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## **SYNTHESIS OF NEW DIMETHYLCARBAMATES, DERIVATIVES OF 2- AND 4- AMINORESORCINOL**

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(Received January 27, 1982)

### **Summary**

The quaternary salts of the bis-dimethylcarbamate esters of the 2- and 4-dialkylaminoacetamidoresorcinol and 2- and 4-dialkylaminopropionamidoresorcinol were synthesized in order to be evaluated as potential anticholinesterase agents.

**Key words:** Synthesis of 2- and 4-dialkylaminoacetamidoresorcinol and 2- and 4-dialkylaminopropionamidoresorcinol -Quaternary salts.

### **Introduction**

The study of the pharmacological activity of physostigmine<sup>1</sup> has proved that its anticholinesterase properties are exclusively attributed to the presence of the urethane group on the aromatic nucleus of this alkaloid. (formula a).

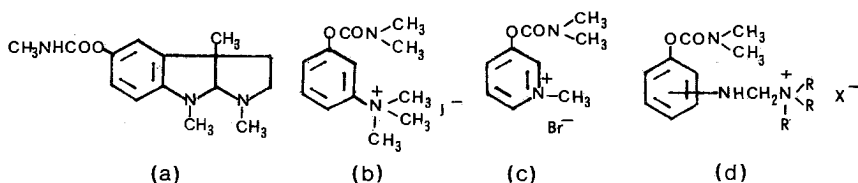
Numerous synthetic compounds of a simpler structure having a mono- or di-substituted carbamate group, have so far been tested as anticholinesterase agents, many of which have gained widespread clinical use (e.g. prostigmine, pyridostigmine<sup>2,3,4</sup>, (formula b, c.)

A broader investigation of the pharmacological properties of these compounds combined with the almost complete elucidation of their mechanism of action has led to the following conclusions.

A) A N-substituted urethane group attached to an aromatic nucleus is necessary, for anticholinesterase activity. Mono-substituted derivatives act faster, but decompose relatively quickly in aqueous media<sup>5</sup>. Di-substituted compounds act slower, but exhibit a longer duration of action and greater stability in the above media.

B) A positively charged nitrogen atom as a quaternary ammonium salt enhances the activity potential as well as the solubility in water<sup>6</sup>. It is noted, however, that the distance between the quaternary nitrogen and the aromatic nucleus is of great importance since it critically influences activity. To study this

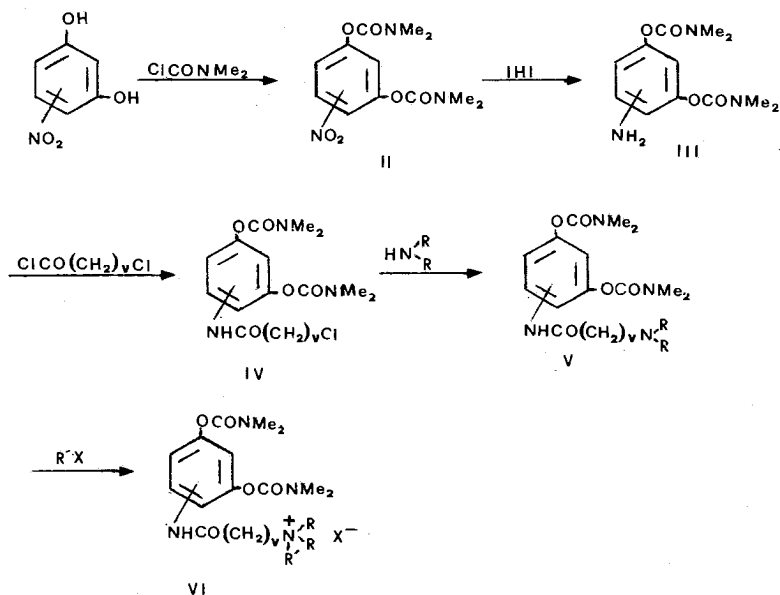
particular effect Tsacotellis<sup>7</sup> has synthesized compounds of the general formula (d) many of which showed a potency only slightly lower than that of prostigmine.



This paper describes the synthesis of new compounds containing two N-substituted urethane groups on a benzene nucleus and a side chain bearing a quaternary nitrogen (general formula VI).

### Discussion

The compounds of the general formula VI were synthesized in five steps outlined in scheme A.



The hydroxyl groups of 4 and 2-nitrosorcinol<sup>8,13</sup> were esterified with dimethylcarbamoyl chloride in dry pyridine<sup>9</sup>.

The nitro group of the above esters was reduced by catalytic hydrogenation<sup>10</sup> under pressure in absolute ethanol. The crude residue reacted with chloroacetyl or

chloropropionyl chloride in chloroform<sup>11,12</sup> to yield the corresponding N-chloroacetyl and N<sup>2</sup>-chloropropionyl derivatives IV.

The intermediate bases V were prepared by reaction of IV with secondary amines in dry benzene. When dimethylamine was employed the reaction took place at room temperature.

Finally, the products V were quaternised by reaction with alkyl halides.

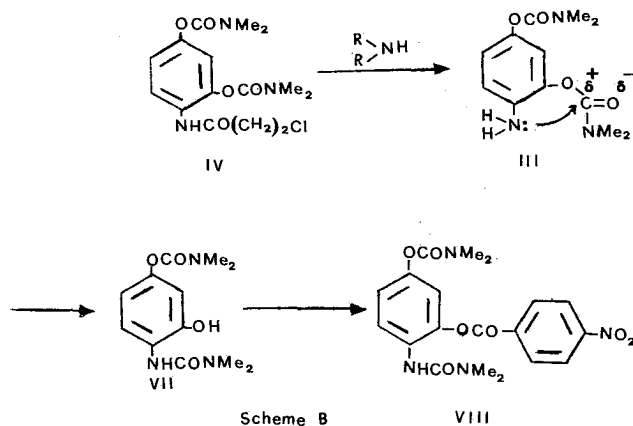
An attempt to obtain 4-(N-N, dialkylaminopropionamido) phenyl 1,3-bis (dimethylcarbamates) (V), by boiling 4-(N-chloropropionamido) phenyl 1,3-bis (dimethylcarbamate) (IV) with various secondary amines led in all cases to the same crystalline product (m.p. 159-60°/ethanol). The examination of the behaviour and chemical properties of this compound gave the following results.

1) The product did not show basic properties, as concluded by its insolubility in acidic solutions.

2) Beilstein's test proved that the compound did not contain chlorine.

3) TLC showed a different R<sub>f</sub> from that of the corresponding chloropropionamide (IV).

These findings led us to the assumption that probably IV was initially aminolysed to 4-aminophenyl-1,3-bis (dimethylcarbamate) (III), which in turn was rearranged by intramolecular aminolysis to N-(2-hydroxy-4-dimethyl (carbamyl-oxy) phenol N, N -dimethylurea VII (Schème B).



This assumption was verified by the following facts.

1) The presence of a free hydroxyl group, was proved by the solubility of VII in dilute alkali. In addition, when VII reacted with p-nitrobenzoylchloride<sup>14</sup>, was formed the corresponding ester VIII, which identified by elemental analysis and IR spectroscopy.

2) I.R. spectra of VII and VIII.

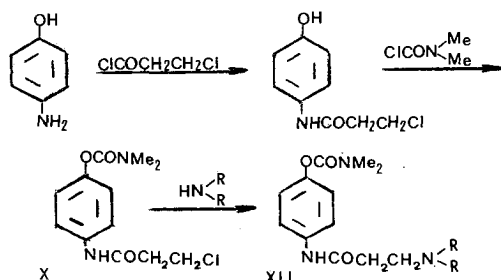
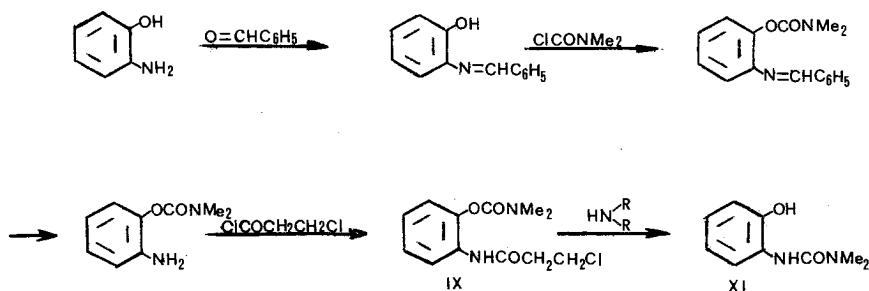
Product VII showed absorption bands at 3450cm<sup>-1</sup>, 1640cm<sup>-1</sup>, and 1720cm<sup>-1</sup> assigned to OH, -C=O of the aryl-substituted urea and carbamate ester -C=O respectively.

Product VIII showed absorption bands at  $3250\text{cm}^{-1}$ ,  $1650\text{cm}^{-1}$ ,  $1720\text{cm}^{-1}$  and  $1520\text{cm}^{-1}$  assigned to  $\text{NH}$ ,  $-\text{C}=\text{O}$  of the aryl-substituted urea, carbamate ester  $-\text{C}=\text{O}$  and  $\text{NO}_2$  respectively.

Analysis VIII:  $\text{C}_{19}\text{H}_{20}\text{N}_4\text{O}_7$  Calc% C:54,8 H:4,8 N:13,4

Found% 54,8 4,7 13,3

In order to prove which of the two carbamyl groups is aminolysed we examined the effect of secondary amines on *o*-(*N*-chloropropionamido) -phenyl *N,N*-dimethylcarbamate (IX) and *p*-(*N*-chloropropionamido) -phenyl *N,N*-dimethyl carbamate (X) prepared as depicted in schemes C and D respectively<sup>7</sup>.



These experiments proved that only the carbamyl group at a position ortho to the acylated group follows the assumed aminolysis pattern.

In fact, the *p*-aminophenol derivative X yielded the expected analog XII. On the contrary the *o*-aminophenol derivative IX yielded 1-(*o*-hydroxyphenyl) 3,3-dimethylurea (XI).

The latter compound was also obtained from another independent route of synthesis<sup>15</sup>.

The final products 4- and 2-(-*N*, dialkylaminopropionamido) phenyl 1,3-bis dimethyl carbamates were synthesized by treatment of the corresponding amides with secondary amines in dry benzene or absolute ethanol, at room temperature.

I.R. spectra. The final products showed absorption bands at  $3250\text{cm}^{-1}$ ,  $1660$

$\text{cm}^{-1}$  and  $1720 \text{ cm}^{-1}$ , assigned to amide NH (amide I band, amide  $-\text{C}=\text{O}$  and urethane  $-\text{C}=\text{O}$ ) respectively<sup>16,17</sup>.

## Experimental

The I.R. spectra were obtained a Perkin-Elmer 177 spectrophotometer. Melting points are uncorrected.

### *2- and 2-nitrophenyl 1,3-bis (dimethylcarbamate) II*

In a warm solution of 0,1 mol 4- or 2-nitroresorcinol in dry pyridine, 0,4 mol dimethylcarbamoyl chloride were added under stirring. The solution was stirred for another 6 hr and then 200 ml benzene or ethyl ether were added. The solution was shaken successively with, 10% HCl solution, 10% aqueous NaOH, and saturated aqueous NaCl until neutrality. The organic layer was dried and the solvent was evaporated.

2-nitrophenyl 1,3-bis (dimethylcarbamate) was obtained as white crystals M.p. 53-55° (yield 76%).

Analysis  $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_6$  Cal.% C:48,5 H:5,1 N:14,1  
Found.% 48,7 5,2 14,2

4-nitrophenyl 1,3-bis (dimethylcarbamate) was obtained as viscous oil and used in the next step without purification.

### *4- and 2-aminophenyl 1,3-bis (dimethylcarbamate) III*

0,03 mol of the appropriate II dissolved in absolute ethanol was hydrogenated under pressure over  $\text{PtO}_2$  or Raney Ni. When the reduction was completed the catalyst was rapidly removed and the solvent was distilled off in vacuum.

2-aminophenyl 1,3-bis (dimethylcarbamate).

White crystals m.p. 186-87° from ethanol (yield 80%).

Analysis. Calc.% C:53,9 H:6,4 N:15,7  
Found.% 53,6 6,4 16

4-aminophenyl 1,3-bis (dimethylcarbamate).

White crystals from ethanol/anhydrous ether m.p. 170-172°.

Analysis.  $\text{C}_{12}\text{H}_{18}\text{N}_3\text{O}_4\text{Cl}$  Calc.% C:47,4 H:6,0 N:13,8 Cl:11,7  
Found% 47,6 6,1 14,1 12,1

### *4- and 2-(N-chloroacetamido) phenyl 1,3-bis (dimethylcarbamate) and*

### *4- and 2-(N-chloropropionamido) phenyl 1,3-bis (dimethylcarbamate) IV.*

In a chloroform solution containing 0,037 mol of the appropriate III and 0,074 mol  $\text{Na}_2\text{CO}_3$ , it was added under stirring and cooling 0,04 mol chloroacetylchloride or chloropropionylchloride.

The stirring was continued for 1 hr. Then, the mixture was cautiously acidified with 10% aqueous HCl solution. The organic layer was separated, washed with saturated NaCl solution, dried and the solvent distilled off.



4-(N-chloroacetamido) phenyl 1,3-bis (dimethylcarbamate). White crystals from benzene m.p. 139-40° (yield 70%).

Analysis.  $C_{14}H_{18}N_3O_5Cl$  Calc.% C:48,9 H:5,3 N:12,2 Cl:10,3  
 Found.% 49 5,2 12,1 10,5

4-(N-chloropropionamido) phenyl 1,3-bis (dimethylcarbamate). Crystalline solid m.p. 128-9° from benzene (yield 76%).

Analysis  $C_{15}H_{20}N_3O_5Cl$  Calc.% C:50,3 H:5,6 N:11,7 Cl:9,9  
 Found.% 50,2 5,6 11,6 9,9

2-(N-chloropropionamido) phenyl 1,3-bis (dimethylcarbamate) Crystalline solid m.p. 173-5° from benzene (yield 80%).

Analysis  $C_{15}H_{20}N_3O_5Cl$  Calc.% C:50,3 H:5,6 N:11,7 Cl:9,9  
 Found.% 50,5 5,5 11,7 10,1

*4- and 2- (N, N-dialkylaminoacetamido) phenyl 1,3-bis (dimethylcarbamate) V.*

0,01 mol of the appropriate IV were dissolved in 50 ml dry benzene and boiled with 0,03 mol of a secondary amine for 6 hr. In the case of dimethylamine the solution was stirred at room temperature for 24 hr. The organic layer was washed with water, dried and the solvent was evaporated.

The products thus obtained are summarised in table I.

*4- and 2- (N, N-dialkylaminopropionamido) phenyl 1,3 -bis (dimethylcarbamate) V.*

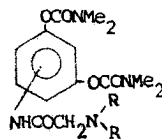
0,014 mol of the appropriate IV were dissolved in dry benzene and stirred with a secondary amine for 24 hr at room temperature. The benzene layer washed with water dried and evaporated. The products thus prepared are summarised in table II.

*Quaternary ammonium salts VI*

The methyl iodide salts were prepared by boiling the bases with methyl iodide in a 1:10 or 1:20 ratio for 2-3 hr. The methyl bromide salts were similarly prepared in dry acetone, at room temperature.

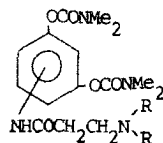
The final products thus obtained are summarised in table III.

TABLE I: 4- and 2- (N, N-dialkylaminoacetamido) phenyl 1, 3-bis- (dimethylcarbamates)



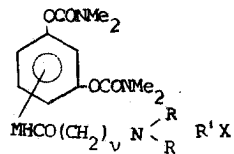
R <sub>2</sub> N-	Position	Salt	Molecular formula	M.P. °C	ANALYSES							
					Calc. %				Found %			
					C	H	N	X	C	H	N	X
	4	picrate	C <sub>22</sub> H <sub>27</sub> N <sub>7</sub> O <sub>12</sub>	215-218	45.4	4.7	16.9		45.6	4.8	16.7	
	4	HCl	C <sub>16</sub> H <sub>25</sub> N <sub>4</sub> O <sub>5</sub> Cl	223-224	49.4	6.5	14.4	9.1	49.3	6.5	14.2	9.1
	2	HCl	C <sub>16</sub> H <sub>25</sub> N <sub>4</sub> O <sub>5</sub> Cl	198-200	49.4	6.5	14.4	9.1	49.3	6.2	14.1	9.1
	4	picrate	C <sub>24</sub> H <sub>31</sub> N <sub>7</sub> O <sub>12</sub>	208-210	47.3	5.1	16.1		47.1	5.2	16	
	2	picrate	C <sub>24</sub> H <sub>31</sub> N <sub>7</sub> O <sub>12</sub>	192-193	47.3	5.1	16.1		47.5	5.2	16.2	
	2	HCl	C <sub>18</sub> H <sub>29</sub> N <sub>4</sub> O <sub>5</sub> Cl	203-205	51.9	7.0	13.4		52.1	7.2	13.2	
	4	picrate	C <sub>25</sub> H <sub>31</sub> N <sub>7</sub> O <sub>12</sub>	155-158	48.3	5.0	15.8		48.7	4.9	15.8	
	4	HCl	C <sub>19</sub> H <sub>29</sub> N <sub>4</sub> O <sub>5</sub> Cl	203-205	53.2	6.8	13.1		53.2	7.0	12.9	
	2	HCl	C <sub>19</sub> H <sub>29</sub> N <sub>4</sub> O <sub>5</sub> Cl	225 dec	53.2	6.8	13.1		53.2	7.0	12.9	
	4	HCl	C <sub>18</sub> H <sub>27</sub> N <sub>4</sub> O <sub>6</sub> Cl	202-204	50.2	6.3	13.0		50.3	6.3	13.0	
	2	HCl	C <sub>18</sub> H <sub>27</sub> N <sub>4</sub> O <sub>6</sub> Cl	230-232	50.2	6.3	13.0		50.3	6.2	13.1	
	2	picrate	C <sub>24</sub> H <sub>29</sub> N <sub>7</sub> O <sub>13</sub>	213-214	42.2	4.7	15.7		42.1	4.8	15.5	

TABLE II: 4- and 2- (N, N-dialkylaminopropionamido) phenyl 1,3 -bis- (dimethylcarbamates)



	Position	Salt	Molecular formula	M.P. °C	ANALYSES								
					Calc. %				Found %				
					C	H	N	X	C	H	N	X	
	4	oxalate	C <sub>21</sub> H <sub>32</sub> N <sub>4</sub> O <sub>9</sub>	147-148	52.9	6.6	11.6			52.7	6.5	11.5	
	2	oxalate	C <sub>21</sub> H <sub>32</sub> N <sub>4</sub> O <sub>9</sub>	129-130	52.9	6.6	11.6			52.5	6.7	11.4	
	4	oxalate	C <sub>22</sub> H <sub>32</sub> N <sub>4</sub> O <sub>9</sub>	135-138	53.2	6.5	11.3			53.4	6.8	10.9	
	2		C <sub>20</sub> H <sub>30</sub> N <sub>4</sub> O <sub>5</sub>	150-153	59.1	7.4	13.8			59.2	7.3	13.9	
	4	oxalate	C <sub>21</sub> H <sub>30</sub> N <sub>4</sub> O <sub>10</sub>	188-189	50.6	6.1	11.2			50.7	6.0	11.2	

TABLE III.



