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CHIMIKA CHRONIKA, *NEW SERIES*

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Chimika Chronika, New Series, 6, 461-469 (1977)

A STUDY ON THE AMINOACIDS CONTAINED IN SEVERAL GREEK WINES.

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(Received March 17, 1976)

Summary

In various Greek wines the amount of free amino acids, after deproteinization with picric acid, as well as, the total amino acid composition after acid hydrolysis, are determined, by automatic amino acid analyzer.

The alcohol content and acidity of the samples used are also given.

The results obtained are discussed as well in comparison with those reported for foreign wines.

In adition the loss of free amino acids for wines clarified with various doses of bentonite after the deproteinization with picric acid is determined and discussed.

Key words: Greek wines, aminoacids, alcohol content, acidity.

Introduction

The presence of amino acids in wines are of particular importance because these affect both their odour[1] and taste (malo-lactic fermentation[2]); Their concentration affects the nutritiousness of the wine, as well as some of its deseases. They also help the fermentation of the must.

The amino acid contents and their changes[3] from the beginning of the fermentation of the must to the aging of the wine, have been determined in foreign wines with paper chromatography,[4] thin layer chromatography[5] and amino acid analyzer.[6,7]

Bentonite has been used as a fining agent but it has been found that it absorbs part of the amino acids; as a result the amount of free amino acids contained in the clarified wine was smaller.[8,9]

The first effort to determine the amount of amino acids in Greek wines was made by Dimotakis[10], Danilatos and Sotiropoulos.[11] The above authors applied paper chromatography.

In this paper the results of the determination of amino acids, by automatic amino acid analyzer, in various Greek wines of different variety and year are given. To determine the free amino acids the wine was deproteinized with picric acid whereas the total ammount of amino acids (free and combined as protein) was determined after acid hydrolysis.

In addition the use of bentonite as a fining agent, for wines which were not clear enough after the deproteinization with picric acid, is studied in respect to the resultant losses of the free amino acids. Thus the proper dose of bentonite for clarification, for a minimum loss of amino acids is determined.

Experimental

Materials

Various samples of genuine wines (dry white, dry red, sweet red) produced in different regions of Greece were obtained from their processing plants.

All the chemicals used were reagent grade.

Instruments - Methods

The pH values were measured with a L. Pusl München 15 Nr ACP Typ 112 pH meter. The alcohol content in the dry wines was determined with the Dujardin-Salleron ebulliometer and this in the sweet wines through distillation. Amino acid analyses were carried out with a JEOL type JLC-5AH automatic amino acid analyzer using two columns, 15 cm and 70cm, filled with JEOL LC-R-1 resin.

Deproteinization

In 100 ml of wine 1g of picric acid was added, the mixture was stirred well and allowed to stay for 30 min at room temperature and then it was centrifuged and filtered. The filtrate was passed through a column 2×2 cm filled with resin Dowex 2×8 (200-400 Mesh) to remove the excess of picric acid.[12,13]

Determination of free amino acids.

The deproteinized wine was mixed with a citrate buffer solution pH 2,2 in ratios 1:1, 1:2, 1:3 depending on the amount of amino acids contained in the wine. The short column was used for the determination of basic amino acids, using a citrate buffer solution pH 5.29 as eluent, and the long column for the determination of acidic and neutral amino acids using as eluents two citrate buffer solutions pH 3,3 and 4.25 succesively. The temperature of the columns was 55°C and the reaction bath of ninhydrin with the amino acids at 95°C. The time for a complete analysis was about six hrs. The peaks area of the aminograms obtained were compared with those of a standard amino acid solution containing 0.1μ mol/ml of each amino acid. The order of elution of amino acids was always the same according to their retention time, as it is shown in Fig. 1.

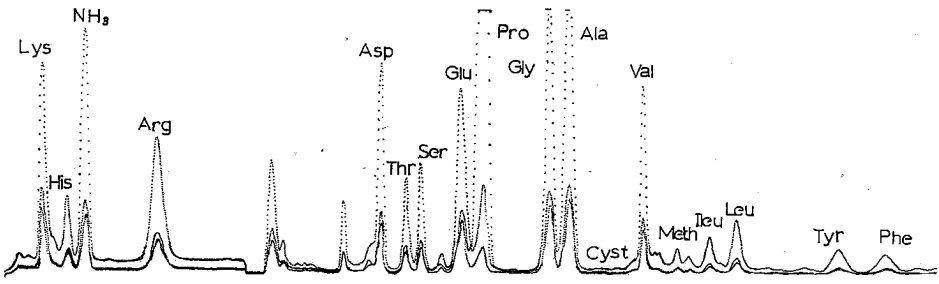

FIG. 1. *Amino Acid Chromatogram of the dry white wine "Kritis 1970" (No 5, Table I)*

Hydrolysis (Determination of total amount of amino acids)

Hydrolysis was carried out according to litarature procedures.[13,14] In a suitable testing tube were put 12,5 ml of wine and evaporated almost completely at 50-55°C. Then 7-8 ml of 6N hydrochloric acid were added, the tube was cooled with dry ice-aceton and the air was removed from the interior of the tube with the use of a rotary pump (0.5 mm Hg). The tube was then sealed by melt and heated in a forced-draft oven at 105°C for 24 hrs. The tube was then opened and the hydrolysate was filtered, washed the residue with distilled water and the filtrate was evaporated to dryness at 50-55°C in a rotator. The residue was re-dissolved in water and concentrated again to dryness, three times, for the complete removal of hydrochloric acid. The residue was then dissolved in a citrate buffer solution pH 2.2, made up to 25 ml and the solution was used for analysis.

Treatment with bentonite

Four volumes of 100 ml of the same wine were mixted with 0.1, 0.2, 0.4 and 1.0 g of bentonite respectively, stirred 10 min., left at room temperature for 20 min and filtered. The filtrate was diluted with a citrate buffer solution pH 2.2 and used for analysis.

Results and discussion

The average value of the alcohol content and the acidity of some kinds of Greek wines examined in this paper are given in Table I. Their average content in

TABLE I. *Alcohol Content and Acidity of various Greek Wines*

	Wines	Alcohol degree	pH	Acidity (as tartaric acid) g/lt
Dry White	Kritis (1967, 1970)*	12.5	3.28	5.4
	Roditis[a] (1973)	12.1	3.50	5.2
	Sideritis (1973, 1974)	11.8	3.28	4.5
Dry Red	Agiorgitico Nemeas (1973, 1974)	13.0	3.44	5.5
	Kritis[a] (1970)	13.5	3.69	3.8
	Kritis Rose[a] (1967)	13.5	3.61	5.4
	Mavrodaphnis[a] (1974)	11.8	3.78	4.1
	Moschato Tyrnavos[a] (1974)	13.4	4.00	2.4
	Rapsanis[a] (1974)	12.7	3.50	5.1
	Stafiditis[b] (1971, 1973, 1974)	13.3	3.26	6.0
	Vafikos Leukados[a] (1973)	11.4	3.31	3.9
Sweet Red	Mavrodaphnis[a] (1973)	15.3	3.74	3.9
	Moschato[a] (Patra 1973)	15.0	3.70	3.9

* Year of crop

a: One sample used

b: Wine made from raisins

free amino acids for the dry white wines is given in Table II and this for the dry red and sweet red wines in Tables III and IV correspondingly.

TABLE II. *Amount of Free Amino Acids in various Greek Dry White Wines*

Amino acid mg/lt	Kritis (1967, 1970)*	Roditis[a] (1973)*	Sideritis (1973, 1974)*
Lysine	41.8	33.1	31.1
Histidine	22.6	10.4	11.0
Arginine	122.8	40.2	98.8
Hydroxyproline	20.9	6.0	11.8
Aspart. acid	42.0	31.0	16.4
Threonine	16.2	12.2	8.5
Serine	12.6	10.0	9.3
Glut. acid	58.9	40.6	26.0
Proline	480.0	398.0	540.0
Glycine	38.7	16.1	11.9
Alanine	57.8	29.6	20.4
Cystine	1.2	4.1	3.3
Valine	20.6	18.0	11.9
Methionine	3.1	4.8	3.9
Isoleucine	7.9	6.8	5.2
Leucine	13.9	20.0	14.5
Tyrosine	15.2	11.0	8.9
Phenylalanine	9.1	9.3	9.3
Total	985.6	701.2	842.6

* Year of crop
a: Results from one sample

Significant differences for the amount of the free amino acids are observed among the examined dry white wines of different origin, as well as, among the dry or sweet red wines (Table II, III, IV). These differences are presumably due to the different variety, degree of ripening and cultivating contitions of the grapes and to different processing of the product. As a result a wide concentration range for each amino acid is observed for each group of these wines and no characteristic differences among dry white, dry red or sweet red wines can be established on account of the wide variation of their amino acid composition.