R <sup>1</sup> -N- R <sup>2</sup>	Position	v	Salts	Molecular Formula	M.P. °C	ANALYSES							
						Calc. %				Found %			
						C	H	N	X	C	H	N	X
	4	1	CH <sub>3</sub> I	C <sub>17</sub> H <sub>27</sub> N <sub>4</sub> O <sub>5</sub> I	160-162	41.3	5.5	11.3	25.7	41.4	5.6	11.3	25.8
	2	1	CH <sub>3</sub> I	C <sub>17</sub> H <sub>27</sub> N <sub>4</sub> O <sub>5</sub> I	228-230	41.3	5.5	11.3		41.0	5.7	11.3	
	2	1	CH <sub>3</sub> Br	C <sub>17</sub> H <sub>27</sub> N <sub>4</sub> O <sub>5</sub> Br	230-232	45.6	6.1	12.5	17.8	45.2	6.0	12.3	18.1
	4	1	CH <sub>3</sub> Br	C <sub>19</sub> H <sub>31</sub> N <sub>4</sub> O <sub>5</sub> Br	163-165	46.2	6.7	11.4		46.4	6.6	11.7	
	4	1	CH <sub>3</sub> I	C <sub>19</sub> H <sub>31</sub> N <sub>4</sub> O <sub>5</sub> I	198-200	42.2	6.1	10.4		42.4	5.8	10.5	
	2	1	CH <sub>3</sub> Br	C <sub>19</sub> H <sub>31</sub> N <sub>4</sub> O <sub>5</sub> Br	185-186	46.2	6.7	11.4		46.2	6.3	11.3	
	2	1	CH <sub>3</sub> I	C <sub>19</sub> H <sub>31</sub> N <sub>4</sub> O <sub>5</sub> I	163-165	42.2	6.1	10.4		42.1	5.7	10.6	
	4	1	CH <sub>3</sub> Br	C <sub>20</sub> H <sub>31</sub> N <sub>4</sub> O <sub>5</sub> Br	163-165	49.3	6.4	11.5		49.5	6.5	11.3	
	4	1	CH <sub>3</sub> I	C <sub>20</sub> H <sub>31</sub> N <sub>4</sub> O <sub>5</sub> I	125-127	44.9	5.8	10.5		45.0	5.6	10.7	
	2	1	CH <sub>3</sub> Br	C <sub>20</sub> H <sub>31</sub> N <sub>4</sub> O <sub>5</sub> Br	188-190	49.3	6.4	11.5		49.3	6.5	11.5	
	2	1	CH <sub>3</sub> I	C <sub>20</sub> H <sub>31</sub> N <sub>4</sub> O <sub>5</sub> I	193-194	44.9	5.8	10.5		45.2	5.9	10.6	
	4	1	CH <sub>3</sub> Br	C <sub>19</sub> H <sub>29</sub> N <sub>4</sub> O <sub>6</sub> Br	130-131	46.6	6.0	11.4	16.3	45.6	6.0	11.4	16.3
	4	1	CH <sub>3</sub> I	C <sub>19</sub> H <sub>29</sub> N <sub>4</sub> O <sub>6</sub> I	180-182	42.5	5.5	10.4		42.3	5.6	10.0	
	2	1	CH <sub>3</sub> Br	C <sub>19</sub> H <sub>29</sub> N <sub>4</sub> O <sub>6</sub> Br	198-199	46.6	6.0	11.4	16.3	46.4	6.2	11.5	16.1
	2	1	CH <sub>3</sub> I	C <sub>19</sub> H <sub>29</sub> N <sub>4</sub> O <sub>6</sub> I	203-205	42.5	5.5	10.4		42.5	5.6	10.3	
	2	2	CH <sub>3</sub> I	C <sub>21</sub> H <sub>33</sub> N <sub>4</sub> O <sub>5</sub> I	208-209	44.0	6.3	10.3	23.3	43.9	6.1	10.6	23.2
	2	2	CH <sub>3</sub> I	C <sub>21</sub> H <sub>33</sub> N <sub>4</sub> O <sub>5</sub> I	208-209	44.0	6.3	10.3	23.3	43.9	6.1	10.6	23.2

## Περίληψη

Σύνθεση δις-διμεθυλοκαρβαμιδικών εστέρων της 2- και 4- διαλκυλαμινοακεταμιδορροσρκινόλης και της 2- και 4- διαλκυλαμινοπροπιοναμιδορροσρκινόλης.

Δις-διμεθυλοκαρβαμιδικοί εστέρες της 2- και 4- διαλκυλαμινοακεταμιδορροσρκινόλης.

Παρασκευάστηκαν με εστεροποίηση των δύο φαινολικών υδροξυλίων της 2- και 4-νιτρορροσρκινόλης με διμεθυλοκαρβαμοϋλοχλωρίδιο και αναγωγή στη συνέχεια της νιτροομάδας προς πρωτοταγή αμινομάδα. Με επίδραση χλωροκετυλοχλωριδίου λαμβάνεται ο δις-διμεθυλοκαρβαμιδικός εστέρας της 2- και 4-χλωρακεταμιδορροσρκινόλης, ο οποίος με επίδραση δευτεροταγών αμινών, δίνει τις αντίστοιχες βάσεις, οι οποίες μετατράπηκαν σε τεταρτοταγή άλατα.

Δις-διμεθυλοκαρβαμιδικοί εστέρες της 2- και 4- διαλκυλαμινοπροπιοναμιδορροσρκινόλης.

Παρασκευάστηκαν με επίδραση β-χλωροπροπιονυλοχλωριδίου επί των δις-διμεθυλοκαρβαμιδικών εστέρων της 2- και 4- αμινορροσρκινόλης και στη συνέχεια με επίδραση δευτεροταγών αμινών επί του σχηματιζόμενου χλωροπροπιοναμιδίου ελήφθησαν αντίστοιχες βάσεις ή προϊόντα αμινόλυσης και στη συνέχεια ενδομοριακής ορθοαμινόλυσης.

Τα τεταρτοταγή άλατα εξετάζονται για πιθανή αντιχολινεστερασική δράση.

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# MONOHALOGENBENZOYLHYDRAZONE I. DARSTELLUNG, EIGENSCHAFTEN, UV-UND IR- SPEKTREN NEUER MONOHALOGENBENZOYLHYDRAZONE VON 2-FURALDEHYD, 2-THIOPHENALDEHYD, 2-PYRROLALDEHYD UND DI-2-PYRIDYLKETON

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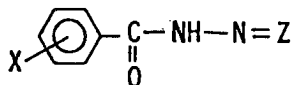
## Zusammenfassung

Darstellung und Eigenschaften der o-, m-, p-, Fluor-, Chlor-, Brom- bzw Jod- Benzoylhydrazonen der 2-Furaldehyd, 2-Thiophenaldehyd, 2-Pyrrolaldehyd und Di-2-pyridylketon werden beschrieben. Es werden ihre UV- und IR- Spektren angegeben und diskutiert. Es wurde gefunden, dass, wenn das Halogenatom die o-Stellung des Benzolkerns besitzt, eine Violettverschiebung der Hauptbande in UV-Spektren sowie eine Verschiebung zu höheren Frequenzen der Valenzschwingung der Carbonylgruppe  $\nu(\text{C}=\text{O})$  in IR-Spektren verursacht.

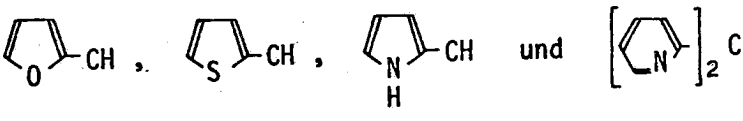
## Einführung

Hydrazone sind bereits seit 30 Jahren als bakteriostatische Verbindungen<sup>1-5</sup> bekannt. In den letzten Jahren erlangten sie besonderes analytisches Interesse als Reagenzien zur Bestimmung verschiedener Kationen<sup>5-11</sup>. Während inzwischen zahlreiche Untersuchungen über Phenylhydrazone und ihre Nitro-, Amino- und Hydroxy-Derivate durchgeführt worden sind, liegen bisher erst relativ wenige Angaben über Halogenbenzoylhydrazone vor.

In der vorliegenden Arbeit berichten wir daher über die Darstellung und Eigenschaften sowie die Elektronen- und Schwingungs-Spektren neuer Monohalogenbenzoylhydrazone von 2-Furaldehyd, 2-Thiophenaldehyd, 2-Pyrrolaldehyd und Di-2-pyridylketon, die der allgemeinen Formel



mit X = F, Cl, Br, I in o-, m- und p- Stellung

und  $\text{Z} =$    $\text{CH}$  ,  $\text{CH}$  ,  $\text{CH}$  und  $\left[ \text{C}_5\text{H}_4\text{N} \right]_2 \text{C}$   
entsprechen.

## Experimenteller Teil

### *a) Darstellung der Verbindungen*

Durch Kondensation der Hydrazide der Monohalogenbenzoesäure mit den oben erwähnten Aldehyden bzw. Ketonen in methanolischer Lösung wurden die entsprechenden Hydrazone nach dem Stuve-Verfahren erhalten<sup>12</sup>. Die Produkte wurden aus Methanol umkristallisiert. Es wurden auf diese Weise 48 Halogenhydrazone hergestellt, die in der Tabelle I aufgeführt sind. Einige von diesen sind schon in früheren Arbeiten erwähnt worden<sup>1,13-19</sup>. Alle Substanzen sind in Wasser, Ether, Tetrachlor- und Schwefelkohlenstoff unlöslich und unter Lichtabschluß nahezu unbegrenzt haltbar. Die Lichtempfindlichkeit ist bei den Iodo-Verbindungen besonders ausgeprägt. In Aceton, Methanol und Chloroform lösen sich die beschriebenen Halogenbenzoylhydrazone gut. Die Eigenschaften dieser Substanzen gehen aus Tabelle I hervor.

### *b) Durchführung der Messungen*

Die Schmelzpunkte wurden mit einem Gerät der Fa. Reichert bestimmt (unkorrigiert).

Die Elektronenspektren wurden mit Spektrophotometern des Typs Beckman ACTA MIV sowie Perkin-Elmer Hitachi 200 aufgenommen. Als Lösungsmittel zur Vermessung wurde Methanol verwendet.

Zur Aufnahme der IR-Spektren (KBr-Presslinge) dienten die Spektrophotometer Beckman IR 4250 sowie Perkin-Elmer 467.

Die C-, H-, N-Bestimmungen wurden mikroanalytisch mittels eines Perkin-Elmer 240 Elementar Analyzers ausgeführt.

## Ergebnisse und Diskussion

### *1. Spektrophotometrische Messungen*

Die Elektronenabsorptionsspektren der untersuchten Hydrazone in neutralen, sauren und alkalischen Lösungen gehen aus Tabelle II hervor.

a. Die Spektren der Monohalogenbenzoylhydrazone von 2-Furaldehyd in neutraler bzw. saurer Lösung zeigen zwei Banden verschiedener Intensität mit Maxima bei 220-260 nm und 304-321 nm. Die Absorption ist auf das chromophore System (Konjugation der  $\pi$ -Elektronen der Benzolkerns mit denen der Carbonylgruppe) zurückzuführen. Die kurzwellige Absorptionsbande ist nur schwach ausgeprägt, erscheint manchmal als Schulter oder wird von der starken langwelligeren Absorptionsbande verdeckt.

Das Spektrum des Benzoylhydrazons von 2-Furaldehyd weist entsprechende Banden auf. Die Einführung eines Halogenatoms in die o-Stellung des Benzolkerns verursacht eine Violettverschiebung um 3-8 nm, während die Halogenierung an m- bzw. p-Stellung eine Rotverschiebung um 1-9 nm (in 0,01 N HCl) bzw. 4-16 nm (in 0,01 N KOH) unter gleichzeitiger Verminderung der Extinktion erbringt. Diese Erscheinungen werden zurückgeführt auf die Unterbrechung der oben erwähnten

TABELLE I: Analytische Daten, Schmelzpunkte und Ausbeuten der hergestellten Hydrazone

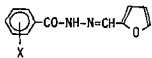
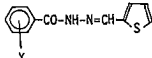
Verbindung	Art und Stellung von Halogen X	Verb. Nr	Reaktionszeit <sup>a</sup>	Ausbeute <sup>b</sup> (%)	Summenformel	Analyse <sup>c</sup>			Schmp. (°C)	Lit. Daten	
						% C	% H	% N			
	o-F	1	5 h	86	C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub> F	gef. 61,68	3,86	11,97	155-160		
	m-F	2	5 h	96		gef. 62,07	3,55	12,34	172-173		
	p-F	3	2 h	85		gef. 61,80	3,85	11,78	202-204		
						ber. 62,07	3,91	12,07			
	o-Cl	4	5 h	90		C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub> Cl	gef. 58,25	3,66	11,33	162-163	Lit. <sup>1</sup> 163°
							gef. 58,57	3,50	11,90	181-182	Lit. <sup>17</sup>
							gef. 58,27	3,52	11,42	210-211	Lit. <sup>13,18</sup> 210-212°
	m-Cl	5	4 h	93			ber. 57,96	3,65	11,27		
							gef. 49,36	2,88	9,51	151-152	Lit. <sup>16</sup> 162-163°
							gef. 49,20	2,95	9,05	196-200	Lit. <sup>15,18</sup> 197-198°
	p-Cl	6	2 h	95			gef. 48,82	3,02	9,73	221-222	Lit. <sup>14</sup> 218-219°
							ber. 49,17	3,09	9,56		
						gef. 41,80	2,60	8,06	176-178		
o-Br	7	5 h	93		C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub> Br	gef. 41,77	2,56	8,03	225-228	Lit. <sup>19</sup> 216°	
						gef. 41,77	2,56	8,03	225-228	Lit. <sup>19</sup> 216°	
						gef. 42,02	2,81	8,45	220-224	Lit. <sup>18</sup> 228°d	
m-Br	8	6 h	96			ber. 42,38	2,67	8,24			
						gef. 41,80	2,60	8,06	176-178		
						gef. 41,77	2,56	8,03	225-228	Lit. <sup>19</sup> 216°	
p-Br	9	3 h	96			gef. 42,02	2,81	8,45	220-224	Lit. <sup>18</sup> 228°d	
						ber. 49,17	3,09	9,56			
						gef. 41,80	2,60	8,06	176-178		
	o-I	10	5 h	90	C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub> I	gef. 41,80	2,60	8,06	176-178		
	m-I	11	3 h	90		gef. 41,77	2,56	8,03	225-228	Lit. <sup>19</sup> 216°	
	p-I	12	2 h	96			gef. 42,02	2,81	8,45	220-224	Lit. <sup>18</sup> 228°d
							ber. 42,38	2,67	8,24		
							gef. 42,02	2,81	8,45	220-224	Lit. <sup>18</sup> 228°d
o-F	13	5 h	86		C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> OSF	gef. 57,82	3,51	11,15	148		
						gef. 58,24	3,38	11,16	183-184		
						gef. 57,87	3,56	11,02	125-227		
						ber. 58,05	3,65	11,28			
m-F	14	5 h	93			gef. 57,87	3,56	11,02	125-227		
						ber. 58,05	3,65	11,28			
p-F	15	2 h	94			gef. 57,87	3,56	11,02	125-227		
						ber. 58,05	3,65	11,28			



TABELLE I (Fortsetzung)

	o-Cl	16	5 h	96	$C_{12}H_9N_2OSCl$	gef.	54,21	3,46	10,57	175-176
	m-Cl	17	5 h	96		gef.	54,56	3,43	10,72	190-191
	p-Cl	18	2 h	95		gef.	54,42	3,48	10,48	201-204
						ber.	54,44	3,43	10,58	
	o-Br	19	5 h	96	$C_{12}H_9N_2OSBr$	gef.	46,26	2,97	9,16	196
	m-Br	20	5 h	96		gef.	46,39	2,54	9,01	224
	p-Br	21	3 h	93		gef.	46,87	2,82	9,02	220
						ber.	46,62	2,93	9,06	
	o-I	22	5 h	84	$C_{12}H_9N_2OSI$	gef.	40,15	2,61	8,16	165-180
	m-I	23	5 h	90		gef.	40,87	2,59	7,96	208-209
	p-I	24	3 h	93		gef.	40,72	2,81	8,61	226-118
						ber.	40,47	2,55	7,86	
	o-F	25	5 h	84	$C_{12}H_{10}N_3OF$	gef.	61,76	4,22	18,38	173-175
	m-F	26	6 h	84		gef.	61,52	4,38	18,06	180-182
	p-F	27	2 h	93		gef.	62,07	4,28	18,33	225-228
						ber.	62,33	4,36	18,17	
	o-Cl	28	8 h	85	$C_{12}H_{10}N_3OCl$	gef.	58,43	4,04	17,29	140-141
	m-Cl	29	5 h	88		gef.	57,65	4,14	17,75	194-197
	p-Cl	30	3 h	93		gef.	58,04	3,90	17,68	233-235
						ber.	58,19	4,07	16,96	
	o-Br	31	5 h	92	$C_{12}H_{10}N_3OBr$	gef.	49,52	3,45	14,35	136-138
	m-Br	32	4 h	93		gef.	49,18	3,37	14,11	202-208
	p-Br	33	6 h	97		gef.	48,08	3,34	14,32	230-231
						ber.	49,34	3,45	14,38	
	o-I	34	5 h	85	$C_{12}H_{10}N_3OI$	gef.	41,94	2,92	12,19	155-162
	m-I	35	5 h	90		gef.	42,00	2,87	12,20	142-145
	p-I	36	5 h	93		gef.	42,08	2,86	12,23	237-241
						ber.	42,50	2,97	12,39	

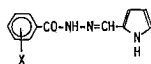
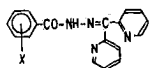


TABELLE I (Fortsetzung)



o-F	<b>37</b>	5 h	93	$C_{18}H_{14}N_4OF$	gef.	67,28	4,15	17,56	150-151
m-F	<b>38</b>	5 h	92		gef.	67,35	4,33	17,46	155-159
p-F	<b>39</b>	2 h	92		gef.	67,09	4,23	17,39	163
					ber.	67,49	4,09	17,49	
o-Cl	<b>40</b>	4 h	90	$C_{18}H_{14}N_4OCl$	gef.	64,15	3,78	15,92	124-125
m-Cl	<b>41</b>	4 h	89		gef.	64,08	3,89	16,64	150-151
p-Cl	<b>42</b>	2 h	95		gef.	64,51	3,88	16,85	182-184
					ber.	64,20	3,89	16,64	
o-Br	<b>43</b>	4 h	96	$C_{18}H_{14}N_4OBr$	gef.	56,90	3,34	14,52	146-148
m-Br	<b>44</b>	4 h	88		gef.	56,44	3,51	14,93	148-150
p-Br	<b>45</b>	2 h	94		gef.	56,54	3,41	14,61	181-182
					ber.	56,71	3,44	14,70	
o-I	<b>46</b>	4 h	85	$C_{18}H_{14}N_4OI$	gef.	50,16	3,17	13,21	153-154
m-I	<b>47</b>	4 h	87		gef.	50,59	3,04	13,15	150
p-I	<b>48</b>	2 h	95		gef.	50,64	3,01	12,92	152-153
					ber.	50,49	3,06	13,08	

<sup>a</sup> Vor Isolierung wurde das Lösungsmittel zur Hälfte abgedampft.