However, comparing the values of the Tables II, III and IV it is observed that the white wines are in general, with a few exceptions, richer in free amino acids than the red ones. This could be attributed to the greater amount of tannin in the red wines, which precipitates the proteins from which these are released. Nevertheless this explanation is not consistent with the greater increase of the amino acid contents in the red wines after the acid hydrolysis of the proteins (Table V). Thus, it might be concluded that the concentration of the free amino acids in these wines is not only depended on the protein content.

TABLE III. *Amount of Free Amino Acids in various Greek Dry Red Wines*

Amino acid mg/lt	Agioritico (Nemeas) (1973, 1974)*	Kritis[a] (1970)*	Kritis[a] (Rose) 1967*	Mavro-daphnis[a] (1974)*	Moschato Tyrnavos[a] (1974)*	Rapsanis[a] (1974)*	Stafiditis (1971)* (1973, 74)*	Vafikos Leukados[a] (1973)*
Lysine	8.5	6.3	26.4	22.4	13.8	9.2	32.6	12.6
Histidine	4.2	5.6	13.3	9.8	15.8	4.5	14.8	4.5
Arginine	6.8	91.2	4.1	trac.	23.7	105.5	43.6	10.8
Hydroxyproline	4.3	3.1	12.3	6.5	19.1	—	6.9	—
Aspart. acid	9.2	3.5	27.8	12.3	25.9	30.0	20.9	6.6
Threonine	5.1	5.6	9.8	4.9	9.4	7.7	7.3	3.6
Serine	5.7	2.4	7.4	4.1	7.3	11.8	7.4	4.2
Glut. acid	10.5	10.3	30.0	17.0	30.2	39.1	27.5	14.4
Proline	355.3	226.0	450.0	314.0	470.0	538.0	408.0	450.0
Glycine	9.0	2.8	21.1	10.1	24.5	20.2	18.4	8.0
Alanine	6.5	10.0	26.3	16.8	28.0	39.1	21.4	16.9
Cystine	1.2	trac.	1.9	4.9	2.1	4.3	3.7	trac.
Valine	4.8	1.2	13.0	9.0	10.4	5.7	11.6	6.7
Methionine	2.1	1.2	2.6	2.3	1.6	36.7	3.7	1.2
Isoleucine	1.9	0.8	5.1	3.5	2.7	48.5	3.4	1.0
Leucine	2.5	2.3	10.3	7.6	4.8	13.4	10.8	3.4
Tyrosine	1.8	2.8	9.8	5.3	9.4	62.4	9.1	1.8
Phenylalanine	2.1	2.8	9.7	5.3	9.1	58.1	7.4	2.1
Total	441.8	388.7	680.9	455.8	707.8	1034.0	659.1	547.8

* Year of crop
a: Results from one sample
b: Wine made from raisins

Among all the free (or free and combined) amino acids, proline is found in all samples of wines in significant highest amounts, whereas the sulfur amino acids, cystine and methionine are found in the lowest amounts.

Arginine and glutamic acid, in an alternative order, are the next predominant amino acids, while an order for the rest amino acids according to their amounts is proved to be different for each sample of wine.

The amounts of free amino acids found in the examined Greek wines, in comparison with those found in foreign wines,[6,16] are approximately the same for some amino acids, whereas for most amino acids these are usually lower in the former wines. However, no definite differences between them can be in general concluded because of the wide variation of amino acid contents, in both wines.

The amount of glutamic acid, glycine and isoleucine, after hydrolysis, increases much more than this of the other amino acids. This increase, for the metioned amino acids, is about two or three times more than their initial contents as free acids (Tables V, II, III). This is explained by the kind of proteins existing in wines, mainly albumins, which contain the greatest amount of these three

TABLE IV. *Amount of Free Amino Acids in two Greek Sweet Red Wines*

Amino acid mg/lt	Mavrodaphnis[a] (1973)*	Moschato[a] Patra (1973)*
Lysine	21.8	26.5
Histidine	17.9	17.9
Arginine	181.2	350.0
Hydroxyproline	5.6	7.8
Aspart. acid	30.6	35.3
Threonine	21.0	30.9
Serine	16.2	25.0
Glut. acid	28.8	30.3
Proline	260.6	270.0
Glycine	13.2	12.6
Alanine	45.6	62.5
Cystine	trace	trace
Valine	19.0	35.0
Methionine	4.7	5.4
Isoleucine	10.0	16.4
Leucine	22.4	30.9
Tyrosine	26.7	25.2
Phenylanine	20.8	18.3
Total	745.6	1000.0

* Year of crop
a: Results from one sample

amino acids.[15] The lower amounts of the sulfur amino acids cystine and methionine found after hydrolysis are attributed to their oxidation during the hydrolysis process.

The results obtained for two wines clarified with different doses of bentonite are shown in Table VI.

As shown in Table VI, the percentage loss of free amino acids increases with the amount of bentonite used and therefore the minimum adequate for clarification dose of the agent (0.1%) must be used whenever it is required.

The percentage loss of amino acids for a definite dose of bentonite, as well as, the relative loss for a higher dose of bentonite varies significantly among the different amino acids and no relationship between this and the initial concentration and the acidic or basic character of the amino acids can be concluded.

TABLE V. *Total Amino Acid Composition of various Greek Wines*

Amino acid mg/lt	DRY WHITE Kritis[a] (1967, 1970)*	Roditis[a] (1973)*	Sideritis[a] (1973, 1974)*	DRY RED Agioritico Nemeas (1973, 1974)*	Stafiditis[b] (1971) (1973, 1974)*	SWEET RED Mavrodaphnis[c] (1973)*
Lysine	50.2	39.1	51.3	15.3	40.2	30.1
Histidine	35.3	14.3	17.3	8.4	30.3	23.1
Arginine	160.2	60.2	133.6	18.1	105.8	201.5
Hydroxyproline	—	15.3	6.9	—	4.5	—
Aspart. acid	68.4	35.4	35.6	26.2	122.1	52.3
Threonine	17.0	20.9	21.0	11.9	90.6	26.6
Serine	29.0	23.1	23.2	14.9	12.4	23.8
Glutam. acid.	116.3	64.2	81.3	63.8	91.7	93.8
Proline	520.0	440.0	540.0	389.0	442.3	300.0
Glycine	55.5	31.0	28.8	28.2	81.3	26.6
Alanine	68.1	80.0	92.7	57.8	38.9	55.4
Cystine	trace	trace	1.0	2.1	2.2	—
Valine	24.4	25.1	19.4	9.3	34.7	24.8
Methionine	3.0	4.6	2.3	2.1	5.2	1.5
Isoleucine	17.6	18.4	17.0	40.1	45.8	19.7
Leucine	18.5	27.7	24.2	8.5	49.2	27.9
Tyrosine	15.0	15.0	12.8	5.9	—	—
Phenylalanine	12.7	10.9	11.5	4.5	—	27.6
Total	1211.2	925.2	1120.1	706.1	1197.2	940.7

*, Year of crop

a, b, c: The amounts of their free amino acids are shown in tables II, III, IV, respectively.