<sup>b</sup> Die Ausbeuten wurden nicht optimiert.

<sup>c</sup> Die Analysen wurden in der Laboratorien den Universitäten Thessaloniki und Bielefeld ausgeführt.

TABELLE II: Bandenmaxima mit Extinktionskoeffizienten der hergestellten Hydrazone  
(in MeOH  $d = 1$  cm).

Verb. Nr.	$\lambda_{\max}$ (nm)	$\epsilon$	$\lambda_{\max}$ (nm)	$\epsilon$	Verb. Nr.	$\lambda_{\max}$ (nm)	$\epsilon$	$\lambda_{\max}$ (nm)	$\epsilon$
	in 0,01 N HCl		in 0,01 N KOH			in 0,01 N HCl		in 0,01 N KOH	
A <sup>a</sup>	230	11650	225	10900	B <sup>a</sup>	266	13000	264	13100
	312	37100	322	27900		318	27550	319	23800
1	223 sh	—	—	—	13	265	12000	260	9200
	309	28950	318	22550		313	26400	322	20200
2	228	10450	225 sh	—	14	267	14000	263	9200
	312	31200	332	22800		317	30600	333	22400
3	230	10900	227 sh	—	15	265	12800	162	9200
	311	32100	326	23700		317	28000	328	22400
4	304	30450	316	23300	16	268 sh	—	262 sh	—
5	230 sh	—	230 sh	—		312	26150	323	20600
	314	30150	333	23200	17	267	11800	262	8200
6	240	14250	235	12750		320	27000	339	20600
	313	33500	333	25300	18	265 sh	—	265 sh	—
7	304	30850	316	23900		320	27450	337	21850
8	314	30700	334	23450	19	269 sh	—	262	7250
9	243	13800	233	11800		312	22350	322	17950
	314	32850	334	24100	20	269 sh	—	260 sh	—
10	225 sh	—	225 sh	—		320	25350	341	20300
	305	31250	317	23700	21	248	10050	236	13600
11	220 sh	—	220 sh	—		320	27150	339	21100
	314	31600	333	24950	22	268 sh	—	262 sh	—
12	260	16350	250	14250		315	32500	325	24950
	321	28350	338	20800	23	268 sh	—	258 sh	—
						313	26600	323	20200
					24	254	13350	245	13350
						314	35450	334	27200
	in 0,01 N HCl		in neutr. Lösung			in 0,01 N HCl		in neutr. Lösung	
C <sup>a</sup>	230	12750	230 sh	—	27	232	13650	230 sh	—
	288	13950	330	28000		288	15050	255 sh	—
25	225	13050	250 sh	—				327	30900
	287	15450	325	30900	28	250 sh	—	250 sh	—
26	227	12730	225 sh	—		288	17600	320	31950
	287	14850	255 sh	—	29	288	18250	255 sh	—
			329	27650				331	27700

TABELLE II (Fortsetzung)

	in 0,01 N HCl		in neutr. Lösung			in 0,01 N HCl		in neutr. Lösung	
<b>30</b>	240	19700	240	16050	<b>40</b>	263	14550	272	16900
	287	11500	330	21600		285 sh	—	307	17800
<b>31</b>	288	15150	250 sh	—	<b>41</b>	330	17600	230 sh	—
			320	29400		263	16450		
<b>32</b>	288	15750	255 sh	—	<b>42</b>	336	19800	321	18600
			332	27900		268	20640	271	21200
<b>33</b>	245	20750	243	15150	<b>43</b>	337	23600	321	22750
	288	14650	331	31030		263	13650	272	15400
<b>34</b>	230 sh	—	230 sh	—	<b>44</b>	329	16400	307	16650
	288	16650	322	28200		263	15850	274	17420
<b>35</b>	288	16950	331	29150	<b>45</b>	285	14750	320	19900
			336	19900		270	18500	270	20050
<b>36</b>	256	23350	254	18200	<b>46</b>	321	20250	321	20250
			332	35600		262	18050	273	20050
D <sup>a</sup>	265	15800	230 sh	—	<b>47</b>	287	17800	318	23800
	284 sh	—	273	17200		338	21600	265	16950
<b>37</b>	256	16350	230 sh	—	<b>48</b>	285 sh	—	321	20450
			282 sh	—		276	16950	337	21100
<b>38</b>	338	18500	317	18800	<b>48</b>	276	18200	322	20600
	257 sh	—	226 sh	—		339	21500	250 sh	—
<b>39</b>	285 sh	—	274	17250	<b>48</b>	276	18200	322	20600
	336	19400	320	18500		339	21500	250 sh	—
<b>39</b>	265	17600	230 sh	—	<b>48</b>	276	18200	322	20600
	285 sh	—	271	18500		339	21500	250 sh	—
<b>39</b>	237	20300	319	20000	<b>48</b>	276	18200	322	20600
	237	20300	319	20000		339	21500	250 sh	—

<sup>a</sup> A = Benzoylhydrazon von 2-Furaldehyd, B = Benzoylhydrazon von 2-Thiophenalddehyd, C = Benzoylhydrazon von 2-Pyrrolaldehyd und D = Benzoylhydrazon von di-2-Pyridylketon.

Konjugation, auf einen sterischen Effekt<sup>20-23</sup> bei o-Stellung des Halogenatoms sowie auf die Bildung des konjugierten Systems  $-\text{CH}=\text{N}-\text{N}=\text{C}(\text{O})$ , das aus der Enolform der Hydrazone in alkalischer Lösung entsteht.

b. Die Spektren der Monohalogenbenzoylhydrazone von 2-Thiophenaldehyd in neutralen, sauren oder alkalischen Lösungen gleichen im grossen und ganzen denen der entsprechenden Monohalogenbenzoylhydrazone von 2-Furaldehyd. So zeigen sie zwei Banden mit Maxima bei 236-269 nm und 312-341 nm. Die Einführung des Halogenatoms in o-Stellung verursacht in neutralen oder sauren Lösungen eine Violettverschiebung um 3-6 nm, während Halogenatome in m- bzw. p-Stellung eine Rotverschiebung um 2 nm erbringen (Ausnahmen bei Fluoro- und Iodo-Benzoylhydrazonen). In alkalischen Lösungen wird nur eine Rotverschiebung um 3-22 nm mit Einführung des Halogenatoms beobachtet. Diese Erscheinungen werden wie oben (1.a.) interpretiert.

c. Monohalogenbenzoylhydrazone von 2-Pyrrolaldehyd in neutraler Lösung zeigen eine starke Bande bei 320-332 nm, die bei Einführung des Halogenatoms in o-Stellung um 5-10 nm nach Violett verschoben ist. In saurer Lösung wird diese Bande nach und nach durch eine neue Bande bei 288 nm, deren Maximum unabhängig von Art und Position des Halogenatoms ist, ersetzt. Die Intensität dieser neuen Absorptionsbande in saurer Lösung ist niedriger als in neutraler Lösung. Eine zweite Bande um 250 nm wird meist verdeckt und erscheint als Schulter. Dieses besondere Verhalten der Hydrazone von 2-Pyrrolaldehyd ist auf eine Strukturänderung infolge ihrer Protonierung zurückzuführen.

d. Die Spektren der Monohalogenbenzoylhydrazone von Di-2-pyridylketon zeigen drei Banden verschiedener Intensität mit Maxima bei 307-339 nm, 270-287 nm und 230-268 nm. Die Einführung eines Halogenatoms in o-Stellung verursacht nur eine Verschiebung der längstwelligsten Hauptbande nach Violett, die Maxima der m- bzw. p-Isomeren werden nicht verändert. In saurer Lösung wird in Vergleich zur neutralen Lösung eine Rotverschiebung des Maximums der Hauptbande beobachtet. Die mittlere Bande wird in saurer Lösung bei abnehmender Intensität nach Rot verschoben und mehr oder weniger von der kurzwelligen Bande höher Intensität verdeckt. Dieses Verhalten wird wie oben (1.a.) interpretiert. Im allgemeinen zeigen die Spektren der betrachteten Monohalogenbenzoylhydrazone das gleiche Bild wie die entsprechenden unsubstituierten Hydrazone. Die Absorptionen sind durch Carbonyl- und Aminocarben-Gruppe sowie Halogenatome als Chromophore bedingt. Die Halogenatome zeigen chromophore Eigenschaften, da sie mit mehreren Systemen in Konjugation treten und dadurch die Lage und die Intensität von Absorptionsbanden verändern<sup>24</sup>. Die Eigenabsorptionen der Halogenatome bzw. der isolierten Systeme liegen so weit im UV, daß sie im allgemeinen bei der Aufnahme von Spektren aus experimentellen Gründen nicht erfasst werden.

Das abweichende Verhalten der Hydrazone von Di-2-pyridylketon ist wahrscheinlich auf die Abwesenheit eines Wasserstoffatoms an dem Kohlenstoffatom, das die Pyridylgruppen trägt, zurückzuführen<sup>23</sup>.

Die beobachtete Rot- bzw. Violettverschiebung lässt sich mittels Konjugation bzw. sterischer Effekte erklären<sup>21-23</sup>; Auswirkungen sterischer Hinderung von Mesomerie auf Elektronenspektren sind bekannt<sup>20</sup>. In Anlehnung an die vorliegenden

Literaturdaten werden hier die kurzwelligen Absorptionen einem Übergang  $\pi^* \leftarrow \pi$  zugeordnet, die langwelligen Banden einem Übergang  $\pi^* \leftarrow n^{25-28}$ .

## 2. IR-Absorptionsspektren

Die im Wellenzahlenbereich von 4000 bis 250  $\text{cm}^{-1}$  aufgenommenen IR-Absorptionsspektren der festen Proben sind in Tabelle III wiedergegeben. In folgenden werden nur einige ausgewählte Schwingungsbanden diskutiert.

TABELLE III : IR-Absorptionsspektren im Bereich von 4000-250  $\text{cm}^{-1}$  (KBr-Preßling)

Verb. Nr.	Absorptionsbande
1	3220 m, 3200 m, 3070 s, 1665 st, 1630 st, 1620 st, 1570 st, 1550 st, 1495 m, 1480 m, 1455 m, 1400 m, 1360 m, 1305 sst, 1230 st, 1165 m, 1155 m, 1145 m, 1105 m, 1025 st, 945 sst, 910 m, 890 m, 820 m, 790 m, 775 m, 755 sst, 660 m, 630 s, 590 m, 540 s, 510 s, 410 m, 280 s.
2	3250 m, 3200 sh, 3150 s, 3060 s, 1650 sst, 1620 sst, 1590 sst, 1560 st, 1540 st, 1475 st, 1440 st, 1345 st, 1290 sst, 1275 sst, 1220 m, 1150 m, 1120 m, 1060 m, 1015 st, 975 m, 960 m, 890 st, 830 sst, 800 st, 785 m, 755 sst, 680 st, 670 m, 590 m, 520 s, 500 m, 405 m, 395 sh.
3	3250 sh, 3230 m, 3150 s, 3060 s, 1650 sst, 1620 m, 1600 st, 1560 m, 1540 st, 1505 sst, 1480 m, 1340 m, 1305 m, 1285 st, 1230 m, 1220 m, 1160 sst, 1060 m, 1015 st, 955 m, 940 st, 885 m, 850 st, 830 s, 815 s, 780 s, 760 m, 740 st, 670 s, 655 s, 610 st, 590 s, 540 m, 490 m, 310 s.
4	3200 sh, 3170 m, 3140 s, 3050 m, 1665 sst, 1630 st, 1595 m, 1570 m, 1550 st, 1485 st, 1435 m, 1400 m, 1335 st, 1310 st, 1265 st, 1225 st, 1165 m, 1075 m, 1065 st, 1050 st, 1020 st, 960 m, 940 st, 905 m, 885 m, 795 m, 760 st, 740 st, 720 m, 650 s, 590 s, 465 s, 430 s, 360 s.
5	3200 sh, 3170 m, 3140 s, 3020 m, 1650 sst, 1630 sst, 1570 sst, 1550 st, 1480 m, 1420 m, 1395 m, 1350 st, 1310 st, 1295 st, 1260 st, 1225 m, 1075 m, 1025 st, 950 m, 940 st, 915 m, 885 st, 815 m, 805 m, 785 m, 750 sst, 735 st, 680 m, 580 m, 490 m, 455 s, 370 s.
6	3230 m, 1180 sh, 3140 s, 3050 s, 1650 sst, 1625 st, 1585 st, 1555 st, 1530 sst, 1480 st, 1470 st, 1330 st, 1300 st, 1290 st, 1270 st, 1160 st, 1145 m, 1095 st, 1015 sst, 940 st, 925 st, 900 st, 885 m, 845 st, 840 m, 785 m, 755 st, 740 st, 650 m, 590 s, 530 m, 465 m, 385 s.

TABELLE III (Fortsetzung)

- 7 3200 sh, 3170 m, 3120 s, 3050 s, 1660 sst, 1620 st, 1590 m, 1540 st, 1480 st, 1340 st, 1300 st, 1260 m, 1160 m, 1060 m, 1015 st, 940 st, 885 m, 770 st, 750 st, 725 m, 700 m, 640 m, 590 m, 560 m, 450 m, 375 s, 325 s.
- 8 3200 m, 3130 s, 3050 s, 1645 sst, 1625 st, 1580 m, 1560 st, 1545 m, 1480 m, 1345 m, 1310 m, 1295 st, 1270 m, 1025 m, 940 m, 750 m, 740 st, 720 m, 680 s, 585 m, 455 m, 375 s, 325 s.
- 9 3260 m, 3200 m, 3130 s, 3060 m, 1650 sst, 1620 sst, 1590 st, 1565 sst, 1545 sst, 1485 st, 1475 st, 1395 m, 1345 st, 1310 st, 1300 st, 1290 st, 1270 st, 1160 st, 1140 m, 1110 m, 1070 st, 1060 st, 1010 st, 940 sst, 900 m, 885 m, 850 m, 840 m, 790 m, 750 st, 740 sst, 680 s, 585 m, 540 s, 500 s, 450 s, 380 s, 325 s.
- 10 3220 sh, 3190 m, 3150 s, 3060 s, 3000 m, 1660 sst, 1630 st, 1585 m, 1575 m, 1550 m, 1480 m, 1400 m, 1355 st, 1310 st, 1290 m, 1275 m, 1270 m, 1225 m, 1165 m, 1060 m, 1025 st, 960 m, 945 st, 795 m, 765 st, 730 m, 695 st, 590 m, 560 s, 455 m, 420 s, 390 s, 315 s.
- 11 3200 m, 3150 s, 3050 m, 1640 sst, 1600 st, 1580 st, 1560 st, 1550 sst, 1480 m, 1340 st, 1310m, 1290 sst, 1270 st, 1155 m, 1135 m, 1070 st, 1010 st, 940 m, 930 m, 905 m, 880 m, 810 m, 780 m, 735 sst, 715 st, 580 m, 450 m, 415 s, 390 s, 300 m, 285 s.
- 12 3190 m, 3100 s, 3070 s, 1640 sst, 1630 sst, 1595 st, 1585 m, 1550 sst, 1480 m, 1365 m, 1325 st, 1300 st, 1280 m, 1220 m, 1140 m, 1040 m, 1010 st, 945 m, 900 st, 855 m, 835 st, 750 m, 720 sst, 655 m, 570 s, 440 m, 325 s, 310 s, 300 s.
- 13 3200 m, 3090 s, 3060 m, 1660 sst, 1615 sst, 1590 m, 1560 sst, 1515 m, 1490 m, 1450 m, 1430 m, 1355 m, 1320 sst, 1310 st, 1285 st, 1275 st, 1225 st, 1215 st, 1170 m, 1115 m, 1110 st, 1040 m, 935 st, 915 st, 855 m, 810 st, 755 st, 710 st, 675 m, 655 st, 560 s, 550 s, 505 s, 400 m, 340 s.
- 14 3270 m, 3200 sh, 3090 m, 1650 sst, 1600 sst, 1590 sst, 1560 sst, 1485 st, 1445 m, 1430 m, 1370 m, 1330 sst, 1315 st, 1290 sst, 1270 sst, 1225 st, 1210 m, 1110 m, 1080 m, 1065 m, 1040 st, 945 m, 890 m, 840 m, 825 st, 805 m, 760 m, 750 st, 735 st, 710 m, 680 st, 620 m, 525 m, 410 m, 350 s.
- 15 3260 m, 3200 sh, 3090 m, 1650 sst, 1605 sst, 1560 sst, 1500 sst, 1430 st, 1370 m, 1330 sst, 1310 st, 1280 sst, 1235 st, 1220 st, 1160 st, 1140 m, 1100 m, 1060 m, 1040 st, 950 m, 900 st, 850 sst, 810 m, 760 sst, 730 sst, 710 m, 640 m, 620 m, 600 sst, 500 m, 485 m, 400 m, 365 s.

TABELLE III (Fortsetzung)

- 16 3230 s, 3200 sh, 3080 s, 1670 sst, 1600 st, 1540 sst, 1520 st, 1480 m, 1430 m, 1380 m, 1340 st, 1300 st, 1275 st, 1250 m, 1230 m, 1160 m, 1080 st, 1060 m, 1050 st, 970 st, 910 st, 860 m, 845 m, 790 m, 760 st, 735 st, 720 sst, 665 m, 650 m, 500 s, 470 s, 400 s, 370 s.
- 17 3200 s, 3180 m, 3020 m, 1655 sst, 1610 st, 1570 st, 1529 s, 1475 m, 1440 m, 1425 m, 1375 m, 1330 st, 1315 m, 1300 st, 1275 m, 1255 m, 1230 m, 1180 s, 1085 m, 1050 st, 980 s, 955 m, 925 m, 895 m, 860 s, 835 s, 800 s, 755 m, 745 st, 705 sst, 680 m, 650 s, 500 s, 465 s, 400 s, 360 s.
- 18 3190 m, 3080 s, 3030 m, 1655 sst, 1610 sst, 1605 sst, 1565 sst, 1520 m, 1495 st, 1435 m, 1375 st, 1365 m, 1330 sst, 1310 sst, 1285 st, 1230 st, 1150 st, 1100 sst, 1065 m, 1050 m, 1020 st, 955 m, 910 st, 865 m, 850 sst, 770 st, 740 m, 725 sst, 675 s, 660 s, 540 m, 460 m, 340 s.
- 19 3220 m, 3200 sh, 3090 s, 1660 sst, 1590 sst, 1540 sst, 1510 m, 1430 st, 1365 m, 1330 st, 1295 st, 1265 st, 1220 m, 1155 m, 1070 m, 1040 m, 1030 m, 960 m, 905 st, 855 m, 835 m, 760 m, 750 st, 710 sst, 655 m, 640 m, 570 s, 540 s, 500 s, 450 s, 400 m, 315 s.
- 20 3220 sh, 3200 m, 1640 sst, 1595 st, 1590 m, 1555 st, 1475 m, 1430 m, 1355 m, 1315 m, 1295 st, 1275 m, 1215 s, 1145 m, 1080 m, 1040 m, 935 s, 915 m, 855 m, 820 s, 800 m, 740 m, 710 st, 670 m, 655 s, 645 s, 580 m, 500 s, 465 s, 445 s, 415 s, 350 s, 325 s, 305 s.
- 21 3280 m, 3220 m, 1670 sst, 1640 sst, 1600 sst, 1560 sst, 1515 s, 1485 st, 1430 m, 1365 m, 1315 sst, 1300 st, 1280 st, 1270 st, 1225 m, 1185 m, 1140 st, 1110 m, 1070 st, 1040 st, 1010 st, 940 m, 900 st, 855 m, 835 st, 760 m, 745 st, 710 sst, 665 s, 650 s, 570 s, 540 m, 500 s, 450 m, 415 s, 395 s, 350 s, 310 s, 300 s, 285 s.
- 22 3240 m, 3090 m, 1660 sst, 1640 sst, 1625 sst, 1600 st, 1580 m, 1550 st, 1495 m, 1465 m, 1430 m, 1370 m, 1330 st, 1285 st, 1225 m, 1145 m, 1080 m, 1045 m, 955 m, 900 st, 855 m, 790 m, 750 st, 735 m, 710 st, 695 m, 570 m, 540 s, 505 m, 365 m, 310 m, 290 s, 280 s.
- 23 3220 m, 3040 s, 1655 sst, 1585 st, 1540 st, 1510 m, 1425 m, 1365 m, 1330 st, 1295 st, 1260 m, 1150 m, 1065 m, 1015 m, 955 m, 905 st, 850 m, 835 m, 745 st, 710 sst, 650 m, 640 m, 630 s, 570 s, 500 s, 395 s, 300 s, 285 s.
- 24 3260 m, 3200 m, 3060 m, 1645 sst, 1620 st, 1585 st, 1560 st, 1540 st, 1475 st, 1390 m, 1345 st, 1310 m, 1300 st, 1270 st, 1155 st, 1140 m, 1110 m, 1065 m,



## TABELLE III (Fortsetzung)

- 1055 st, 1015 st, 1005 st, 940 sst, 900 m, 885 m, 850 m, 790 m, 745 st, 735 sst, 680 s, 620 s, 585 m, 535 s, 440 s, 390 s, 290 s.
- 25** 3230 st, 3120 s, 3080 m, 1660 sst, 1610 sst, 1570 sst, 1545 sst, 1490 st, 1455 m, 1425 st, 1340 sst, 1320 sst, 1290 st, 1285 m, 1230 st, 1140 m, 1115 m, 1100 m, 1075 m, 1035 st, 980 m, 950 m, 915 st, 885 m, 815 st, 755 sst, 740 st, 660 m, 600 m, 560 s, 540 s, 515 s, 440 s, 410 m, 285 s.
- 26** 3420 s, 3250 st, 3070 m, 1660 sst, 1615 sst, 1590 sst, 1555 st, 1535 st, 1485 m, 1475 m, 1425 m, 1415 m, 1350 st, 1310 st, 1290 sst, 1270 st, 1225 st, 1120 m, 1085 st, 1060 st, 1030 st, 965 m, 895 st, 880 m, 830 sst, 800 st, 790 st, 745 sst, 680 st, 670 m, 660 st, 635 m, 570 st, 520 s, 500 s, 400 m, 280 m.
- 27** 3270 m, 3160 s, 3060 m, 1655 sst, 1640 sst, 1615 sst, 1595 sst, 1565 m, 1515 sst, 1450 st, 1365 sst, 1325 st, 1295 st, 1285 m, 1250 st, 1230 m, 1165 st, 1150 st, 1100 m, 1065 st, 1050 st, 910 m, 885 m, 850 st, 815 m, 790 m, 760 m, 750 m, 740 st, 615 m, 545 s, 500 s, 410 s, 385 s, 305 s.
- 28** 3270 st, 3200 st, 3060 m, 1660 sst, 1610 sst, 1575 m, 1560 st, 1535 st, 1480 m, 1440 st, 1425 st, 1415 m, 1350 st, 1335 st, 1310 st, 1280 m, 1265 st, 1170 m, 1160 m, 1140 st, 1100 m, 1075 st, 1030 sst, 995 m, 975 m, 910 st, 885 m, 810 m, 795 m, 755 st, 740 sst, 695 m, 600 m, 570 s, 475 s, 460 s, 440 s, 355 s.
- 29** 3300 st, 3220 st, 3030 m, 1670 st, 1625 sst, 1560 sst, 1480 m, 1425 st, 1345 sst, 1300 m, 1275 s, 1170 s, 1125 st, 1080 m, 1000 st, 910 m, 890 st, 800 st, 740 sst, 685 sst, 650 m, 550 s, 460 st, 415 s, 400 s, 340 st.
- 30** 3430 m, 3300 m, 3260 st, 1660 sst, 1640 st, 1625 sst, 1600 st, 1565 st, 1545 st, 1495 st, 1435 m, 1340 st, 1310 st, 1280 m, 1150 m, 1135 m, 1120 m, 1100 sst, 1080 m, 1040 m, 1030 m, 980 m, 950 m, 900 m, 880 m, 855 st, 790 m, 760 st, 745 sst, 670 m, 640 s, 580 s, 525 m, 470 s, 390 s, 350 s.
- 31** 3200 m, 3120 s, 3060 s, 1660 sst, 1610 sst, 1595 m, 1565 m, 1535 st, 1475 m, 1430 st, 1340 st, 1310 st, 1260 m, 1160 m, 1125 m, 1090 m, 1035 sst, 975 m, 905 m, 885 m, 795 m, 745 sst, 600 m, 565 s, 450 s, 385 s, 330 s.
- 32** 3300 s, 3200 st, 3050 s, 1640 sst, 1605 sst, 1560 st, 1550 st, 1445 m, 1420 m, 1350 sst, 1310 m, 1290 m, 1270 m, 1140 st, 1095 m, 1060 st, 1035 st, 950 s, 900 s, 880 m, 800 m, 775 m, 735 st, 720 m, 685 s, 670 m, 590 m, 560 s, 450 s, 410 s, 330 s, 300 m.

TABELLE III (Fortsetzung)

- 33 3420 st, 3250 st, 1655 sst, 1615 sst, 1565 sst, 1545 m, 1485 st, 1420 m, 1340 m, 1310 st, 1285 m, 1145 m, 1070 m, 1030 st, 1010 m, 970 m, 945 m, 900 m, 880 s, 835 m, 815 m, 780 m, 735 sst, 665 s, 590 m, 575 m, 490 s, 440 s, 380 s, 325 s, 300 s, 285 m.
- 34 3400 m, 3220 m, 3050 s, 1645 sst, 1610 sst, 1585 m, 1550 st, 1530 st, 1450 m, 1425 st, 1350 m, 1335 st, 1300 sst, 1265 m, 1255 m, 1115 m, 1065 m, 1035 st, 1020 m, 955 m, 905 m, 885 m, 815 m, 745 st, 695 m, 640 m, 575 m, 560 m, 515 s, 445 s, 375 s, 365 s, 320 s, 300 s, 290 s.
- 35 3190 m, 3120 s, 3040 s, 1635 sst, 1600 sst, 1560 m, 1540 st, 1440 m, 1350 st, 1300 m, 1285 m, 1265 m, 1135 st, 1090 m, 1055 m, 990 m, 950 m, 895 s, 880 m, 800 m, 755 m, 735 st, 705 m, 685 m, 670 s, 590 s, 560 s, 445 s, 310 s, 285 s.
- 36 3300 s, 3220 m, 3150 s, 3070 s, 1645 sst, 1610 sst, 1590 m, 1550 st, 1485 m, 1450 m, 1360 m, 1340 m, 1310 st, 1135 m, 1060 m, 1040 m, 1010 st, 980 m, 950 m, 905 m, 885 m, 840 st, 790 m, 745 st, 670 m, 595 s, 545 s, 450 s, 385 s, 290 s.
- 37 3110 s, 3070 s, 1695 sst, 1615 m, 1595 st, 1580 m, 1565 m, 1500 st, 1485 sst, 1475 sst, 1440 st, 1430 st, 1330 sst, 1290 st, 1280 st, 1235 st, 1220 m, 1135 sst, 1085 m, 1055 s, 1000 m, 900 m, 825 s, 810 st, 790 m, 760 st, 750 st, 740 st, 670 m, 660 st, 650 st, 580 s, 540 m, 525 m, 420 m, 410 m, 380 s.
- 38 3100 s, 3050 s, 1690 sst, 1590 sst, 1575 st, 1565 m, 1545 st, 1515 m, 1485 st, 1465 st, 1445 st, 1435 sst, 1425 m, 1330 sst, 1290 st, 1260 sst, 1190 m, 1150 m, 1125 sst, 1050 m, 1000 m, 895 s, 835 sst, 805 st, 740 st, 735 m, 720 st, 680 s, 650 st, 615 m, 575 m, 525 s, 410 m, 400 m, 370 s.
- 39 3110 s, 3060 s, 1700 sst, 1610 sst, 1590 st, 1580 m, 1565 m, 1550 m, 1505 sst, 1475 st, 1435 st, 1330 st, 1310 m, 1285 st, 1265 st, 1255 st, 1240 sst, 1235 st, 1170 st, 1155 m, 1140 st, 1105 m, 1055 s, 1000 m, 900 m, 755 m, 740 m, 725 m, 685 m, 670 m, 655 st, 640 m, 615 m, 575 m, 500 s, 410 s, 365 s.
- 40 3180 s, 3140 s, 3070 s, 1695 sst, 1595 m, 1590 m, 1570 s, 1500 st, 1470 st, 1440 st, 1425 m, 1410 m, 1330 st, 1280 m, 1270 m, 1250 st, 1140 st, 1125 m, 1105 m, 1080 st, 1055 m, 1050 s, 1000 st, 965 m, 900 st, 810 st, 790 m, 775 m, 750 st, 740 st, 715 m, 670 m, 650 st, 640 m, 580 s, 465 s, 400 m, 355 s.
- 41 3100 s, 3060 s, 1695 sst, 1590 m, 1575 st, 1545 m, 1510 m, 1465 st, 1330 st, 1285 st, 1245 st, 1140 m, 1110 m, 1080 m, 1000 m, 975 s, 905 s, 805 st, 785 st, 755 m, 740 st, 715 st, 680 s, 650 m, 575 s, 475 s, 400 s, 340 s.

TABELLE III. (Fortsetzung)

- 42 3100 s, 3060 s, 1680 sst, 1590 sst, 1565 m, 1550 m, 1520 st, 1490 sst, 1470 sst, 1335 sst, 1305 sst, 1295 m, 1285 st, 1270 sst, 1255 sst, 1185 m, 1160 m, 1140 st, 1115 st, 1095 st, 1080 st, 1055 m, 1010 st, 1000 m, 905 st, 890 st, 855 sst, 835 m, 805 st, 760 m, 750 st, 735 st, 685 m, 670 m, 660 st, 615 st, 590 m, 525 st, 410 m, 350 m.
- 43 3170 s, 3080 s, 1690 sst, 1585 m, 1500 st, 1465 st, 1430 sst, 1420 m, 1325 st, 1275 m, 1265 m, 1250 st, 1150 m, 1140 st, 1120 m, 1075 m, 1000 st, 900 st, 790 st, 780 st, 680 m, 650 st, 580 m, 400 m, 375 s.
- 44 3090 s, 3060 s, 1695 sst, 1590 s, 1580 m, 1565 m, 1545 m, 1520 m, 1465 st, 1430 st, 1330 st, 1310 m, 1285 st, 1265 st, 1245 st, 1145 st, 1075 m, 1000 m, 905 m, 875 m, 810 st, 785 m, 750 m, 740 st, 720 m, 710 st, 675 m, 655 m, 615 m, 580 s, 400 s, 375 s.
- 45 3130 s, 3050 s, 1675 sst, 1585 sst, 1560 m, 1545 m, 1520 m, 1480 st, 1465 st, 1430 st, 1330 st, 1300 st, 1280 m, 1265 st, 1250 st, 1150 m, 1135 st, 1110 st, 1080 st, 1070 st, 1050 m, 1005 st, 995 m, 900 st, 885 st, 850 st, 830 m, 800 st, 750 st, 740 st, 725 st, 705 m, 680 m, 665 m, 655 st, 610 m, 580 m, 500 m, 400 m, 325 m.
- 46 3280 s, 3070 s, 1685 sst, 1670 st, 1630 st, 1585 m, 1530 st, 1490 m, 1470 st, 1430 sst, 1330 sst, 1290 m, 1265 st, 1255 m, 1150 m, 1140 st, 1115 m, 1085 m, 1065 m, 1005 m, 900 m, 810 st, 765 m, 740 st, 690 sst, 675 m, 655 st, 620 m, 580 s, 400 s, 340 s.
- 47 3100 s, 3060 s, 1690 sst, 1590 m, 1555 st, 1540 st, 1520 m, 1460 st, 1430 st, 1405 m, 1325 st, 1310 m, 1280 st, 1260 st, 1245 m, 1140 st, 1135 m, 1075 m, 1050 m, 995 m, 965 m, 900 m, 875 m, 805 st, 785 m, 740 st, 705 st, 675 m, 650 m, 610 m, 575 s, 460 s, 410 s, 400 s, 310 s, 300 s.
- 48 3090 s, 3050 s, 1685 sst, 1580 st, 1560 s, 1510 m, 1465 st, 1430 st, 1420 st, 1325 st, 1300 m, 1280 m, 1260 st, 1250 st, 1130 st, 1105 st, 1070 m, 1050 s, 1005 st, 995 m, 895 m, 885 m, 835 m, 800 st, 740 st, 720 st, 650 st, 610 m, 580 m, 400 s, 315 s, 300 s.

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Intensität der Absorptionsbande: sst = sehr stark, st = stark, m = mittelstark, s = schwach, sh = Schulter.

Die IR-Spektren der Hydrazone weisen eine sehr starke Bande im Bereich 1700-1635  $\text{cm}^{-1}$  auf, welche der Valenzschwingung der Carbonylgruppe  $\nu(\text{C}=\text{O})$  oder Amidbande I zugeordnet werden kann<sup>8,29-32</sup>. Diese Bande und das gleichzeitige

Auftreten der (N-H)-Valenzschwingung bei  $3430\text{--}3170\text{ cm}^{-1}$  weisen auf die Keto-Struktur der Hydrazone in festem Zustand hin (bei bekanntem Gleichgewicht zwischen Keto- und Enol-Form).

Ein Vergleich der IR-Spektren der drei (o-, m-, p-) Isomeren zeigt, daß die Wellenzahl der (C=O)-Valenzschwingung bei o-Isomeren gegenüber den m- bzw. p-Isomeren bis zu  $20\text{ cm}^{-1}$  zu höheren Frequenzen (mit Ausnahme der Verbindungen 28, 37 und 43) verschoben ist, da die Halogenatome +R und -I-Effekt verursachen<sup>23,28</sup> und bei o-Stellung einen zusätzlichen sterischen Effekt erbringen<sup>20-23</sup>.

In Bereich  $1630\text{--}1500\text{ cm}^{-1}$  werden neben den (C=O)-Absorptionen noch zwei bis vier weitere starke bis mittelstarke Banden beobachtet. Von diesen sind die kurzwelligen der Aminocarbenschwingung  $\nu$  (C=N) zuzuordnen<sup>33-36</sup>; die übrigen lassen sich noch nicht eindeutig zuordnen, weil im selben Bereich auch die Amidbande II sowie die Absorptionen von  $\nu$  (C=C) bzw. des aromatischen Kerns liegen<sup>29</sup>.