TABLE VI. *Percentage loss of Free Amino Acids for Wines clarified with different doses of Bentonite*

SIDERITIS (1974) (dry white)					
Amino acids mg/lt	Initial content	0.1% bentonite, loss %	0.2% bentonite, loss %	0.4% bentonite, loss %	1% bentonite, loss %
Lysine	30.1	3.6	9.9	23.3	33.3
Histidine	7.4	1.3	1.3	5.4	18.9
Arginine	19.2	1.0	2.0	11.4	20.8
Aspartic acid	15.1	5.3	17.2	33.1	58.2
Threonine	10.4	18.3	30.7	48.0	50.0
Serine	9.3	10.7	21.5	50.5	60.2
Glutamic acid	24.6	2.4	5.2	23.5	60.5

continue

Amino acids mg/lt	Initial content	0.1% bentonite, loss %	0.2% bentonite, loss %	0.4% bentonite, loss %	1% bentonite, loss %
Proline	540.0	2.0	12.9	25.9	33.3
Glycine	8.2	12.2	17.0	63.4	73.1
Alanine	16.0	3.7	11.2	39.3	62.5
Cystine	4.1	21.9	24.3	36.5	48.7
Valine	13.6	19.1	23.5	55.8	75.0
Methionine	3.9	2.5	0.0	15.3	25.6
Isoleucine	5.7	12.2	38.5	42.1	54.3
Leucine	16.0	5.6	10.6	25.0	53.1
Tyrosine	8.3	24.0	30.1	42.1	56.6
Phenilalanine	7.5	6.6	25.3	26.6	44.0
Hydroxyproline	7.8	8.9	8.9	—	28.2

STAFIDITIS (1973) (dry red)

Amino acids mg/lt	Initial content	0.1% bentonite, loss %	0.2% bentonite, loss %	0.4% bentonite, loss %	1% bentonite, loss %
Lysine	32.9	2.7	2.7	4.5	17.0
Histidine	19.8	4.0	13.6	20.2	36.8
Arginine	70.3	3.1	14.3	24.6	34.5
Aspartic acid	34.7	16.4	30.8	38.6	44.3
Threonine	11.7	11.9	28.2	41.0	63.2
Serine	10.9	7.3	22.0	36.6	42.2
Glutamic acid	40.1	8.9	33.9	35.6	53.3
Proline	450.0	11.1	11.1	17.5	17.3
Glycine	23.6	14.8	19.9	24.1	32.2
Alanine	31.9	8.7	27.5	29.4	36.3
Cystine	3.1	0.0	25.8	—	—
Valine	18.9	58.2	69.3	71.9	72.4
Methionine	5.7	29.8	28.0	40.3	47.3
Isoleucine	6.5	0.0	26.1	23.0	50.7
Leucine	18.6	24.1	26.8	36.0	33.3
Tyrosine	16.1	13.6	40.3	45.9	45.3
Phenilalanine	11.8	9.3	34.7	67.7	43.2
Hydroxyproline	7.1	8.4	—	5.6	—

Περίληψη

Μελέτη τῶν ἀμινοξέων ποὺ περιέχονται σὲ διάφορους ἑλληνικοὺς οἴνους.

Σὲ διάφορα ἑλληνικὰ κρασιὰ προσδιορίζονται μὲ αὐτόματο ἀναλυτὴ ἀμινοξέων, τὰ ἐλεύθερα ἀμινοξέα μετὰ ἀπὸ ἀπολευκωμάτωση μὲ πικρικὸ ὀξύ, καθὼς καὶ τὰ ὁλικὰ ἀμινοξέα (ἐλεύθερα + ἑνωμένα ὑπὸ μορφὴ πρωτεϊνῶν) μετὰ ἀπὸ ὄξινη ὑδρόλυση.

Τὰ ἀποτελέσματα ποὺ προκύπτουν συζητοῦνται καὶ συγκρίνονται μὲ αὐτὰ γιὰ κρασιὰ ἀλλοδαπῆς ποὺ ἀναφέρονται στὴ βιβλιογραφία.

Ἐπιπλέον προσδιορίζεται καὶ συζητεῖται ἡ ἀπώλεια τῶν ἐλεύθερων ἀμινοξέων σὲ κρασιὰ ποὺ διαυγάζονται μὲ διάφορες ποσότητες μπετονίτη μετὰ τὴν ἀπολευκωμάτωση μὲ πικρικὸ ὀξύ.

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DERIVATIVES OF 1 — (3′,4′ — DIMETHOXY-PHENYL) — 2 — AMINO-ACETYLAMINO-ETHANOL

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(Received April 17, 1976)

Summary

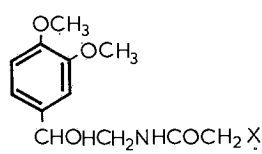
The synthesis of 1 - aryl - 2 - amino-acetylaminoethanols bearing alkoxy-groups on the aryl moiety is described. The products are obtained in fair yield by the action of chloracetyl chloride, followed by suitable amines on the 1-aryl-2-aminoethanols. The products were tested for local anesthetic and probable cholinergic activity.

Introduction

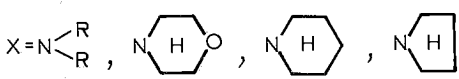
Substituted arylaminoethanols have been known for a long time for their sympathomimetic activity. The basic structure of the most widely used representative of this class includes a primary, secondary or tertiary amine as part of the side chain together with a secondary alcoholic group a- to the amino-group; the ring on the other hand may or may not bear free hydroxyl groups.

This configuration allows the characterization of the influence of the various groups on the sympathomimetic properties of this molecule in relation to the pharmacological action of adrenaline.

Retaining the basic structural requirements for sympathomimetic activity, we have in the present work, introduced other pharmacologically active groups such as the acetylaminoacyl moiety and have synthesized compounds of the general formula (I).



(I)



R=Me, Et, Isobutyl .

The pharmacological action of these compounds synthesized according to scheme 1, was studied and is described in a later section.

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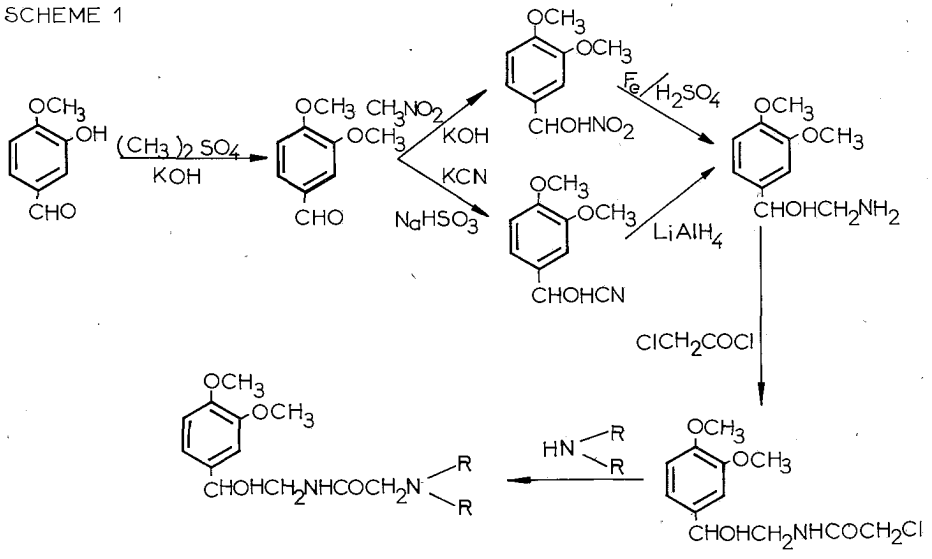
Starting point for the synthesis of I was isovanilin which was further methylated yielding the corresponding dimethoxybenzaldehyde.[1,2] The dimethoxyphenylaminoethanols were then obtained via two routes, i.e. (a) reaction with nitromethane in alkaline media yielding the corresponding nitroethanol followed by reaction to the corresponding aminoethanol[3] and (b) reaction with potassium cyanide in the presence of sodium bisulphite giving the cyanohydrin which is further reduced with lithium aluminum hydride to the aminoalcohol[4].

Route (a) was then preferably followed due to the higher yields thus obtained. Reaction of the aminoethanol with chloracetyl-chloride in alkaline media gave the chloracylamino-derivatives, which on reaction with various amines yielded (I).

The hydrochlorides of (1) could not be purified due to their highly hygroscopic nature and the pharmacological control had to be performed with freshly prepared hydrochlorides.

SCHEME 1



Experimental

The infrared spectra reported in this work were run on a Perkin-Elmer 521 infrared spectrophotometer and were in accordance with the proposed structures. The reagents employed were purified by standard procedures; melting points are uncorrected. Veratraldehyde was prepared by methylation of vanillin with dimethylsulfate and was purified by distillation under reduced pressure.[1,2]

1-(3',4'-Dimethoxy-phenyl) - 2 - nitro - ethanol

3,4-Dimethoxybenzaldehyde (220 g, 132 mmole) and nitromethane (7.5g 123mmole) dissolved in methanol (100ml) were cooled to -10°C and an ice-cold solution of potassium hydroxide (10g) in aqueous methanol (18ml water in 30ml methanol) was added dropwise under vigorous stirring taking care not to allow the temperature to exceed 0°C. When the addition was completed, the reaction mixture was poured into a 50% aqueous solution of acetic acid (22ml) frosen to 0°C, under vigorous stirring.