Bei Fluoro- und Chloro-benzoylhydrazonen tritt je eine starke Bande im Bereich  $1100\text{--}1000\text{ cm}^{-1}$  bzw.  $750\text{--}700\text{ cm}^{-1}$  auf, die der Valenzschwingung der (C-F)- bzw. (C-Cl)-Gruppe zuzuordnen ist<sup>38</sup>, während bei Bromo- und Iodo-hydrazonen keine derartigen charakteristischen starken Einzelbanden im Bereich der zu erwartenden (C-Br)- bzw. (C-I)-Valenzschwingungen erscheinen sondern viele schwache bis mittelstarke Banden.

Die (N-N)-Valenzschwingung ist ebenfalls nur wenig charakteristisch und liegt im Bereich  $1040\text{--}970\text{ cm}^{-1}$ <sup>39,41</sup>, in dem gleichzeitig viele andere Banden auftreten; aus den vorliegenden Daten ist daher keine eindeutige Zuzuordnung möglich.

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## Summary

### *Monohalogenobenzoylhydrazones I.*

*Preparation, properties, u.v. and i.r. spectra of new monohalogenobenzoylhydrazones of 2-furaldehyde, 2-thiophenylaldehyde, 2-pyrrolaldehyde and di-2-pyridylketone*

New o-, m-, p-, fluoro-, chloro-, bromo- and iodo- benzoylhydrazones of 2-furaldehyde, 2-thiophenylaldehyde, 2-pyrrolaldehyde and di-2-pyridylketone have been prepared and characterised. u.v. and i.r. data for the mentioned compounds are reported and discussed. The orthoposition of the halogen atoms at the benzene ring causes a hypsochromic effect on the main band of the u.v. spectra as well a shift of  $\nu$  (C=O) in the i.r. spectra.

**Key words :** Monohalogenobenzoylhydrazones, fluorobenzoylhydrazones, chlorobenzoylhydrazones, bromobenzoylhydrazones iodobenzoylhydrazones, 2-furaldehyde, 2-thiophenylaldehyde, 2-pyrrolaldehyde, di-2-pyridylketone, preparation, u.v. spectra, i.r. spectra.

## Περίληψη

### *Μονοαλογονοβενζοϋλοϋδραζόνες I.*

*Παρασκευή, ιδιότητες και φάσματα u.v. και i.r. νέων μονοαλογονοβενζοϋλοϋδραζονών της 2-φουραλδεϋδης, 2-θειοφαιναλδεϋδης, 2-πυρρολαλδεϋδης και δι-2-πυριδυλοκετόνης*

Παρασκευάζονται και χαρακτηρίζονται νέες ορθο-, μετα- και παρα- φθορο-, χλωρο-, βρωμο- και ιωδο- βενζοϋλοϋδραζόνες της 2-φουραλδεϋδης, 2-θειοφαιναλδεϋδης και δι-2-πυριδυλοκετόνης. Παρέχονται και συζητούνται τα δεδομένα των φασμάτων υπεριώδους-ορατού και υπερύθρου των ενώσεων αυτών. Διαπιστώνεται ότι, όταν το αλογόνο στον βενζολικό πυρήνα βρίσκεται σε ορθο- θέση, προκαλεί μία υψιχρωμική μετατόπιση της κυρίας ταινίας στα φάσματα υπεριώδους-ορατού, καθώς και της χαρακτηριστικής απορροφήσεως της ν (C = O) στα φάσματα υπερύθρου προς υψηλότερες συχνότητες.

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## **THERMODYNAMICS OF LOCALIZED AND NON - LOCALIZED ADSORPTION OF GAS MIXTURES ON HOMOGENEOUS SURFACES**

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### **Summary**

A generalized model for the mixed-gas adsorption on homogeneous surfaces is developed by means of lattice statistical thermodynamics. On the basis of this model the adsorption isotherms and the various thermodynamic functions are derived both for mobile and localized monolayers and the main approximations involved in this treatment are discussed.

**Key Words** : Lattice statistical thermodynamics, Hole theory, Physical adsorption.

### **I. Introduction**

In a series of previous publications<sup>1,2</sup> the monolayer pure gas adsorption on homogeneous surfaces has been studied by means of the hole theory. This study has revealed that the hole theory can offer an almost quantitative description of the adsorption isotherm as well as of the other adsorption parameters under the condition that the adsorbed particles on the adsorption surface form a liquid-like layer. It was also shown that a quantitative description of the liquid state by this theory implies a satisfactory description for liquid mixtures<sup>3</sup>. Therefore the hole theory is expected to equally well describe the mixed gas adsorption when on the adsorption surface a two-dimensional liquid-like mixture is formed by the adsorbed particles.

The scope of the present work is to extend the hole theory to mixed gas adsorption on homogeneous surfaces. In particular our purpose is to develop a generalized model including either mobile or localized adsorption and further on the basis of this model to determine the adsorption isotherms and the main thermodynamic functions of the adsorption layer for the case of mixed gas adsorption.

### **II. Theoretical Treatment**

#### *a. The model*

The adsorption layer is considered as a two-dimensional closed system of N

molecules arranged on it according to a regular lattice structure. In this system we also assume that each molecule occupies only one lattice site. The number of sites  $L$  is greater than  $N$  so that there will be a number of empty sites or holes on the adsorption layer. The sites may be considered as fixed points (localized adsorption) or as cells into which the adsorbed molecules can move (mobile adsorption).

If the system is composed of  $r$  components, then the  $L$  lattice sites are occupied by  $N_1$  molecules of type 1,  $N_2$  molecules of type 2, ...,  $N_r$  molecules of type  $r$ , while there are  $L-N$  holes on the adsorption layer. It is supposed that all molecules have similar diameters and they are under the influence of (a) the field of the adsorption surface and (b) the field of the nearest neighbouring molecules (nearest neighbouring statistics).

### b. Partition function

In order to determine the partition function of the adsorption layer we consider the holes as being the  $r+1$  component of the system. Thus the adsorption layer is considered as a two-dimensional mixture of  $L$  "molecules" of  $r+1$  different species.

The partition function  $q_{ij}$  of the  $j$ th molecule of type  $i$  ( $i=1, \dots, r+1$ ) is

$$q_{ij} = q_{\text{int}(ij)} q_{\text{trans}(ij)} \exp\left(\frac{U_i}{kT}\right) \exp\left(-\frac{w_i}{kT}\right) \quad (1)$$

with  $q_{r+1,j} = 1$ .

In Eq. (1)  $q_{\text{int}(ij)}$  and  $q_{\text{trans}(ij)}$  are the internal and the translational partition functions of the  $j$ th molecule, respectively. Evidently, when the lattice sites are considered as points we have

$$q_{\text{trans}(ij)} = 1 \quad (2)$$

whereas, when the lattice sites are considered as cells into which the adsorbed molecules can move, we have

$$q_{\text{trans}(ij)} = \lambda_i a_{fij} \quad (3)$$

where  $\lambda_i$  is equal to  $2\pi m_i kT/h^2$ ,  $m_i$  is the mass of a molecule of type  $i$ ,  $T$  is the absolute temperature,  $k, h$  are Boltzmann's and Planck's constants, respectively and  $a_{fij}$  is the free surface area available for the motion of the  $j$ th molecule in its cell.

Finally the last two factors in Eq. (1) stand for a correction for the energy zero.  $U_i$  is the adsorbate-adsorbent interaction energy, while  $w_i$  is the adsorbate-adsorbate interaction energy. This last term can be calculated on a random distribution basis<sup>4</sup>, with each molecule at the centre of its cell. If  $c$  is the coordination number of lattice of the adsorption layer,  $u_{kh}(0)$  the interaction energy between a pair of nearest neighbouring molecules of type  $k$  and  $h$  respectively when they are in the centre of their cell and  $\theta_i$  is the degree of coverage



of the adsorption surface from the molecules of type  $i$ , then the interaction energy per molecule of type  $i$  is given by :

$$\frac{w_i}{kT} = \frac{c\theta_i u_{ii}(0) + 2 \sum_{\ell>i} c\theta_\ell u_{i\ell}(0)}{2kT} \quad (4)$$

The total partition function of the adsorption layer can be obtained by multiplying  $q_{ij}$  and adding over all the permissible arrangements of the  $N$  molecules:

$$Q = \sum_{\langle N \rangle} \prod_{ij} q_{ij} \quad (5)$$

Assuming that the internal degrees of freedom do not depend on the presence of other molecules in the lattice, we have

$$\prod_{ij} q_{\text{int}(ij)} = \prod_i (q_{\text{int}(i)})^{N_i} \quad (6)$$

The sum in Eq. (5) is easily calculated by the Bragg-Williams approximation<sup>4</sup>, in which a random distribution of the adsorbed molecules is assumed. The general expression for the partition function obtained may be represented by:

$$Q = \frac{L!}{\prod_i N_i! (L-N)!} \prod_i \left\{ \exp \frac{N_i U_i}{kT} (q_{\text{int}(i)} q_{\text{trans}(i)})^{N_i} \right\} \exp \left\{ -\frac{Lu(0)}{2kT} \right\} \quad (7)$$

where

$$u(0) = c \sum_{i=1}^r \left[ \theta_i^2 u_{ii}(0) + 2 \sum_{\substack{\ell \neq i \\ \ell > i}}^r \theta_i \theta_\ell u_{i\ell}(0) \right] \quad (8)$$

In Eq. (7)  $q_{\text{trans}(i)}$  is taken approximately the same for all molecules of type  $i$  due to the random distribution approximation.

### c. Adsorption isotherms

1. *Mobile adsorption.* In this case the adsorbed phase is considered as a two-dimensional liquid-like layer. Thus we have<sup>1,5,6</sup>

$$q_{\text{trans}(i)} = \lambda_i a_f \quad (9)$$

where the free area  $a_f$  is assumed to be approximately the same for all the molecules due to the random distribution approximation and also because all molecules were assumed to be of similar dimensions.

For the calculation of the adsorption isotherms it is necessary to approximate the free area by means of a formalistic expression. In the present work we will make use of the linear approximation<sup>6</sup>,

$$a_f = \theta a_f(0) + (1-\theta)\omega \quad (10)$$

which has been successfully employed to the study of pure gas adsorption when the adsorbed molecules form a mobile layer<sup>1,2</sup>.

In Eq. (10)  $\theta$  is the fraction of the total surface covered with adsorbed molecules and is given by:

$$\theta = \frac{N}{L} = \sum \frac{N_i}{L} = \sum \theta_i \quad (11)$$

The parameter  $\omega$  in Eq. (10) is the free area of an adsorbed molecule having empty all its nearest neighbouring sites. This area is given by:

$$\omega = A/L$$

where  $A$  is the area of the adsorption surface. For a hexagonal close packed configuration we have

$$\omega = \sqrt{3}\alpha^2/2 \quad (12)$$

where  $\alpha$  is the nearest neighbouring distance between the adsorbed molecules.

Finally, the parameter  $a_f(0)$  in Eq. (10) is the free area when  $L = N$ . In the case of a mixture,  $a_f(0)$  depends on the composition of the adsorption surface<sup>7</sup> i.e. it depends on  $\theta$ . However the area  $a_f(0)$  is so small that it can be approximately set:

$$a_f = (1 - \theta) \omega \quad (13)$$

The chemical potential of the  $i$  molecule in the adsorption layer may now be calculated from

$$\frac{\mu_i}{kT} = - \left( \frac{\partial \ln Q}{\partial N_i} \right)_{L, T, N_{i \neq i}} \quad (14)$$

which yields

$$\frac{\mu_i}{kT} = -\ln(\lambda_i q_{int(i)} \omega) + \ln \frac{\theta_i}{(1-\theta)^2} + \frac{\theta_i}{1-\theta} - \frac{U_i}{kT} + \sum_{\ell=1}^r \theta_\ell \frac{cu_{i\ell}(0)}{kT} \quad (15)$$

At equilibrium,  $\mu_i$  in Eq. (15) must equal the chemical potential of the  $i$  component of the gas phase:

$$\mu_i = \mu_i^{\text{gas}} \quad i = 1, 2, \dots, r \quad (16)$$

For a perfect gas we have

$$\frac{\mu_i^{\text{gas}}}{kT} = \ln P_i - \ln(kT q_{int(i)}^{\text{gas}} \lambda_i^{3/2}) \quad (17)$$

where  $P_i$  is the partial pressure of the  $i$  gas in the bulk gas phase.

The adsorption isotherms obtained from Eqs. (16) may be expressed by:

$$\ln P_i = \ln \frac{\lambda_i^{1/2} kT q_{int(i)}^{\text{gas}}}{q_{int(i)} \omega} - \frac{U_i}{kT} + \ln \frac{\theta_i}{(1-\theta)^2} + \frac{\theta}{1-\theta} + \sum_{\ell=1}^r \theta_\ell \frac{cu_{i\ell}(0)}{kT} \quad (18)$$

$$\text{or } \frac{\theta_i}{(1-\theta)^2} \exp \frac{\theta}{1-\theta} \exp \left( \sum_{j=1}^r \theta_j A_{ij} \right) = P_i K_i \quad (19)$$

where

$$A_{ij} = cu_{ij}(0) / kT \quad (20)$$

and

$$K_i = (q_{\text{int}(i)} \omega / \lambda_i^{1/2} kT q_{\text{int}(i)}^{\text{gas}}) \exp(U_i / kT) \quad (21)$$

We observe that a system of  $r$  isotherms with  $r$  unknowns, vis  $\theta_i$ , is obtained. The molecular parameters of these isotherms can be determined from the corresponding experimental isotherms. In the case of relatively simply structured, non polar, molecules these parameters can be determined theoretically by means of the molecular properties of the adsorbed gases, except the gas-solid interaction  $U_i$  which is usually determined from experimental data<sup>1,2</sup>. Thus for the various parameters we have:

The partition functions  $q_{\text{int}}$ ,  $q_{\text{int}}^{\text{gas}}$  can be calculated from the vibration and rotation partition functions of the adsorbed molecules<sup>7,8</sup>.

The potentials  $u_{hk}(0)$  assuming that the adsorbate-adsorbate interactions can be represented by the Lennard-Jones 6:12 potential, are given by

$$u_{hk}(0) = 4\varepsilon_{hk} \{ (\sigma_{hk}/\alpha)^{12} - (\sigma_{hk}/\alpha)^6 \} \quad (22)$$

The parameters  $\varepsilon_{hh}$ ,  $\sigma_{hh}$  can be determined from the properties of the pure components, while the determination of  $\varepsilon_{hk}$ ,  $\sigma_{hk}$  ( $h \neq k$ ) calls for the use of a certain mixing rule. The relationships usually involved are the following<sup>3</sup>:

$$\sigma_{hk} = (\sigma_{hh} + \sigma_{kk}) / 2 \quad (23)$$

$$\varepsilon_{hk} = \xi_{hk} (\varepsilon_{hh} \cdot \varepsilon_{kk})^{1/2} \quad (24)$$

where  $\xi_{hk}$  is an empirical factor used to correct deviations from the geometric mean. In practice it is used to employ  $\xi_{hk}$  as an adjustable parameter<sup>9,10</sup>.

Finally  $\omega$  can be determined from Eq. (12) provided that  $\alpha$  is approximately equal to the mean value of  $2^{1/6} \sigma_{hk}$ , or, more refined, it can be calculated by minimizing the Helmholtz free energy,  $A$ , of the adsorbed phase<sup>1,3,6,11</sup>. This thermodynamic function is related to the partition function  $Q$  by the equation

$$A = -kT \ln Q \quad (25)$$

which results to

$$\frac{A}{kT} = \sum N_i \left\{ \frac{1}{\theta} \ln(1-\theta) + \ln \frac{\theta_i}{(1-\theta)^2} - \frac{U_i}{kT} - \ln(q_{\text{int}(i)} \lambda_i \omega) \right\} + \frac{Lu(0)}{2kT} \quad (26)$$

Therefore  $\omega$  can be calculated from the equation

$$(\partial A / \partial \omega)_{A, T, N, N_i} = 0 \quad (27)$$

2. *Localized adsorption.* In this case each adsorbed molecule is restricted on a single adsorption site being unable to perform translational motion on the adsorption layer. Thus we have

$$q_{\text{trans}(i)} = 1 \quad (28)$$

The partial chemical potential of the  $i$ th adsorbed molecule is then

$$\frac{\mu_i}{kT} = \ln \frac{\theta_i}{1-\theta} - \frac{U_i}{kT} + \sum_{\ell=1}^r \theta_\ell \frac{cu_{i\ell}(0)}{kT} - \ln q_{\text{int}(i)} \quad (29)$$

and equating to the partial potential of the  $i$ th component in the gas phase, we have

$$\ln P_i = \ln \frac{\lambda_i^{3/2} kT q_{\text{int}(i)}^{\text{gas}}}{q_{\text{int}(i)}} - \frac{U_i}{kT} + \ln \frac{\theta_i}{1-\theta} + \sum_{\ell=1}^r \left\{ \theta_\ell \frac{cu_{i\ell}(0)}{kT} \right\} \quad (30)$$

or

$$\frac{\theta_i}{1-\theta} \exp \left( \sum_{\ell=1}^r \theta_\ell A_{i\ell} \right) = P_i K_i \quad (31)$$

where

$$A_{i\ell} = cu_{i\ell}(0)/kT \quad (32)$$

and

$$K_i = (q_{\text{int}(i)}/\lambda_i^{3/2} kT q_{\text{int}(i)}^{\text{gas}}) \exp(U_i/kT). \quad (33)$$

As it was expected, in the case of localized adsorption, a system of  $r$  Frumkin's type isotherms is obtained<sup>12</sup>.

#### d. Thermodynamic functions

The various thermodynamic functions can be determined by statistical mechanics by means of the partition function  $Q$ , equation<sup>7</sup>. Thus we have<sup>2,7</sup>:

##### 1. Mobile adsorption.

The internal energy,  $E$ , is related to the partition function  $Q$  by the equation<sup>7</sup>

$$E = kT^2 \cdot \left( \frac{\partial \ln Q}{\partial T} \right) \quad (34)$$

which yields

$$E = \sum_{i=1}^r N_i \left\{ -U_i + kT + kT^2 \frac{\partial \ln q_{\text{int}(i)}}{\partial T} \right\} + \frac{Lu(0)}{2} \quad (35)$$

The isosteric heat  $Q_{\text{st}(i)}$  of the  $i$ th adsorbed component is given by<sup>13</sup>.

$$Q_{st(i)} = H_{g(i)} - \left( \frac{\partial E}{\partial N_i} \right) = H_{g(i)} - RT + U_i - RT^2 \frac{\partial \ln q_{int(i)}}{\partial T} - \sum_{l=1}^r \theta_l \frac{cRu_{il}(0)}{k} \tag{36}$$

where  $H_{g(i)}$  is the enthalpy of the  $i$ th component in the bulk gas phase.

Finally, the integral entropy,  $S$ , can be determined by the equation

$$S = \frac{E}{T} + k \ln Q \tag{37}$$

which gives

$$\frac{S}{k} = \sum_{i=1}^r N_i \left\{ 1 + T \frac{\partial \ln q_{int(i)}}{\partial T} + \ln(q_{int(i)} \lambda_i \omega) - \ln \frac{\theta_i}{(1-\theta)^2} - \frac{1}{\theta} \ln(1-\theta) \right\} \tag{38}$$

2. Localized adsorption

The thermodynamic properties of this model are given by the following relations:

$$\frac{A}{kT} = \sum N_i \left\{ \frac{1}{\theta} \ln(1-\theta) + \ln \frac{\theta_i}{1-\theta} - \frac{U_i}{kT} - \ln q_{int(i)} \right\} + \frac{Lu(0)}{2kT} \tag{39}$$

$$E = \sum N_i \left\{ -U_i + kT^2 \frac{\partial \ln q_{int(i)}}{\partial T} \right\} + \frac{Lu(0)}{2} \tag{40}$$

$$Q_{st(i)} = H_{g(i)} + U_i - RT^2 \frac{\partial \ln q_{int(i)}}{\partial T} - \sum_{k=1}^r \theta_k \frac{cRu_{ik}(0)}{k} \tag{41}$$

$$\frac{S}{k} = \sum N_i \left\{ T \frac{\partial \ln q_{int(i)}}{\partial T} + \ln q_{int(i)} - \ln \frac{\theta_i}{1-\theta} - \frac{1}{\theta} \ln(1-\theta) \right\} \tag{42}$$

III. Discussion

In the present work a generalized model of the mixed gas adsorption on homogeneous surfaces was developed. The over all elaboration was kept on a purely theoretical level. The analysis of mobile as well as of localized adsorption by means of this model apparently covers all the experimental systems involving physical monolayer adsorption and chemisorption. However the fundamental assumptions which have been made impose certain restrictions to the choise of the experimental systems to which this treatment is applicable. These assumptions are the following: (1) The adsorption surface must be energetically uniform. Actual surfaces deviate to a certain degree from this assumption due to the existence of impurities, cracks, dislocations, different crystal surface etc.<sup>14</sup> Therefore, before any application of this model we must assure that the effect of the non-uniformity of the adsorbent surface

is negligible on the adsorption process. (2) The adsorbed phase must be composed of spherical molecules of equal size interacting with isotropic field forces. This is a critical assumption especially when mobile adsorption is examined. As it has been shown<sup>3</sup> for the case of liquid mixtures, the hole theory provides a quantitative description of these mixtures only when this requirement is fulfilled.

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## Περίληψη

*Θερμοδυναμική της τοπικής και κινητής προσρόφησης αέριων μιγμάτων σε ομογενείς επιφάνειες.*

Στην εργασία αυτή αναπτύχθηκε ένα γενικευμένο μοντέλο της μικτής προσρόφησης αερίων πάνω σε ενεργειακά ομογενείς επιφάνειες. Η στιβάδα προσρόφησης θεωρείται σαν ένα διδιάστατο κλειστό σύστημα, τα σωματίδια της οποίας κατανέμονται ακολουθώντας τη γεωμετρία ενός κανονικού πλέγματος. Κάθε προσροφημένο σωματίδιο καταλαμβάνει μόνο μία πλεγματική θέση. Ο αριθμός αυτών των θέσεων είναι πάντα μεγαλύτερος από τον αριθμό των προσροφημένων σωματιδίων, με αποτέλεσμα στη στιβάδα προσρόφησης να υπάρχει ένας αριθμός κενών πλεγματικών θέσεων (οπών). Υποθέτοντας μία τυχαία κατανομή οπών και προσροφημένων σωματιδίων προσδιορίζεται η συνάρτηση κατανομής του συστήματος και ακολούθως με βάση αυτήν προσδιορίζονται οι ισόθερμες προσρόφησης και οι κυριότερες θερμοδυναμικές συναρτήσεις της προσροφημένης στιβάδας. Η κινητή και η τοπική προσρόφηση αποδεικνύεται ότι προκύπτουν σαν μερικές περιπτώσεις του γενικευμένου αυτού μοντέλου.

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## **FREE LIME PRODUCED DURING THE HYDRATION OF FLY ASH CEMENT**

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### **Summary**

The hydration of fly ash cement is not a simple process, and has not been studied completely yet. Chemical characteristics play an important role and are easily measured, in comparison. The aspect of free lime, produced during the hydration reactions and the influence of fly ash content are examined in this paper. A 20 % partly replacement of cement by fly ash in mortars gave very promising results.

**Key words:** Calcium hydroxide, lime, fly ash, Portland cement, hydration, pozzolanic reaction.

### **Introduction**

The prospects for using the vast range of pozzolanic materials in the cement industry have been recently reviewed<sup>1</sup>. Among these materials particular emphasis is placed on fly ashes, produced from pulverized burnt coal in thermoelectric plants, not only for aspects linked with energy shortage and the possible use of industrial by-products, but essentially for the positive effects these materials produce, when mixed with Portland cement.

In this field research is particularly fostered, in our country as well<sup>2</sup>. During 1983 the expectations for the production of lignite fly ash from the plants go up to  $4.44 \times 10^6$  t, while the cement industries estimate to buy this year approximately  $1.25 \times 10^6$  t for their own needs. Today's industrial practice is an addition of fly ash of around 15 %.

The above figures give just a rough idea of the whole problem, and we believe that it is a good reason for our laboratory's research to be going on<sup>3</sup>, particularly from the chemical point of view. Different parameters of test mortars were measured with promising results, and among them the compressive strength (which is considered to be one of the most important and representative properties) in order to evaluate the quality of pozzolana. It was thought that experimental work on the pozzolanic reactivity of the greek fly ash should follow. Other aspects of fly ash utilization are also under study by us, as for example the possibility of germanium recovery<sup>2</sup>.

Nowadays, much is known<sup>4</sup> on cement hydration, in which actually two mechanisms are involved: direct topochemical reactions, or a through solution mechanism, starting with the dissolution of reactants. The calcium silicates (alite  $C_3S$  and belite  $C_2S$ ) make up approximately 70 % of the cement, and their hydration products will determine mainly the properties of set cement. It is noted that in cement chemistry each oxide is usually described by a single letter and this is adopted here, namely  $CaO = C$ ,  $SiO_2 = S$ ,  $Al_2O_3 = A$ ,  $Fe_2O_3 = F$ ,  $H_2O = H$ , and  $SO_3 = \bar{S}$ . Generally, hydration is indeed a complex phenomenon.

The main cement hydration products are calcium silicate hydrate having the shape of short fibres, with average composition  $C_3S_2H_3$  (sometimes referred as tobermorite gel) and calcium hydroxide, these from the reaction of calcium silicates with water. Also, monosulphate  $C_4A\bar{S}H_{12}$  from tricalcium aluminate ( $C_3A$ ), and phases containing alumina and iron oxide, such as  $C_4AF\bar{S}$ . aq, from the ferrite phase ( $C_4AF$ ). The presence of  $Ca(OH)_2$  makes cement pastes highly alkaline (pH = 12.5) and this explains why such pastes provide good protection to embedded steel against corrosion, but in the meantime why they are very sensitive to acid attack.

It must be said that these products take time to develop and that any other added substance would also take part in the hydration as a reactant. So, gypsum is added to cement to delay its setting. According to the available reactants, hydration products could be later converted, as for example ettringite  $C_6A\bar{S}_3H_{31}$  (which is the immediate hydration product of tricalcium aluminate) converts from about the second day to monosulphate. The ferrite phase reacts in a similar way and when sulphate ions are exhausted, they are replaced by hydroxide ions, as described by Soroka<sup>4</sup>.

Taylor<sup>5</sup> stated recently that much basic work remains to be done on blended cements (mixtures with waste materials), as our knowledge on their hydration chemistry is rather limited. The scope of this paper is to present some of our results on the aspect of free lime, produced during the hydration of cement mixed with fly ash from the Ptolemaida region, which is a pozzolanic material.

## Methods and Results

The cement used in the experimental part<sup>6</sup> was a mixture of clinker, gypsum and blastfurnace slags (without any fly ash) ground together, which was taken from a cement manufacturer in the Thessaloniki area. The fly ash added has been previously crushed in the laboratory in a ball mill. Chemical and other physical characteristics of both cement and fly ash are given in *Table I*. Chemical analysis was done by x-ray, while specific surface by Blaine permeability apparatus.

Four series of test mortars were made, each having the same composition, by mixing sand 68.18% (of the total material) and water 9.09 %; one series had only cement 22.73 %, and the other only fly ash 22.73 %. The other two were blended cements with proportion in fly ash respectively 20 % and 40 % of the total [cement + fly ash] - the latter expression was found more useful. The specimens



were cylinders having a base area of  $4.9 \times 10^{-4} \text{ m}^2$ , height 0.038 m and density around  $1,880 \text{ kg/m}^3$ .

TABLE I: Chemical Composition and Characteristics (% unless stated)

	Cement	Fly Ash
SiO <sub>2</sub>	21.40	25.45
Al <sub>2</sub> O <sub>3</sub>	5.40	16.17
Fe <sub>2</sub> O <sub>3</sub>	4.65	7.97
CaO	62.44	31.91
MgO	1.70	2.78
SO <sub>3</sub>	2.20	8.01
(K,Na) <sub>2</sub> O	0.66	0.53
Loss on ignition	1.88	6.83
HCl acid - insolubles	1.06	16.70
Free CaO	2.21	9.65
Fineness, +90 μm	1.65	7.80
Specific surface (cm <sup>2</sup> /g)	2,400-2,800	~ 5,150

The mortars after made, were put for 24 hours in a place saturated with water vapours and afterwards, were kept for curing in a water bath having temperature  $19 \pm 1 \text{ }^\circ\text{C}$ . Before each measurement of free lime, the test specimen was dried to constant weight (for approximately two hours) in  $110 \text{ }^\circ\text{C}$ . Then it was ground, uniformly mixed and finely crushed so that all the compound passed the sieve of  $150 \text{ }\mu\text{m}$ . From that, samples of 0.2 g were taken, in 200 ml conical flasks for extraction by 100 ml of solvent in a refluxing assembly. The solvent used was a mixture of ethyl acetoacetate and isobutyl alcohol in a 3:20 ratio by volume. Care should be taken in the experiments for moisture, which would give higher results.

The method followed was a modification of the older Franke method, known also as multiple extraction method<sup>7</sup>. Two newer modifications have been proposed<sup>8,9</sup>, performing only a single extraction on each sample, one referred as solvent variation method, and the other one referred as time variation method. The latter was chosen for reasons of solvent economy. These two methods were found in agreement, and has been also checked with x-ray quantitative analysis<sup>8</sup>.

The procedure involved extractions for different periods of time, and extrapolation of the data back to zero time, as illustrated in *Figure 1*. The hydration products contain easily extractable free calcium hydroxide and difficulty extractable combined calcium oxide. In any given extraction, consequently, all or at least a large part of the free calcium hydroxide may be removed and simultaneously, a small amount of the combined calcium oxide. So, a correction was needed.

The researchers from a theoretical analysis<sup>8</sup>, proposed that the total calcium oxide removed in an extraction,  $C_t$ , followed an equation of the form:

$$C_t = C_e + k_3 t$$

where  $t$  is the time and  $k_3$  is a constant. Therefore, a plot of  $C_t$  against  $t$  is a straight line with intercept  $C_e$ , the free calcium oxide. Noting that for the time variation method the amount of firmly bound calcium oxide,  $C_n$ , was given by the simple relation:  $\Delta C_n = k_3 t$ .

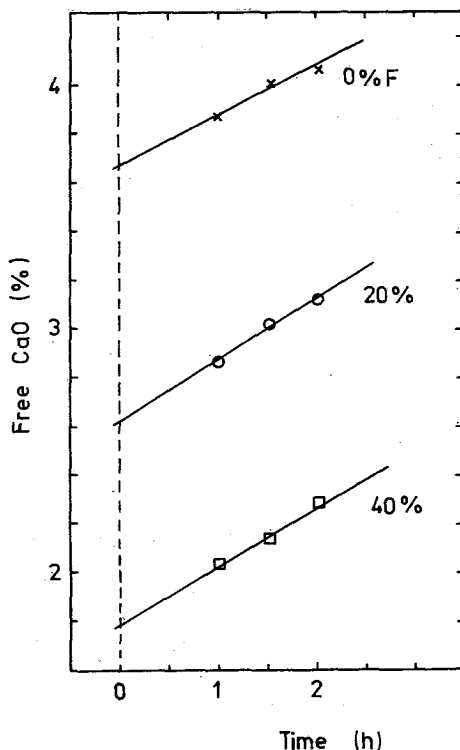


FIG. 1. Example of free calcium oxide evaluation with time of extraction, for test mortars of 28 days at different fly ash (F) content.

The sample and solution obtained from the extraction apparatus was rapidly cooled, filtered in a vacuum assembly and washed, both flask and residue, with small increments of isobutyl alcohol. The solution was then titrated with dilute perchloric acid, adding drops of thymol blue as indicator, according to method ASTM C114-81<sup>9</sup>.

The possibility of presence of calcium hydroxide should be kept in mind, when applied to cement or aged clinker, since the method do not distinguish between total free calcium oxide and hydroxide. An approximate determination of the calcium hydroxide present and hence, by subtracting it from the total, of the free calcium oxide may be obtained, by an additional estimation of the water combined as calcium hydroxide, by means of a simple thermal analysis (and also other techniques).

On heating the cement, water combined in hydrated cement compounds other than calcium hydroxide is mostly evaporated below 350 °C, while that combined in hydroxide is lost almost entirely over the range 350-550 °C. This loss of water may, after a small correction, be used as a measure of the hydroxide content. The correction is due to a small loss of water occurring between 350 and 550 °C from the hydrated cement compounds. It was found with set cements that this second loss at 550 ° is higher, by a factor varying from about 1.07 to 1.12, that at 350 °C<sup>7</sup>.

The results obtained from the experiments are shown in *Figure 2*. The test specimens containing 40 % fly ash exhibited the lower content of free lime. Also after approximately 45 days, the content was quite constant. Generally, it is known that the pozzolanic reaction is slow and the early phenomena are also due to adsorption.

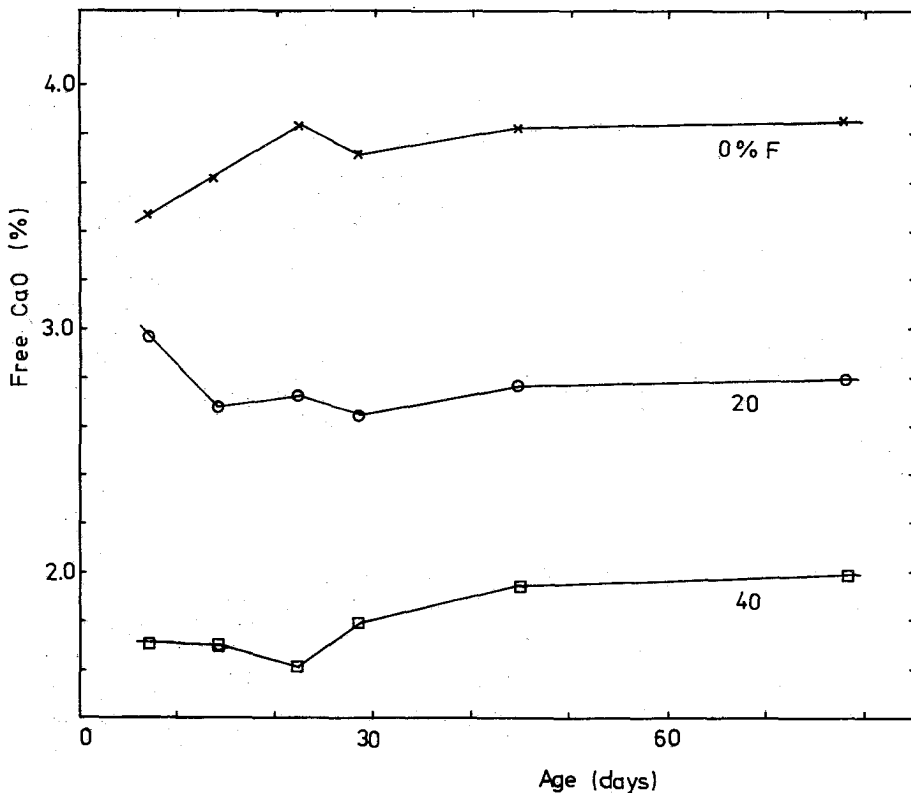


FIG. 2. Free calcium oxide variation in test mortars as a function of the time of wet curing.

The curve of pure cement showed somehow a different shape at early stages. It was possible that, besides, we had here the influence of the slags hydration, which is complex too<sup>10</sup>. After 28 days in this case, there was an increase in the value of free lime. It seems that the slag could not be able to capture any more calcium hydroxide, at least at the rate of its production.

The free lime that the specimens should have as contribution of the free lime content of 0 % and 100 % fly ash proportionally, has been also estimated theoretically, and the values are given for comparison in *Table II*. The experimental values, shown in Figure 2, for free lime were never higher than the theoretical ones.

Finally, calculations were made for the quantity (in g) of calcium hydroxide reacted with 100 g of fly ash, for the cases of 20 % and 40 % fly ash mortars, and are presented as *Figure 3*. These calculations were based on the difference of the experimental from the theoretical value of free lime for the two proportions, with the necessary corrections for the weight of the sample, and the molecular weights ratio to convert to calcium hydroxide.