The mixture was then poured into a separating funnel containing 450ml of water and 3,4-dimethoxyphenyl-2-nitroethanol appeared after a few minutes as a yellowish layer at the buttom of the funnel. This was separated (18.1g, 60%) and was recrystallised from petroleum ether-benzene to give off-white meedles of 3,4-dimethoxy-phenyl-2-nitro ethanol m.p. 96°C, (Found: C, 53.30; H, 5.64%. $C_{10}H_{13}NO_5$ requires: C 52.87, H 5.70%).

1-(3',4'-Dimethoxy-phenyl)-2-amino - ethanol[3,4]

Sodium bisulphite (27.0g) in water (100ml) was added to 3,4-Dimethoxy benzaldehyde (32.0g, 192mmole) and the mixture was stirred at room temperature for 0.5hrs. More water (c.a. 100ml) was then added followed by ether (300ml) and the mixture was cooled to 0°C.

An ice-cold solution of potassium cyanide (23.5g, 356mmole) in water (c.a. 60ml) was then added under vigorous stirring, followed by more sodium bisulphite and the stirring was continued for 3hrs more.

The organic layer was then separated and the aqueous layer was extracted with ether. The combined ethereal extracts were washed with 20% aqueous sodium bisulphite and then with water and the solvent was distilled off. The residue was dried by azeotropic distillation with benzene (c.a. 40ml) and light petroleum was added.

The cyanohydrine thus precipitated was filtered, it was washed with petr. ether and dried (c.a. 33g). A solution of crude 3,4-dimethoxybenzaldehyde cyanohydrin (20g) in absolute ether (200ml) was added in very small portions to a vigorously stirred, ice-cold mixture of lithium-aluminum hydride (7.6g) in absolute ether (200ml) and the mixture was stirred for c.a. 17hrs at room temperature. The complex was then decomposed by the addition of a little water which was followed by sodium hydroxide solution and more water. The ethereal layer was separated, it was dried over anhydrous sodium sulphate, and the solvent was distilled off to leave crude *1-(3',4'-dimethoxy-phenyl)-2-amino-ethanol* as a yellow oil (c.a. 12g, 32% based on 3,4-dimethoxybenzaldehyde). This was distilled under reduced pressure (110°C/80μHg) to give an off-white oil (Found: C, 60.58; H, 7.88% $C_{10}H_{15}NO_3$ requires: C, 60.91; H, 7.61%).

Unfortunately, the picrate of this amine, although readily formed, could not be accurately analysed due to its extreme hygroscopic nature.

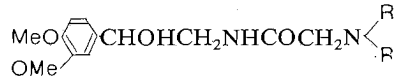
Reduction of 1 - (3',4' - dimethoxy-phenyl) - 2 - nitro-ethanol

Sulphuric acid (1:1, 230ml) was added in small portions under vigorous stirring to a cooled solution of 1 - (3',4' - dimethoxy-phenyl) - 2 - nitro - ethanol (30g) in ethanol (250ml), followed by the addition of ferric powder. The mixture was then gently warmed on a steam-bath for three hours, while a little ferric powder and a little sulphuric acid were added from time to time.

The mixture was then allowed to cool, water was added (c.a. 800ml and the precipitate was separated by filtration.

The solution was extracted with ether and the aqueous layer was rendered alkaline (c.a. pH10) by the addition of a concentrated solution of sodium hydroxide. The free amine was salted out and was extracted with ether, it was dried over magnesium sulphate and the solvent was removed to leave the crude amine (18g, 71%) which on distillation gave a white oil identified as *1 - (3',4' - dimethoxy-phenyl) - 2 - aminoethanol* by infrared spectroscopy (comparison with an authentic sample).

TABLE I



Product	-NRR	Yield %	base or salt	formula	b.p/ μ.Hg	m.p	Analysis Calc. C	H	N	Found C	H	N
x_1	$-N(CH_3)_2$	90	base	$C_{14}H_{22}N_2O_4$	160/100		59,57	7.80	9.94	59,34	7,94	9,58
x_3	$NHCH(CH_3)_2$	83	base	$C_{16}H_{26}N_2O_4$	170/100		61,94	8,34		61,69	8,64	
x_6	$-N(C_2H_5)_2$	90	base	$C_{16}H_{26}N_2O_4$	165/100		61,91	8,44	9,03	61,58	8,85	9,42
			picrate	$C_{22}H_{29}N_5O_{11}$		138-40	48,98	5,38		49,27	5,57	
x_2	N⟨H⟩O	80	base	$C_{16}H_{24}N_2O_5$	185/300		59,19	7,43	8,65	59,30	7,80	8,15
	»		picrate	$C_{22}H_{27}N_5O_{12}$		170-2	47,74	4,88	12,65	48,23	4,96	13,01
	»		Iodo-methylate	$C_{17}H_{27}JN_2O_5$		176	43,77	5,79	5,98	44,10	6,01	5,62
x_5	N⟨H⟩	90	base	$C_{17}H_{26}N_2O_4$	175/150		63,35	8,07	8,69	63,85	8,34	8,35
x_4	N⟨H⟩	83	base	$C_{16}H_{24}N_2O_4$	165/30		62,34	7,79	9,08	62,73	7,90	9,52

1 - (3',4' - Dimethoxy-phenyl) - 2 - chloracetaminoethanol

Sodium carbonate (2.2g) was added to a solution of 1 - (3',4' - dimethoxy-phenyl) - 2 - aminoethanol (11.0g, 55mmole) in chloroform (80ml) and the mixture was stirred at room temperature while chloracetylchloride (3.8ml 65mmole) was added dropwise. Stirring was continued for 1hr after which the mixture was left overnight.

It was then filtered and the filtrate was washed with dilute hydrochloric acid and then with water until neutral. The solution was dried over magnesium sulphate and the solvent was distilled off to leave 1 - (3',4' - dimethoxy-phenyl) - 2 - chloracetaminoethanol as a viscous oil (10.5g, 70%) which was employed without further purification in the preparation of the amines.

1 - (3',4' - Dimethoxy-phenyl) - 2 - dimethylacetaminoethanol

1 - (3',4' - Dimethoxy-phenyl) - 2 - chloracetaminoethanol (6.0g, 22mmole) and a 30% ethanolic dimethylamine solution (17ml, 115mmole) were sealed in a glass tube and were left at room temperature for several days. The reaction mixture was then filtered and the solvent as well as excess dimethylamine were removed under vacuo from the filtrate. The remainder was rendered alkaline with aqueous sodium hydroxide and it was extracted with ether.

The organic layer was dried over magnesium sulphate and it was distilled off to leave oily 1 - (3',4' - dimethoxy-phenyl) - 2 - dimethylacetaminoethanol.

1 - (3',4' - dimethoxy-phenyl) - 2 - morpholinoacetaminoethanol

Morpholin (5.9g 72mmole) was added to a solution of 1 - (3',4' - dimethoxy-phenyl) - 2 - chloracetaminoethanol (6.5g, 24mmole) in benzene (30ml) and the mixture was heated under reflux for 3hrs.

The mixture was then filtered to remove morpholin hydrochloride and the filtrate was treated with sodium bicarbonate solution and then with water. The organic layer was dried over magnesium sulphate and the solvent was removed to leave crude 1 - (3',4' - dimethoxy-phenyl) - 2 - morpholinoacetaminoethanol (6.1g 80%) which was distilled under reduced pressure (185°C/300μ.Hg) to give the pure amine (c.a. 5g) identified in the form of its picrate.

Pharmacological Section

Surface local anesthetic action

The compounds described above were pharmacologically examined by the supression of the reflexes on the cornea of guinea pigs following the technique introduced by M.R.A. Chance *et al*[5] where the activity of the product is found by determining the minimum concentration required for elimination of reflex action lasting over five minutes. The results are shown in table II.

TABLE II

Compound	DL_{50}(1) (gr/kg*)	DE50(2)	Anesthesia compared to procaine = 2
x_1	0.023	6.00	0.33
x_2	0.013	5.00	0.40
x_3	0.010	5.00	0.40
x_4	0.010	3.30	0.50
x_5	0.025	3.35	0.50
x_6	inactive		

(1) Mean lethal dose calculated Grosso Modo by the method of Litshfield and Wilcoxon.
(2) The mean of the active concentration is determined from the curve resulting from the logarithm of the concentration in each solution versus its integer percent response on the special Log/brobit chart.

The compounds were tested for C.N.S. action on white mice and quantitative results were obtained based on standard behaviour.

General behaviour (general comportement)

The compounds affected the motor activity of the animals subjected to test, while they had no effect on respiration and reflexes.