TABLE II: Theoretical Values of Free CaO

Fly ash content (%)	Age (days)	7	14	22	28	44	77
20		3.03	3.18	3.33	3.34	3.33	3.36
40		2.63	2.80	2.89	2.65	2.92	2.94

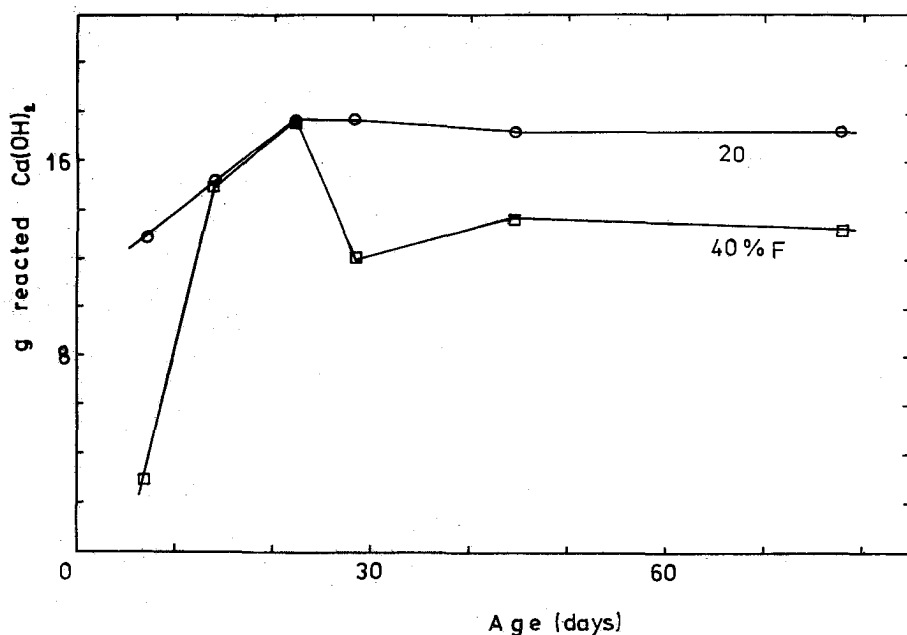


FIG. 3. Degree of pozzolanic reaction expressed in terms of the quantity of bound calcium hydroxide/100 g of fly ash.

## Discussion and Conclusions

For the pozzolanic reaction, currently it is accepted<sup>11</sup> that it is a diffusion-controlled dissolution reaction, which rate determining step (if the kinetics are considered) is the dissolution of unhydrates and the precipitation of products in the early stage, and the diffusion of ions or ion radicals, through amorphous surface layer of pozzolana and precipitated hydrates on the surface of pozzolana, in later stage.

Research has been carried out on the hydration of blended cements, but the conclusions arrived at are not necessarily in agreement<sup>12</sup>. In simple words, the pozzolanas combine with free calcium hydroxide, formed from the silicates hydration. The resulting reduction in the calcium hydroxide content is an explanation, but not the only one, for the improvement in cement qualities, when substituted partly by suitable pozzolanas; for example, the sulphate resistance of concrete.

Sulphate expansion is mainly due to the formation of ettringite. One of the theories advanced to explain the beneficial effect of pozzolanas, attributed that to the effect of calcium hydroxide on the solubility of hydrated calcium aluminates, which is very low in saturated lime solution. Hence, the topochemical (solid state) nature of the sulphate reaction and the resulting expansion.

The decrease in the calcium hydroxide concentration, due to reaction with pozzolana, increases the solubility of the hydrated calcium aluminates and consequently, the sulphate reaction occurs through solution and therefore without expansion. Lea<sup>7</sup>, however, considered this explanation incomplete, and suggested that the improved sulphate resistance results mainly from the greater inhibition of the reaction, by formation of protective calcium silicate hydrate films over the aluminate compounds. Cement corrosion is our current research interest, not only from the point of engineering interest, but also to explain the whole cement behaviour as its properties are interrelated.

Free lime reduction in pozzolanic mortars is attributed mainly to the reaction of silica with calcium hydroxide. It was proved that the silica that takes part in this reaction is only the active fraction, represented by the soluble part in hydrochloric acid. For the fly ash examined this was represented by the 65.6 % of the total silica.

It is also known that the fineness of fly ash (or pozzolana) is a crucial factor. Finer fly ash means more active in the reaction<sup>3</sup>. The solid waste as produced in our power stations has generally a fineness of 15-20% (residue) on the sieve of 90  $\mu\text{m}$ .

The study of pozzolanic activity obviously is not simple, since it presents interlinked aspects (physical, chemical and mechanical) difficult to correlate. The activity could be explained by the thermodynamic instability of the system, composed of lime, pozzolana and water. Besides this reason, it is possible in the pozzolanas to find characteristics more easily measurable and perhaps correlatable with their activity. Among these, the chemical composition plays an important role.

Observations from Figure 3 shows for the 20% fly ash test specimen, after 22 days of wet curing, a rather constant value of the calculated bound mass of calcium

hydroxide per 100 g of fly ash, which seems to be the bind ability of the fly ash sample. However, the 40 % mortar shows a maximum value (about the same with the former) and then a decrease to a lower constant value.

Somehow, in this case lime was unbound from fly ash around 22 days. A possible explanation is the influence of the sulphate content of fly ash, which was quite high in our test sample (see Table I) and of course more in the 40 % specimen.

Vaguier and Carles-Gibergues<sup>13</sup> studying fly ash in contact with saturated lime solution, noticed an early period (from 15 to 20 days) characterized by sulphate solubilization and a lime decrease attributed to an absorption process. Then, there was a simultaneous decrease of calcium and sulphate ions with ettringite and gypsum formation. Subsequently, in a third period there was a considerable increase both of lime and sulphate in the solution, probably due to a slow solubilization of silica, with tobermorite formation to the detriment of ettringite or gypsum formation. If the ashes had been devoided of most sulphates through leaching, the solution composition evolved in a very regular manner, which shows a considerable influence of sulphate ion on the lime-pozzolana reaction.

Considering finally the high mechanical strength (near the maximum value) of the 20% fly ash mortar obtained and also the small expansion observed<sup>3</sup>, if a selection had to be made between these two proportions - from the range investigated - it could be concluded that the 20 % mixture is a more realistic solution, at least with our current experience. Further research study is needed, as each fly ash has each own characteristics, for example Ptolemaida's is different than Megalopoli's fly ash (which are the main production areas in Greece), and any extrapolating assumption based on the foreign bibliography would be dangerous.

## Περίληψη

*Η Παραγόμενη Ελεύθερη Άσβεστος κατά την Ενυδάτωση του Τσιμέντου με Ιπτάμενη Τέφρα*

Η ιπτάμενη τέφρα παράγεται κατά χιλιάδες τόννους το χρόνο στους Ατμοηλεκτρικούς Σταθμούς Παραγωγής Ηλεκτρικής Ενέργειας της ΔΕΗ από την καύση λιγνιτών. Η δυνατότητα αξιοποίησής της έχει μεγάλη σημασία, γιατί το στερεό αυτό βιομηχανικό απόβλητο βρίσκει έτσι μια χρησιμοποίηση σαν παραπροϊόν στην τσιμεντοβιομηχανία σε μια εποχή που υπάρχει έλλειψη καυσίμων, αλλά κύρια για τα θετικότερα αποτελέσματα που λαμβάνονται στις ιδιότητες του τσιμέντου Portland, όταν προστεθεί η ιπτάμενη τέφρα που είναι ένα υλικό ποζολανικό. Τα υλικά αυτά έχουν την τάση να δεσμεύουν την ελεύθερη άσβεστο που σχηματίζεται κατά την ενυδάτωση του τσιμέντου, παρουσία νερού. Η ενυδάτωση είναι μια σύνθετη λειτουργία διαδοχικών και παράλληλων αντιδράσεων όλων των συστατικών του τσιμέντου. Η ελεύθερη άσβεστος παράγεται από τα πυριτικά του ασβεστίου και είναι ιδιαίτερα ευπρόσβλητη στα όξινα διαλύματα (διάβρωση

τσιμέντου). Η ποζολανική ενεργότητα απαιτεί τη μελέτη φυσικών, χημικών και μηχανικών ιδιοτήτων, πολλές από τις οποίες αλληλοσχετίζονται. Το εργαστήριό μας έχει αναλάβει εδώ και χρόνια μια έρευνα πολλών παραμέτρων του σχηματιζόμενου τσιμεντοκονιάματος με ενθαρρυντικά αποτελέσματα. Ο τομέας της παραγόμενης ελεύθερης ασβέστου εξετάζεται σ' αυτή την εργασία, σε σύνδεση με την πρόσφατη βιβλιογραφία.

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## MASS SPECTROMETRY OF SOME SUBSTITUTED N-CHLOROACYLBENZYLAMINES

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### Summary

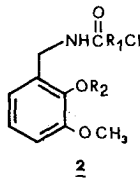
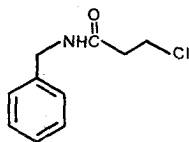
The mass spectra of seventeen 2-alkoxy-3-methoxy-N-chloroacylbenzylamines have been recorded, and the effect of variation of the alkoxy group (e.g. methoxy, ethoxy, n-propyloxy, isopropyloxy and n-butyloxy) together with variation (chain branching and increasing chain length) of the acyl group on the mode of fragmentation have been studied. It is concluded that four major fragmentation pathways are available for this type of structure.

A plausible structure for the  $m/e$  136 ion, which is the base peak in nine of the spectra and is prominent in the remainder, is deduced, and rearrangement processes are discussed.

**Key words:** N-Chloroacylbenzylamines, mass spectrometry.

### Introduction

In a previous paper<sup>1</sup>, two of us<sup>a,b</sup> in an attempt to improve the activity of beclamide (1), described the synthesis and biological activity a series of seventeen compounds (Table I) of the general type 2.



In the present paper we report the results of our studies on the mass spectra of the 2-alkoxy-3-methoxy-N-chloroacylbenzylamines (Table I).

Mass spectra were obtained using electron impact, by direct insertion into the source of an AEI MS 902 mass spectrometer under low resolution conditions.



TABLE I. 2-Alkoxy-3-methoxy-N-chloroacylbenzylamines



Compound	R <sub>1</sub>	R <sub>2</sub>	Formula	m.p. °C
3	CH <sub>2</sub>	CH <sub>3</sub>	CH <sub>11</sub> H <sub>14</sub> ClNO <sub>3</sub>	95 - 99
4	CH(CH <sub>3</sub> )	CH <sub>3</sub>	CH <sub>12</sub> H <sub>16</sub> ClNO <sub>3</sub>	85 - 86
5	CH <sub>2</sub> CH <sub>2</sub>	CH <sub>3</sub>	CH <sub>12</sub> H <sub>16</sub> ClNO <sub>3</sub>	85 - 86
6	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	CH <sub>3</sub>	CH <sub>13</sub> H <sub>18</sub> ClNO <sub>3</sub>	76 - 78
7	CH <sub>2</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>12</sub> H <sub>16</sub> ClNO <sub>3</sub>	92 - 95
8	CH(CH <sub>3</sub> )	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>13</sub> H <sub>18</sub> ClNO <sub>3</sub>	93 - 96
9	CH <sub>2</sub> CH <sub>2</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>13</sub> H <sub>18</sub> ClNO <sub>3</sub>	107 - 110
10	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>14</sub> H <sub>20</sub> ClNO <sub>3</sub>	81 - 82
11	CH <sub>2</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CH <sub>13</sub> H <sub>18</sub> ClNO <sub>3</sub>	80 - 82
12	CH(CH <sub>3</sub> )	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CH <sub>14</sub> H <sub>20</sub> ClNO <sub>3</sub>	81 - 82
13	CH <sub>2</sub> CH <sub>2</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CH <sub>14</sub> H <sub>20</sub> ClNO <sub>3</sub>	77 - 78
14	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CH <sub>15</sub> H <sub>22</sub> ClNO <sub>3</sub>	66 - 68
15	CH <sub>2</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>13</sub> H <sub>18</sub> ClNO <sub>3</sub>	66 - 67
16	CH(CH <sub>3</sub> )	CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>14</sub> H <sub>20</sub> ClNO <sub>3</sub>	83 - 84
17	CH <sub>2</sub> CH <sub>2</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>14</sub> H <sub>20</sub> ClNO <sub>3</sub>	78 - 79
18	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>15</sub> H <sub>22</sub> ClNO <sub>3</sub>	71 - 72
19	CH <sub>2</sub> CH <sub>2</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CH <sub>15</sub> H <sub>22</sub> ClNO <sub>3</sub>	75 - 76

## Results and Discussion

The mass spectra of the compounds listed in Table I can be rationalised in terms of four major fragmentation pathways.

Molecular ions were observed in all cases, with two ions of abundance ratio 3:1, separated by two mass units, indicating the presence of one chlorine atom in the molecule (see Table II). Ions of mass one unit higher were also observed at lower abundances, and were attributed to ion-molecule reactions in the source. Loss of a hydrogen radical from the molecular ion was not observed. The relative intensity of the molecular ion was found to decrease with increasing molecular weight.

Loss of the groups -R<sub>2</sub> and -OR<sub>2</sub> from the molecular ion was common to all the compounds studied, with the exceptions where R<sub>2</sub> = isopropyl (structures 15-18), when a C<sub>3</sub>H<sub>6</sub> molecule was eliminated, and where R<sub>2</sub> = n-butyl (structure 19),

TABLE II. Major ions of some 2-alkoxy-3-methoxy-N-chloroacylbenzylamines\*

Structure	M <sup>+</sup>	-Cl	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{CR}_1 \end{array}$	$-\text{CR}_1\text{Cl}$	$-\text{R}_2(+\text{H})$	$-\text{NH}_2$	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{H}_2\text{NCR}_1\text{Cl} \end{array}$	Others
3	243(90)	208(100)	166(56)					136(24),91(21),77(10),65(13),51(11)
4	257(32)	222(100)	166(50)					136(50),91(35),77(14),65(25),51(13)
5	257(27)			166(100)				136(47),91(17),77(10),65(13)
6	271(23)			166(100)				136(50),91(18),77(12),65(11)
7	257(70)	222(100)	180(37)		152(46)			136(53),91(11),77(11),65(23),51(11)
8	271(52)	236(100)	180(50)		152(46)			136(49),91(10),77(13),65(27),51(11)
9	271(24)			180(100)	152(76)			136(71),91(10),77(11),65(28),51(12)
10	285(27)			180(100)	152(60)			136(52),77(12),65(12)
11	271(37)	236(31)	194(73)		152(35)	136(100)		77(10),65(17),51(12)
12	285(35)	250(40)		194(100)	152(35)	136(100)		65(25)
13	285(16)			194(30)	152(27)	136(100)		65(15)
14	299(18)			194(46)	152(36)	136(100)		77(11),65(16)
15	271(11)	194(66)	152(28)		229(30)	136(100)		77(10),65(25),51(11)
16	285(25)	208(95)	152(23)		243(43)	136(100)		65(16)
17	285(17)				243(50)		136(100)	65(13)
18	299(23)				257(57)		136(100)	77(11),65(11)
19	299(20)				243(12)		136(100)	

\* m/e values are followed by relative intensities in parenthesis. All ions of m/e  $\geq 50$  and intensity  $\geq 10\%$  are tabulated. For those ions containing chlorine, only the most abundant isotope ion is quoted.

when a  $C_4H_8$  molecule was eliminated. The  $(M^+ - R_2)$  and  $(M^+ - OR_2)$  fragment ions were all of extremely low abundance. The corresponding alkyl cations were observed at  $m/e$  29 ( $C_2H_5^+$ ),  $m/e$  43 ( $C_3H_7^+$ ) and  $m/e$  57 ( $C_4H_9^+$ ).

Elimination of the  $-R_2$  group as in Figure 1 permits formation of the stable quinonoid ion (a)<sup>3</sup>.

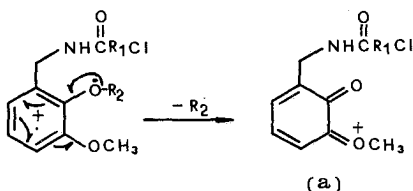


FIG. 1

$\alpha$ -Cleavage, involving loss of Cl, leads to the formation of an ion which is the base peak when  $R_1 = CH_2$  or  $CH(CH_3)$  and  $R_2 = CH_3$  or  $CH_2CH_3$  (structures 3, 4, 7 and 8). When  $R_1 = CH_2$  or  $CH(CH_3)$  and  $R_2 = CH_2CH_2CH_3$  or  $CH(CH_3)_2$  (structures 11, 12, 15 and 16) some Cl loss from the molecular ion is observed, but is generally a less favoured process and gives ions of much lower abundance.

No  $\alpha$ -cleavage was observed when  $R_1 = (CH_2)_2$  or  $(CH_2)_3$  and  $R_2 = CH_3$ ,  $CH_2CH_3$ ,  $CH_2CH_2CH_3$ ,  $CH(CH_3)_2$  or  $CH_2CH_2CH_2CH_3$ , illustrating the loss of influence of the carbonyl group as the chain length increases. An ion of low abundance corresponding to the loss of the HCl molecule from the molecular ion was observed in the spectra of structure 18 and 19 and was attributed to a thermal elimination occurring before ionisation.

As expected, the size and spatial distribution of groups  $R_1$  and  $R_2$  have a marked effect on the mode of fragmentation of these compounds (see Figure 2). For example, when  $R_1 = CH_2$  and  $R_2 = CH_3$  or  $CH_2CH_3$ , (structures 3 and 7) a molecule of ketene is lost from the  $(M^+ - Cl)$  ion. Similarly, when  $R_1 = CH(CH_3)$  and  $R_2 = CH_3$  or  $CH_2CH_3$  (structures 4 and 8), a corresponding loss a  $CH_3CHCO$  molecule from the  $(M^+ - Cl)$  ion is observed. A distinct difference is noted between the two isomeric propyl compounds when  $R_1 = CH_2$ . When  $R_2 = n$ -propyl (structure 11), loss of a  $C_3H_6$  molecule occurs *after* consecutive losses of Cl and ketene from the molecular ion, whereas the isopropoxy compound (structure 15) exhibits loss of a  $C_3H_6$  molecule *before* the consecutive Cl and ketene eliminations. A similar fragmentation pattern is observed with the isopropoxy compound when  $R_1 = CH(CH_3)$ , (structure 16) i.e. consecutive losses of  $C_3H_6$ , Cl and  $CH_3CHCO$ ; whilst the *n*-propoxy analogue (structure 12) is anomalous in that although Cl loss from the molecular ion is observed, a following loss of  $CH_3CHCO$  is not readily apparent. An alternative pathway is evident in the loss of  $OCCH(CH_3)Cl$  from the molecular ion, followed by elimination of a  $C_3H_6$  molecule.