Thermoregulative activity

The compounds described cause a fall of temperature in general, as well as fall of the fever caused on mice by amphetamine; an example of such action is shown in Fig. 1.

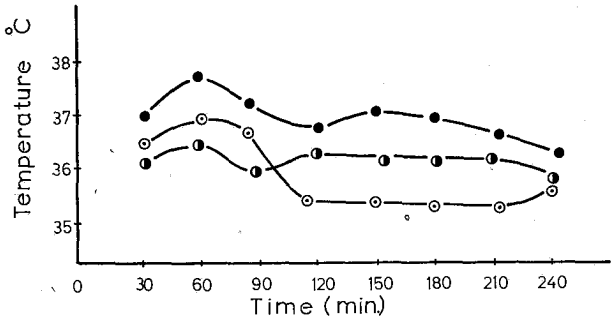


FIG. 1: *Thermoregulative activity of X_1*

Other effects

All the aforementioned compounds were tested on neuromuscular preparations (phrenic-diaphragm) and an increase in the intensity of contractions was observed for x_1 and x_5.

Further testing in combination with drugs blocking the neuromuscular synapses such as curare is in progress and will be reported later.

Acknowledgements

The authors wish to thank Prof. G. Tsatsas for suggesting the project. Thanks are also extended to the N.R.C. "Demokritos" analytical Laboratory for elemental analyses and the Laboratory of Experimental Pharmacology of the University of Athens for offering the guinea pigs required.

Περίληψη

Παράγωγα τῆς 1 - (3',4' - διμεθοξυ-φαινυλο) - 2 - αμινο-ακετυλαμινο-αιθανόλης.

Περιγράφεται ἡ σύνθεσις νέων παραγώγων τῆς 1 - (3',4' - διμεθοξυ-φαινυλο) - 2 - αμινο-ακετυλαμινο-αιθανόλης. Τὰ προϊόντα λαμβάνονται μὲ καλὴν ἀπόδοσιν δι' ἀντιδράσεως τῶν 1 - αρυλο - 2 - αμινοαιθανολῶν μὲ χλωρακετυλοχλωρίδιον καὶ ἐν συνεχείᾳ μὲ καταλλήλους ἀμίνας. Ἀνακοινοῦται ἐπίσης ἡ δρᾶσις τῶν συντεθεισῶν ἑνώσεων ὡς τοπικῶν ἀναισθητικῶν καὶ χοληνενεργῶν μέσων.

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"IR SPECTRA OF 9-METHYLADENINE, Pt (9-METHYLADENINE H)Cl_3 AND THEIR DEUTERATED DERIVATIVES"

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Summary

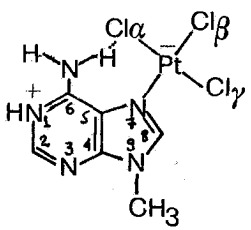
The IR spectra of 9-methyladenine its deuterio analog (ND_2, ^+ND, CD_3, C_8-D), the complex Pt(9-methyladenine H)Cl_3 and Pt(9-methyladenine D)Cl_3 have been recorded in the region 4000-200 cm^{-1}. A qualitative assignment of the various observed spectral bands is attempted. The group frequencies NH_2, NH^+, CH_3 are in many cases recognized and are helpfull in structural assignments of the complex.

Key words: IR spectra, (9-methyladeninium) trichloroplatinum (II), 6-amino-9-methylpurine, 9-methyladenine, Platinum (II) complexes.

Introduction

The recent discovery of the antitumour activity of platinum coordination compounds,[1,2] has given a great importance in studies of the interactions of platinum inorganic salts with the constituents of nucleic acids. This is because, it is believed that the metal exhibits its biological action by reacting with DNA[3]. Therefore, the general reactivity behavior of the bases, constituents of DNA, towards platinum, as well as the binding sites, are some of the main problems in such studies in vitro.[4-6]

9-methyladenine, although not a natural constituent of nucleic acids, can serve as model in such interactions. The crystal structure of Pt(9-methyladenine H)Cl_3 prepared in 3N HCl acid solution has been resolved by X-rays diffraction work,[7,8] and it is a zwitterion, as follows:



Structure of the complex

There is a weak hydrogen bonding between the chlorine Cl_α and one of the hydrogen atoms of the group NH_2. A stronger hydrogen bond also exists between the chlorine atom Cl_γ and the proton at the N_1 site of another molecule in the unit cell.[7,8]

In the present report a tentative assignment of the fundamentals is attempted, based on the ir spectra of the ligand (L) the deuterated ligand (LD) and the complexes $Pt(LH)Cl_3$ and $Pt(LD)Cl_3$ (ND_2, C_8-D, CD_3) partially or completely deuterated. This study may help in structural assignments of this or other similar complexes.[5]

IR spectra

(a) Region 4000-2000 cm^{-1}

In this region the NH_2 stretching bands of the free ligand appear at 3312 and 3256 cm^{-1} and they are shifted to 2450 cm^{-1} upon deuteration (See Fig. 1 and Table I). In the complex $Pt(LH)Cl_3$ these bands are observed at 3323 cm^{-1} and 3260 cm^{-1} and are shifted to 2513 and 2426 cm^{-1} in the complex $Pt(LD)Cl_3$.

In the deuterated ligand L (C_8-D, CD_3, ND_2) there is observed only one weak band at 3010 cm^{-1}, which can be assigned to the C_2-H stretching motion. The remaining C-D stretching are observed as a broad band at 2260 cm^{-1}. In the partially deuterated complex $Pt(LD)Cl_3$ bands were observed at 3077, 3046, 3012 and 2943 cm^{-1}. The first two are undoubtedly due to the methyl group, the third to C^2-H and the fourth to C^8-H. The corresponding C-D bands are at 2303, 2267 and 2204 cm^{-1}. The absence of a massif absorption around 2500 cm^{-1} in the non deuterated complex, indicates the absence of a strong intra-molecular hydrogen bonding, involving the N_1H^+ proton and the Cl_y in infinite chains, as in the case of 6-mercaptopurine riboside complexes[4]. The unit cell contains only two hydrogen bonded molecules.[7,8] Existence of a strong hydrogen bonding NH^+ ... Cl^-, reduces the NH^+ stretching frequency in the case of pyridinium[9], pyrimidinium[10] and purine.[11]

(b) Region 2000-1200 cm^{-1}

The first band in this region occurs at 1662 cm^{-1} in the ligand which is attributed to the NH_2 bending vibration, because it is removed upon deuteration. The same conclusion has also been reached by Kyogoku *et al.*[12], *for the band at 1677 cm^{-1}* in the ir spectrum of 9-methyl adenine single crystals. Therefore, the second band of the ligand at 1594 cm^{-1} is the first ring stretching band of the purine skeleton. This band moves to higher frequencies when the N_1 nitrogen atom is protonated.[4,5,9-13] While in the complex $Pt(LH)Cl_3$ we only observe one band at 1662 cm^{-1} which cannot distinghuish between NH_2 bending or ring stretching of the protonated form, in the complex $Pt(LD)Cl_3$ there appear a band at 1648 with a shoulder at 1663 cm^{-1} (partial deuteration). The 1648 cm^{-1} band is the first ring stretching frequency. This shift, by 54 cm^{-1} from the ligand to the complex in the ring stretching vibration, is a good indication for N_1-H^+ protonation[4,9-13]. The second ring stretching frequency, due also to the purine ring is observed at 1565 cm^{-1} in the non deuterated ligand and at 1555 cm^{-1} in the deuterated one. In the non deuterated complex we have two bands at 1585 and 1568 cm^{-1}, which appear at 1589 and 1572 cm^{-1} in the deuterated one and are also assigned to ring stretchings by analogy with purine itself.[11,14] The 1585 cm^{-1} band diminishes in intensity in the deuterated complex and it can be associated with the ND^+ deformation motion of the deuterated ring. Some assignments of ring stretching vibrations by analogy with purine[11,14] are given in Table I.

The C-H deformation mode of the methyl group occurs at 1453 cm^{-1} in the single crystal of 9-methyladenine[12] and possibly at 1469 cm^{-1}, in the KBr disk. On passing from the non deuterated complex to the deuterated one, there is a re-ordering of the bands at 1420 cm^{-1}, which indicates the presence of C-H deformation modes in this region. A strong band at 1263 cm^{-1} has been assigned to the C-NH_2 stretching by Kyogoku *et al.*[12] in 9-methyladenine. In KBr disks we

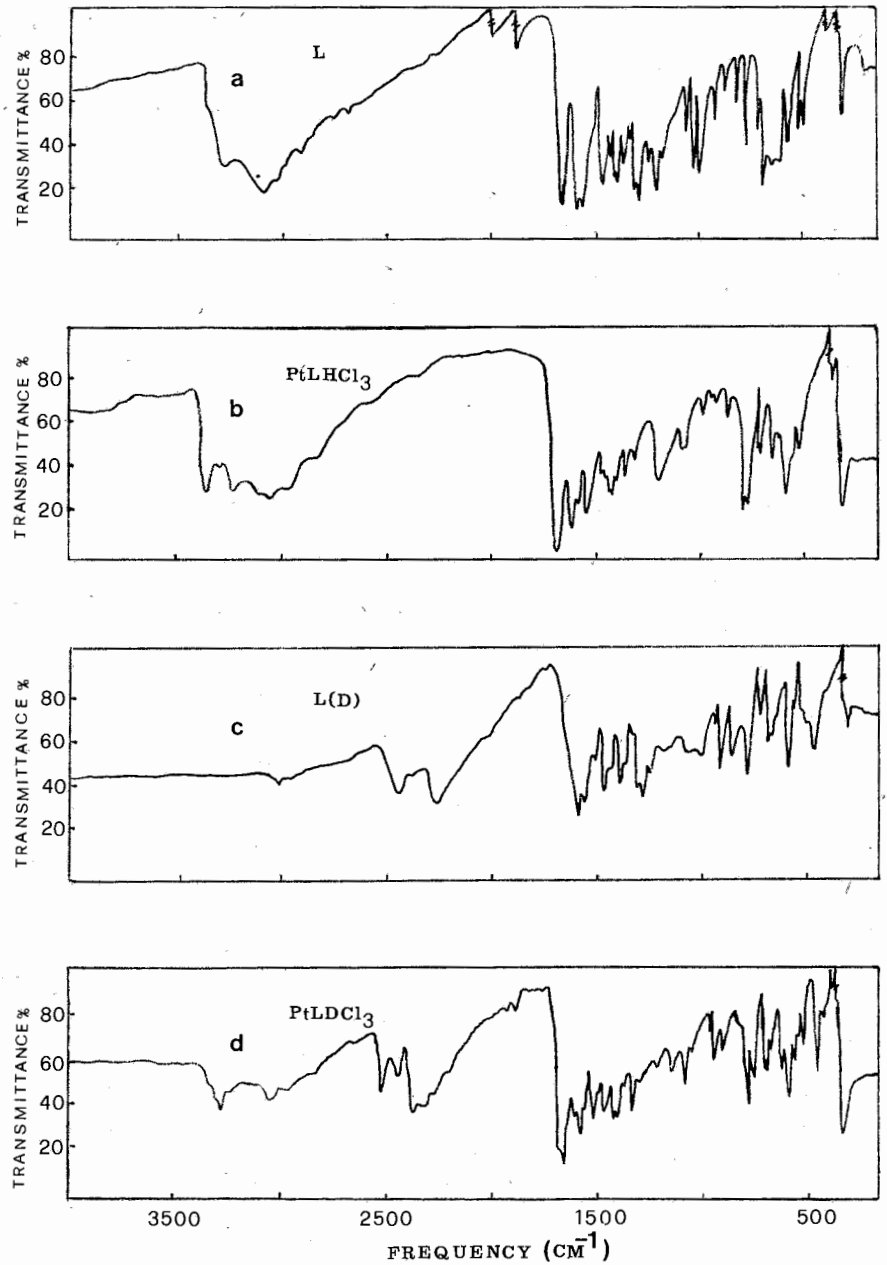


FIG: 1. *IR spectra in the region 4000-200 cm^{-1} of: (a) The ligand L=9-methyladenine, (b) the complex Pt(LH)Cl$_3$, (c) the deuterated ligand L and (d) the deuterated complex Pt(LD)Cl$_3$ (ND$_2$, ND$^+$, CD$_3$, C$_8$-D).*

TABLE I: *IR data of 9-methyladenine = L its platinum complex and their deuterated derivatives*

(LH)	$Pt(LH)Cl_3$	(LD) (ND_2, CD_3, C_8-D)	$Pt(LD)Cl_3$ (ND_2, CD_3, C_8-D) partially	Assignment
3312 m	3323 vs	—	3322 w	
—	—	—	3285 m	NH_2 stretchings
3256 s	3260 s	—	3268 m	
—	3198 vs	—	—	NH^+ stretchings
3065 vs	3035 vs	—	3077 s	
—	—	3010 w	3046 s	
2904 s	2928 vs	—	3012 w	
—	—	—	2943 w	
2703 w	—	—	—	
2606 w	—	—	—	
—	—	—	2513 m	ND_2, ND^+ and
—	—	2448 s	2440 w	
—	—	—	2426 w	C-D stretchings
—	—	2369 w	2363 s	
—	—	—	2303 s	
—	—	2263 vs	2267 m	
—	—	—	2204 w	
1662 vs	1662 vs	—	1663 sh	δNH_2
—	—	—	1648 s	ring stretching py + NH^+
1591 vs	1585 vs	1594 vs	1589 m	
1565 m	1568 m	1555 s	1572 s	
1506 w	1525 s	—	1524 s	ring stretching Im
—	—	1498 m	1486 w	
1469 s	1452 w	1464 s	1455 m	ring stretching Im+py
1432 m	1440 w	1428 m	1430 m	C-H deformation +
—	1426 m	—	—	ring stretching
1414 s	1412 m	—	—	
1403 s	1392 m	1387 s	1395 m	ring stretching py
1368 m	1362 w	1366 m	1366 w	ring stretching Im
1341 w	1343 ms	—	1347 m	
—	—	1332 w	1326 w	ring stretching Im +
1319 s	—	1312 s	1319 w	NH or CH_3 deformation
1302 s	1301 m	1295 s	1300 w	
—	—	—	1280 w	CH_3 deformation +
1246 m	1229 w	1252 m	1256 w	C-N stretching
—	—	—	1243 w	
1223 s	—	1209 w	—	
1192 m	1187 s	1191 w	1185 ms	γ NH_2

TABLE I: *(continued)*

(LH)	$Pt(LH)Cl_3$	(LD) (ND_2, CD_3, C_8-D)	$Pt(LD)Cl_3$ (ND_2 CD_3, C_8-D) partially	Assignment
—	1129 w	1173 w	1145 m	
1079 m	1076 m	1073 w	1073 ms	
1043 s	1068 m	1047 w	1042 w	
1016 s	—	1009 w	—	γ C-H
943 m	985 m	—	—	
—	—	953 w	959 w	ϱ NH_2
—	—	940 w	—	
—	942 w	925 m	939 w	
—	921 w	—	917 w	
900 m	—	—	898 w	
839 m	868 m	861 s	869 m	γ C-H
—	—	792 s	—	
797 s	773 vs	732 m	773 s	ring motion
737 s	762 vs	—	761 s	ring motion
715 s	708 s	696 m	701 s	ring motion
—	—	680 m	675 w	
667 vs, br	656 s	—	658 w	
—	—	—	631 s	
—	583 vs	595 s	591 w	ω NH_2
—	—	571 w	573 w	
—	—	—	561 m	
542 s	549 w	—	554 m	
531 s	—	536 m	—	
—	523 m	517 m	519 m	ring motion
—	—	476 m	453 s	ω ND_2
—	—	—	416 w	
353 ms	369 w	398 w	—	
—	317 s	—	330 s	ν Pt-Cl stretching
—	—	328 w	—	

s = strong, m = medium, w = weak, v = very, br = broad, Im = Imidazole, py = pyrimidine, ν = stretching, δ, γ = deformation, ϱ = rocking, ω = wagging.

have the medium bands at 1246 cm^{-1} in 9-methyladenine, at 1252 cm^{-1} in the deuterated analog and at 1229 cm^{-1} in $Pt(LH)Cl_3$ and 1280 cm^{-1} in $Pt(LD)Cl_3$, which may be related to the same motion. In the complex $Pt(LH)Cl_3$, we have bands at 1343 and 1301 cm^{-1} and in the $Pt(LD)Cl_3$ at 1326 cm^{-1} only. This implies that the first two bands are probably due to coupling of CH_3 deformation motion with one skeletal vibration.[11,14] The 1326 cm^{-1} band therefore is a pure ring imidazolic stretching motion.[11,14]

(c) Region below 1200 cm^{-1}

The 1187 cm^{-1} band of $Pt(LH)Cl_3$ must be composite in nature, since it is much simplified upon deuteration and it must contain the NH_2 rocking vibration, hydrogen bonded with Cl_a. It removes to 959 cm^{-1} upon deuteration. In free 9-methyladenine this frequency was assigned at 1082 $cm.^{-1}$ [12] It is known that this band increases in frequency upon coordination or formation of hydrogen bonding.[15] The 985 cm^{-1} band is removed upon deuteration from $Pt(LH)Cl_3$ to $Pt(LD)Cl_3$ and it may be due to the C-H rocking frequency, which occurs at 943 cm^{-1} in the non deuterated ligand.[12] The 840 cm^{-1} band of 9-methyladenine has also been assigned to a C-H rocking motion.[12] The corresponding 868 cm^{-1} of $Pt(LH)Cl_3$ is also missing from $Pt(LD)Cl_3$ and assigned to the same motion.