As the chain-length of group  $R_1$  increases another mode of fragmentation becomes apparent. When  $R_1 = CH_2CH_2$ , loss of  $OCCH_2CH_2Cl$  from the molecular ion leads to an ion which is the base peak when  $R_2 = CH_3$  (structure 5, base

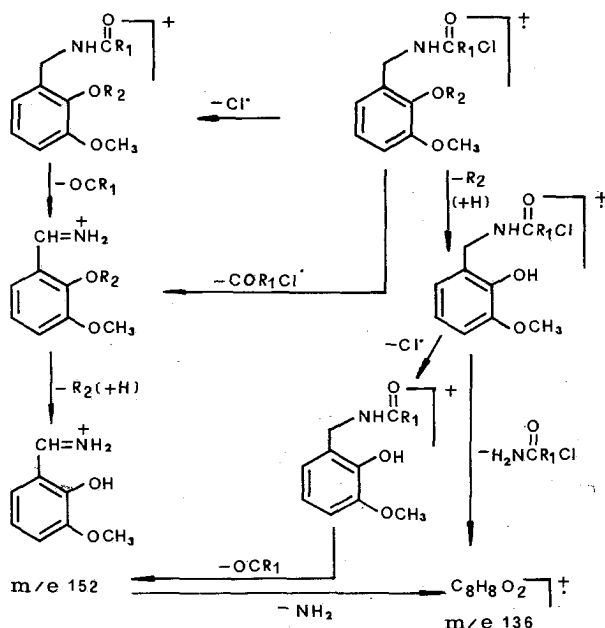


FIG. 2. Major fragmentation pathways of 2-alkoxy-3-methoxy-N-chloroacylbenzylamines.

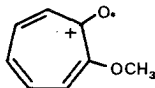
peak  $m/e$  166) and  $R_2 = \text{CH}_2\text{CH}_3$  (structure 10, base peak  $m/e$  180). The *n*-propyloxy analogues of these compounds i.e. when  $R_1 = \text{CH}_2\text{CH}_2$  or  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$  and  $R_2 = \text{CH}_2\text{CH}_2\text{CH}_3$  (structure 13 and 14) are similar in that they eliminate  $\text{OCCH}_2\text{CH}_2\text{Cl}$  and  $\text{OCCH}_2\text{CH}_2\text{CH}_2\text{Cl}$  respectively, from the molecular ion. This is followed in both cases by loss of a  $\text{C}_3\text{H}_6$  molecule, but does not lead to an ion which is the base peak of the spectrum.

The remaining compounds exhibit yet another mode of fragmentation, where the isopropoxy compounds possessing long chain groups at  $R_1$  i.e. when  $R_1 = \text{CH}_2\text{CH}_2$  (structure 17) or  $\text{CH}_2\text{CH}_2\text{CH}_2$ , (structure 18) first lose a molecule of  $\text{C}_3\text{H}_6$  from the molecular ion, followed by elimination of an amide fragment corresponding to  $\text{H}_2\text{NCOCH}_2\text{CH}_2\text{Cl}$  and  $\text{H}_2\text{NCOCH}_2\text{CH}_2\text{Cl}$  respectively to form an ion which is the base peak ( $m/e$  136) in both cases<sup>4</sup>.

This process is again observed when  $R_1 = \text{CH}_2\text{CH}_2$  and  $R_2 = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  where consecutive losses of  $\text{C}_4\text{H}_8$  and  $\text{H}_2\text{NCOCH}_2\text{CH}_2\text{Cl}$  are evident, leading to an ion at  $m/e$  136 which is again the base peak. All the major fragmentation pathways discussed above are supported by appropriate metastable ions in each case.

The  $m/e$  136 ion was prominent in all of the spectra examined and was found to increase in abundance as the mass of the substituent group  $R_2$  was increased, and was in fact, the base peak of the spectrum when  $R_2 = n$ -propyl, isopropyl or *n*-butyl. The structure of this ion is open to speculation, but the 2-methoxy tropone structure (b) is proposed as a reasonable hypothesis, based on the formation of a carbonyl group consequent to the elimination of the  $R_2$  group and the wellknown

ring expansion of a benzyl group to form a tropylium ion under electro-impact conditions. Metastable transitions are observed for the loss of  $\text{H}_2\text{CO}$  and  $\text{CHO}$  from this ion, lending support to the postulate<sup>5</sup>.



(b)

Other fragments common to all of the compounds studied may be attributed to ions involving the benzene ring e.g.  $m/e$  91 ( $\text{C}_7\text{H}_7^+$ ) which can eliminate a  $\text{C}_2\text{H}_2$  molecule to form an ion of mass  $m/e$  65 ( $\text{C}_5\text{H}_5^+$ ), and  $m/e$  77 ( $\text{C}_6\text{H}_5^+$ ) which can also eliminate a molecule of  $\text{C}_2\text{H}_2$  to yield an ion  $m/e$  51 ( $\text{C}_4\text{H}_3^+$ ).

*Rearrangements process.* The spectra of the compounds which possess an ethoxy group all show elimination of a fragment of mass 28 amu from the  $m/e$  180 ion, the loss being supported by the appropriate metastable ion. This is attributed to the loss of ethylene from the ethoxyl group by means of a four-centered rearrangement (Figure 3).

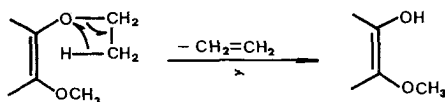


FIG. 3

A similar type of rearrangement would account for the *n*-propyloxy, isopropyloxy and *n*-butyloxy analogues eliminating the corresponding olefins,  $\text{C}_3\text{H}_6$  and  $\text{C}_4\text{H}_8$ .

Somewhat surprisingly, there is no indication of the familiar McLafferty rearrangement in any of the compounds studied where  $\text{R}_1 = \text{CH}_2\text{CH}_2\text{CH}_2$ , although the necessary  $\gamma$ -hydrogen is available<sup>7</sup>. This cannot be due to a steric effect as no such rearrangement is observed when  $\text{R}_2 = \text{methyl, ethyl, propyl, or isopropyl}$ . It must therefore be concluded that the more facile elimination of  $\text{OCCH}_2\text{CH}_2\text{CH}_2\text{Cl}$  fragment (when  $\text{R}_2 = \text{methyl, ethyl or propyl}$ ) or the  $\text{H}_2\text{NCOCH}_2\text{CH}_2\text{CH}_2\text{Cl}$  fragment (when  $\text{R}_2 = \text{isopropyl}$ ) from the molecular ion, is a lower-energy process than that required for the formation of the six-centred McLafferty rearrangement.

## Περίληψη

*Φασματομετρία Μάζας υποκατεστημένων Ν-χλωροακυλοβενζυλαμινών.*

Περιλαμβάνεται η μελέτη δεκαεπτά φασμάτων μάζας 2-αλκοξυ-3-μεθοξυ-Ν-χλωροακυλοβενζυλαμινών. Πιο συγκεκριμένα, μελετάται η επίδραση της μεταβολής της αλκοξυ-ομάδας (μεθοξυ-αιθοξυ, καν.-προπυλοξυ, ισοπροπυλοξυ και

καν.-βουτυλο) σε σχέση με την μεταβολή της ακυλο-ομάδας (διακλάδωση και αύξηση του μήκους της αλυσίδας), πάνω στον τρόπο σχάσης. Όπως έδειξαν τα αποτελέσματα, οι σημαντικότεροι τρόποι σχάσης της δομής αυτής είναι τέσσερις.

Αναφέρεται επίσης η πορεία του σχηματισμού του ιόντος  $m/e$  136, που αποτελεί τη βασική κορυφή εννέα φασμάτων N-χλωρο-ακυλοβενζυλαμινών.

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## SHORT PAPER

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*Chimika Chronika, New Series, 12, 225-228 (1983)*

### ALTERNATIVE PROCEDURE FOR THE SYNTHESIS OF DI-HYDROCERAMIDE TRIMETHYLAMINOETHYL PHOSPHONATES

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#### Introduction

In previous papers<sup>1,2</sup> was reported the synthesis of trans-D-erythro ceramide-N,N,N-trimethylaminoethyl phosphonate (phosphono-sphingomyelin) and in a subsequent paper<sup>3</sup> the unusual chromatographic behaviour of the above compound was examined. In this latter paper was reported that phosphono-sphingomyelin was eluted from a silicic acid column in the cardiolipin fraction with 5% methanol in chloroform. This property is also shared by acetyl glycerylether phosphonocholine (phosphono-AGEPC)<sup>4,5</sup>. A number of similar compounds have been synthesized and subjected to column chromatography to determine their behaviour under these conditions.

In the course of this investigation, it was decided to synthesize the dihydroceramide trimethylaminoethylphosphonates to examine their elution pattern from a silicic acid column. The method employed was essentially that of Baer et al.<sup>6,7</sup> for the synthesis of dihydroceramide aminoethylphosphonates, with the exception that the ceramide was unprotected at the 3-O position and the coupling of the ceramide with 2-bromoethyl phosphonic acid monochloride was accomplished in the presence of triethylamine and within five minutes of the start of the reaction. By this means the primary hydroxyl group reacts preferentially with the stoichiometric quantity of the acid monochloride with comparable yields.

#### Experimental

All reagents used were ANALAR grade and were distilled before use. Anhydrous and ethanol free chloroform was obtained by distilling chloroform from phosphorous pentoxide just before use. Triethylamine was dried over sodium hydroxide pellets.

2-bromoethyl phosphonic acid was prepared according to a previous method<sup>6,7</sup>.

Trimethylamine was purchased from Eastman-Kodak USA and the N-palmitoyl and N-lignoceryl dihydroceramides were purchased from Serdary Research Labs., Ontario, Canada.

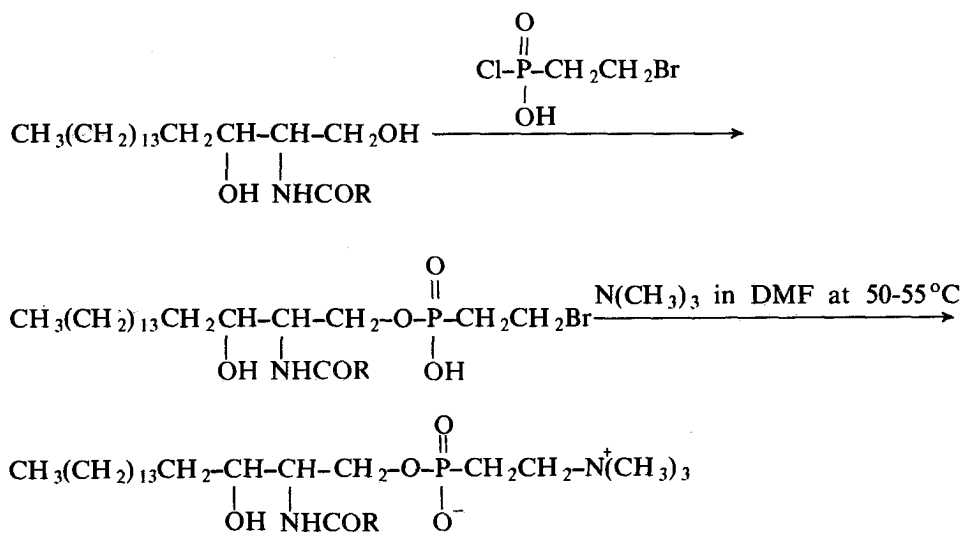
Purity of products was tested with TLC on silica gel G F<sub>254</sub> pre-coated plates, Riedel, of layer thickness 0.2 mm, using methanol/water (2:1, v/v) and chloroform/methanol/water (65:25:4, v/v/v) as solvents.

Total nitrogen was determined by the micro-Kjeldahl method and lipid phosphorous by the Allen procedure<sup>8</sup>.

IR spectra were recorded on a Perkin-Elmer 197 grating Infra Red spectrophotometer and mass spectra were recorded in England by Roche Products Ltd, on a low resolution mass spectrometer.

*Erythro-N-palmitoyl-DL-dihydrosphingosyl-1-(2-bromoethyl) phosphonate*

The 2-bromoethyl phosphonic acid monochloride was prepared according to the procedure of Baer et al.<sup>6,7</sup>.



Reaction scheme : *synthesis of dihydroceramide (trimethylaminoethyl) phosphonate.*  
*R = palmitoyl or lignoceryl residue.*

Phosphonylation was done as follows: the 2-bromoethyl phosphonic acid monochloride was dissolved in 4.0 ml of anhydrous and ethanol-free chloroform; to this cooled solution (about 10°C) was added a solution of 40 mg (0.058 mmole) of erythro-N-palmitoyl-DL-dihydrosphingosine and 0.02 ml (0.14 mmole) of anhydrous triethylamine in 4.0 ml of purified chloroform, under anhydrous conditions and with stirring over a period of five minutes. The reaction mixture was allowed to stand at room temperature for 20 hours. At the end of this period, 0.2 ml of water was added and the mixture was stirred vigorously for two hours. The solvent and excess of triethylamine were distilled under reduced pressure and a bath temperature of 30-35°C and the residue was dissolved in a mixture of 6.0 ml of chloroform, 3.0 ml of methanol and 0.3 ml of water. The solution was stirred for two hours with



0.5 ml of Amberlite IR-120(H+). The solution was filtered, the Amberlite was washed with a small volume of solvent and the whole evaporated to dryness under reduced pressure and a bath temperature of 30-35 °C.

The product was dried in a vacuum desiccator overnight and was used in the following step without purification.

*Erythro-N-palmitoyl-DL-dihydrosphingosyl-1-(trimethyl aminoethyl) phosphonate*

The reaction of the phosphorylated dihydroceramide with trimethylamine in anhydrous dimethylformamide was carried out as described previously<sup>6,7</sup>.

The final product was dried over phosphorous pentoxide in a vacuum desiccator for 24 hours and 7.3 mg (38.42% of theory) of pure erythro-N-palmitoyl-DL-dihydrosphingosyl-1-(trimethylaminoethyl) phosphonate were obtained.

Found N 3.97 P 4.71%

Calculated N 4.06 P 4.68%

One spot was obtained on TLC, where the  $R_f$  value of the compound in methanol/water (2:1, v/v)<sup>9</sup> was 0.66 and in chloroform/methanol/water (65:25:4, v/v/v) was 0.25. The IR spectrum of the compound gave the characteristic frequencies for the phosphonates<sup>3,4</sup>. Mass spectroscopic data furnished results (mass ions 151, 211, 239, 254, 284, 566, 631, 641, etc. corresponding to the fragmentation of the phosphorylcholine and the N-acyl residues) which point to the fact that the monophosphonate compound was formed.

*Erythro-N-lignoceryl-DL-dihydrosphingosyl-1-(trimethyl aminoethyl) phosphonate*

The same procedure was followed as for the N-palmitoyl analog. 6.9 mg (36.30% of theory) of the pure compound were obtained.

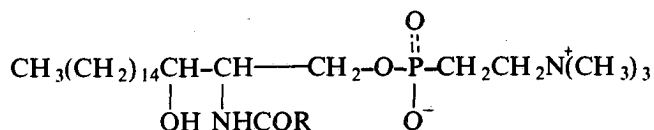
Found N 3.49 P 4.01%

Calculated N 3.46 P 3.99%

One spot was obtained on TLC, where the  $R_f$  value of the compound in methanol/water was 0.71 and in chloroform/methanol/water was 0.26. The IR spectrum of this compound compared well with those reported in the literature<sup>2,4</sup>. The fact that the monophosphonate compound was formed is also supported by mass spectroscopic data (mass ions: 29, 59, 71, 76, 99, 151, 167, 211, 323, 351, 475, 490, etc.).

## Results and Discussion

From the data furnished above is evident that the monophosphonate compounds were prepared. The IR spectra have furnished frequencies for  $\nu(\text{OH})$  and the accompanying TLC and analytical data support the above conclusion. The procedure is suitable for the synthesis of ceramide trimethylaminoethyl phosphonates where the hydroxyl group at the 3-O position need not be suitably protected. The compound synthesized possesses the structure that follows :



## Abstract

In this paper is described the synthesis of dihydroceramide trimethylaminoethylphosphonates by a modification of the procedure employed by Baer for the synthesis of trimethylaminoethylphosphonates. Both Erythro-N-palmitoyl-DL-dihydrosphingosyl-1-(N,N,N-trimethylaminoethyl) phosphonate and Erythro-N-lignoceryl-DL-dihydrosphingosyl-1-(N,N,N-trimethylaminoethyl) phosphonate have been synthesized by reacting the corresponding unprotected dihydroceramides with 2-bromoethyl phosphonic acid monochloride in the presence of triethylamine and subsequently reacting with anhydrous trimethylamine in dimethyl formamide at 50-55°C for three days.

Characterisation of the products was accomplished by TLC, IR spectroscopy and mass spectrometry.

## Περίληψη

### Σύνθεση των φωσφονο-διυδροκηραμιδίων

Η παρούσα εργασία περιγράφει τη σύνθεση των (τριμέθυλοαμινοαιθύλο)-φωσφονο-διυδροκηραμιδίων με μια τροποποίηση της μεθόδου των Baer et al. για τη σύνθεση των ενώσεων αυτών<sup>1,2</sup>.

Περιγράφεται η σύνθεση των N-παλμιτόυλο και N-λιγνοσέρυλο φωσφόνο διυδροκηραμιδίων με αντίδραση των αντίστοιχων μη-προστατευομένων διυδροκηραμιδίων με το μονοχλωρίδιο του 2-βρωμιοαιθύλο φωσφονικού οξέος σε χλωροφόρμιο και με την παρουσία τριαιθυλαμίνης. Η αντίδραση με άνυδρη τριμεθυλαμίνη έγινε σε διμέθυλοφορμαμίδιο στους 50-55° για τρεις μέρες.

Η ταυτοποίηση των προϊόντων έγινε με TLC, υπέρυθρο φασματοσκοπία και φασματοσκοπία μάζας.

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