The 773, 762 and 708 cm^{-1} bands of the $Pt(LH)Cl_3$ are not removed upon deuteration and appear at 773, 761 and 701 cm^{-1} in the deuterated complex. They are therefore assigned to skeletal vibrations. The corresponding bands in the non-deuterated ligand are at 797, 737 and 715 cm^{-1} and at 792, 732 and 696 cm^{-1} in the deuterated one. The NH_2 wagging motion, is assigned to the 583 cm^{-1} band of $Pt(LH)Cl_3$ which is shifted to 453 cm^{-1} in $Pt(LD)Cl_3$. In the ligand it has been assigned at 690 (490).[12] This difference may be due to N^+-H ...Cl_a bonding. 9-methyladenine removes the 675 cm^{-1} (ϱ_w) to 630 cm^{-1} upon complex formation with 5-bromo-3-methyl uracil.[16] The band at 523 cm^{-1} of $Pt(LH)Cl_3$ does not remove upon deuteration, appearing at 519 cm^{-1} in $Pt(LD)Cl_3$ and it is therefore attributed to a skeletal vibration too. The ν Pt-Cl appears as a single medium sharp band at 317 cm^{-1} in the non deuterated complex, in agreement with Cl ... H bonding in the complex.[17] It moves to 330 cm^{-1} in the deuterated species.

Experimental

IR spectra:

The IR spectra were recorded using a Perkin-Elmer 621 spectrophotometer calibrated with polystyrene. The spectra were recorded in KBr disks. The positions of the absorptions are given within ± 2 cm^{-1}.

Deuterated and non deuterated ligand and complexes

The preparation of the complex Pt(9-methyladenine H)Cl_3 has been described[5]. 9-methyladenine (D_8, ND_2, CD_3) was obtained by treating a 0.05 M solution of ligand in D_2O, at 70°C under vacum for three days[5]. The corresponding complex Pt(9-methyladenine D)Cl_3, (ND_2, C_8-D, CD_3, N_1D^+) was prepared from the deuterated ligand in 3N DCl solution. The partially ND_2, CD_3, $N_1{}^+D$ complex was prepared from the non-deuterated ligand in 3N DCl.

Περίληψη

Φάσματα ὑπερύθρου τῶν 9-μεθυλαδενίνης, Pt(9-μεθυλαδενίνη H)Cl_3 καὶ τῶν δευτεριωμένων παραγώγων των.

Μελετῶνται τὰ φάσματα ὑπερύθρου, περιοχῆς 4000-200 cm^{-1} τῆς 9-μεθυλαδενίνης, τοῦ δευτεριωμένου παραγώγου της (ND_2, ND^+, CD_3, C_8-D), τοῦ συμπλόκου Pt(9-μεθυλαδενίνη H)Cl_3 καὶ τοῦ δευτεριωμένου παραγώγου του. Ἐπιχειρεῖται ποσοτικὸς χαρακτηρισμὸς τῶν διαφόρων παρατηρουμένων φασματικῶν ταινιῶν. Αἱ συχνότητες τῶν ὁμάδων NH_2, NH^+, CH_3 χαρακτηρίζονται ἐπιτυχῶς εἰς πολλὰς περιπτώσεις καὶ μαζὶ μὲ ἄλλας ταινίας βοηθοῦν εἰς τὸν δομικὸν χαρακτηρισμὸν τοῦ συμπλόκου.

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DITHIOCARBAMATES OF VANADIUM (III)

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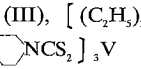
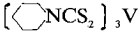
Summary

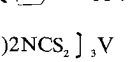
The preparation and spectral properties are reported for the new complexes obtained by the reaction of vanadium trichloride and N,N′ disubstituted dithiocarbamate ligands. The general formula of the complexes is $V(dtcb)_3$; where dtcb are diethyl-, dimethyl-, morpholine-, piperidine- and pyrrolidine- dithiocarbamate. The crystal field parameters for the complexes are given.

Key words: Tris (dithiocarbamate) vanadium (III), preparation, spectra, crystal field parameters.

Abbreviations: $V(detc)_3$ Tris (diethyldithiocarbamato) vanadium (III), $[(C_2H_5)_2NCS_2]_3V$

$V(mdtc)_3$ Tris (morpholinedithiocarbamato) vanadium (III), []$_3$V

$V(pmtc)_3$ Tris (pentamethylenedithiocarbamato) vanadium (III), []$_3$V

$V(tmtc)_3$ Tris (tetramethylenedithiocarbamato) vanadium (III), []$_3$V

$V(metc)_3$ Tris (dimethyldithiocarbamato) vanadium (III), $[(CH_3)2NCS_2]_3V$

$V(mdtc)_2Cl$ Bis (morpholinedithiocarbamato) vanadium (III) chloride

$V(tmtc)_2Cl$ Bis (tetramethylenedithiocarbamato) vanadium (III) chloride

Introduction

Continuing our study on the dithiocarbamates of both transition and main group elements,[1-3] we report here the preparation and characterization of some dithiocarbamato-Vanadium (III) complexes as well as the major assignments for the IR, UV-visible and NMR spectra, which are discussed.

The complexes that are reported have the general formulae $V(dtcb)_3$ or $V(dtcb)_2Cl$ and they have been prepared by direct reaction of vanadium trichloride with anhydrous sodium dithiocarbamates.

Experimental

All reactions and manipulations were carried out under dry oxygen-free conditions. The IR spectra were recorded as KBr discs in the range 4000 - 200 cm^{-1} using a Perkin-Elmer 467 spectrophotometer. The electronic spectra were obtained with a PMQII Zeiss spectrophotometer. The proton NMR spectra were recorded on a Varian 60 Mc/MHz instrument using TMS as the internal standard.

The preparation of tris vanadium (III) complexes

The preparation of $V(mdtc)_3$ illustrates the method used for the synthesis of the derivatives. Vanadium trichloride 0.96 g (6.1 mmoles) was added to a suspension of 3.3 g (18.3 mmoles) of sodium morpholinodithiocarbamate (mdtc) in 50 ml of solvent (chloroform or alcohol) and after stirring for one hour gave an orange precipitate. The precipitate was treated with CH_2Cl_2 and the mixture was filtered to separate sodium chloride. The complex was isolated from the filtrate by precipitation with petroleum ether. After 24 hours attempts to recrystallize the complexes resulted in decomposition.

The preparation of the chlorovanadium (III) complexes of pyrrolidine and morpholine

These derivatives were prepared by addition of 0.96 g (6.1 mmoles) vanadium trichloride to a suspension in chloroform of 12.2 mmoles sodium pyrrolidinodithiocarbamate (tmtc) or morpholinodithiocarbamate (mdtc). After filtration petroleum ether was added to the filtrate to precipitate the product.

Results and discussion

Generally the reaction of vanadium trichloride with sodium dithiocarbamate in ethanol or methanol produces compounds having the formula $V(dtcb)_3$. Only in the case of the morpholino- and pyrrolidino- dithiocarbamate the obtained complexes were also the $V(mdtc)_2Cl$ and $V(pyrdtc)_2Cl$. The list of the complexes prepared, their analyses and some properties are shown in Table I. All these complexes are nonelectrolytes and are soluble in common organic solvents. They are not stable after exposure to the atmosphere and for this reason freshly prepared samples were used for all measurements and characterization procedures. The complexes are immediately hydrolysed in water.

The general assignments of the infrared spectra of the dithiocarbamates have been discussed extensively by many authors[4-7] and only a few important details relevant to the V(III) complexes reported are mentioned. The band in the region 1460 cm,$^{-1}$ assigned to the partly double bond character of C⋯N bond.[8] In the chloro-derivatives as expected, the stretching vibration of C⋯N bond showed a blow shift attributed to -I inductive effect induced by the halogen atom.[9]

The C⋯S stretching frequencies are in the range 950-1000 cm^{-1} and this is an indication that the dithiocarbamate groups act as bidentate ligands.[10]

Metal-sulfur stretching vibrations have been observed in the region 340-440 cm^{-1} for the dithiocarbamate complexes. Absorption bands attributed to vanadium-sulfur stretching vibrations for vanadium (IV) dithiocarbamate complexes have been reported at 345-361 cm^{-1} [11-13]. For the tris- complexes reported here a medium strength band is observed in the same region. For the chlorocomplexes this band is shifted to about 380 cm^{-1}. This shifting for the chlorocomplexes may be due to a back-donation effect.

The obtained NMR spectra in chloroform solutions gave peaks in two distinct regions with δ values ca. 3.8 and ca. 1.3, which easily assigned to methylene and methyl protons respectively. The differences between the NMR spectra of the tris- and bis-dithiocarbamates of V(III) and those of the dithiocarbamates of other elements were of no significance.

Electronic spectra of the complexes

Solution spectra were measured over the range 6000-40000 cm^{-1}. While it is clear that the complexes decompose to some extent, the measurements were made

TABLE I: Analytical data and some properties of the Vanadium (III) Dithiocarbamate Complexes

	% Calcd						% Found							
Compound	V	C	N	H	S	Cl	V	C	N	H	S	Cl	Color	Mp[a], °C
1) V $(detc)_3$	10.30	36.36	8.48	6.06	38.78	-	9.86	35.13	8.69	5.83	38.13	-	red-brown	146
2) V $(mdtc)_3$	9.49	33.51	7.82	4.46	35.75	-	8.94	33.13	7.34	4.16	35.39	-	yellow	124
3) V $(pmtc)_3$	9.58	40.67	7.90	5.64	36.15	-	9.80	39.28	7.67	5.33	36.45	-	red-brown	156
4) V $(tmtc)_3$	10.41	36.80	8.58	4.90	39.26	-	10.16	36.00	8.21	4.58	38.94	-	brown	106
5) V $(mdtc)_2Cl$	12.40	29.20	6.81	3.90	31.20	8.65	12.00	30.00	6.93	4.10	31.20	7.96	gray-green	97
6) V $(tmtc)_2Cl$	13.49	31.74	7.40	4.23	33.86	9.39	13.30	30.87	7.11	4.12	34.20	8.35	brown-green	102

a = With decomposition in each case

TABLE II: *Infrared spectra* (cm^{-1})

Compound	ν(C···N)	ν(C···S)	ν(M···S)
$V(detc)_3$	1480 1510 vs	995 s	355 vs
$V(mdtc)_3$	1480 1500 vs	1000 sh 1020 vs	335 m
$V(pmtc)_3$	1480 vs	975 vs 995	345 s
$V(tmtc)_3$	1490 vs	988 vs	340 vs
$V(mdtc)_2Cl$	1460 vs	1020 s	380 m
$V(tmtc)_2Cl$	1500 s	995 vs	380 m

rapidly. The measurement of a given region was repeated three to five times always with a freshly prepared solution each time.

The electronic spectra are typical of those exhibited by V(III) in an octahedral enviroment.[14] The absorptions in the range 6000 and 20000 cm^{-1} are assigned to d-d transitions while the bands between 20000 and 30000 are assigned as charge transfer, probably d-π^* transition. The expected three d-d transitions in the normal order of increasing energy are the following:
$\nu_1(^3T_{2g} \leftarrow {}^3T_{1g}(F))$, $\nu_2(^3T_{1g}(P) \leftarrow {}^3T_{1g}(F))$ and $\nu_3(^3A_{2g} \leftarrow {}^3T_{1g}(F))$.

Taking ν_1 and ν_2 for the two spin allowed transitions, the ligand field splitting parameter (10 Dq) and Racah parameter (B) were calculated (Table III). These values are in aggrement with those of nephelauxetic series of Jörgensen.[15] Band ν_2 is quite obvious only in the $V(mdtc)_3$ complex for the other complexes observed as a shoulder. As pointed out by Ballhausen[16] the Dq values are calculated as well only from the ν_1 values.

The higher energy band (ν_3) is in the region where charge transfer or intra ligand transitions are expected. This transition corresponds configurationally to the simultaneous excitation of the two electrons ($e^2_g \leftarrow t^2_{2g}$), high improbable. It is expected to be very weak, obscure by the strong charge-transfer bands. The energy of ν_3 was calculated from the values of Dq and B.

Another band was observed in the region 10000 cm^{-1}. This low energy band is raised from the distortion of octahedral d^2 complexes due either to a solvent effect and/or to the oxidation of V(III) complexes.

TABLE III: *Electronic spectral data and crystal field parameters* (cm^{-1})

Compound	ν_1	ν_2	Dq	B	$\beta=(\frac{B}{B_o})$**
$V(detc)_3$	14000(1,3)*	24390	1541	786	0,91
$V(mdtc)_3$	14493(1,96)	24691	1591	774	0,90
$V(pmtc)_3$	13698(1,5)	25000	1516	850	0,98
$V(tmtc)_3$	14285(1,7)	25000	1573	810	0,94
$V(metc)_3$	14184(1,6)	25316	1565	839	0,97

* values of log ε.
** Bo = Racah parameter of V(III) ion.

For chloro complexes was very difficult to arrive in sufficient measurements in the near- infrared spectra (d - d - transitions) arising from stereochemical changes with the addition of extra electron density from the electron - rich halogen atom.

Περίληψις

Διθειοκαρβαμιδικὰ σύμπλοκα τοῦ τρισθενοῦς βαναδίου

Στὴν ἐργασία αὐτὴ παρασκευάζονται καὶ μελετῶνται τὰ νέα τρισδιθειοκαρβαμιδικὰ σύμπλοκα τοῦ βαναδίου (III), τοῦ γενικοῦ τύπου $V(S_2CX)_3$ ὅπου X = $N(CH_3)_2$, $N(C_2H_5)_2$, μορφολίνη, πιπεριδίνη καὶ πυρρολιδίνη. Ἀναφέρεται ἀκόμη ἡ παρασκευὴ τῶν συμπλόκων δισ(μορφολινοδιθειοκαρβαμιδικοῦ) χλωριούχου V(III) καὶ δισ(πυρρολιδινοδιθειοκαρβαμιδικοῦ) χλωριούχου V(III). Ἐπίσης δίδονται καὶ ἑρμηνεύονται τὰ κύρια χαρακτηριστικὰ στοιχεῖα τῶν φασμάτων ὁρατοῦ ὑπεριώδους, ὑπερύθρου καὶ πυρηνικοῦ μαγνητικοῦ συντονισμοῦ τῶν παρασκευασθέντων συμπλόκων. Ἡ δομὴ τῶν τριπαραγώγων εἶναι ὀκταεδρικὴ καὶ οἱ τιμὲς τῶν παραμέτρων τοῦ κρυσταλλικοῦ πεδίου ὑπολογίζονται ἀπὸ τὰ ἠλεκτρονικὰ φάσματά τους (πίναξ III).

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MASS SPECTRAL STUDIES OF SUBSTITUTED PHENYLIODINE DIBENZOATES

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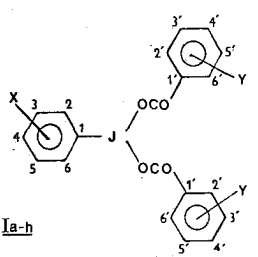
Summary

The mass spectra of eight substituted phenyliodine dibenzoates have been recorded and examined; ion fragment correlations, useful for diagnostic purposes, are indicated. The most interesting feature of their fragmentation mode is a number of rearranged ions; the mechanisms of their formation are briefly discussed. Certain fragment ions arise according to known thermolytic decompositions, while some other thermal reactions are observed for the first time.

Introduction

Although aryliodine dibenzoates of the general type *I* have been studied chemically in some detail,[1,2,3,4] their behaviour upon electron impact has not received any attention. In this paper the mass spectra of a number of substituted phenyliodine dibenzoates *(Ia-h)* are reported and their characteristic fragment ions are indicated and discussed.

Ia: X=Y=H
Ib: X=H, Y=4′ - CH_3
Ic: X=H, Y=2′ - CH_3
Id: X=H, Y=4′ - Cl
Ie: X=2 - Cl, Y=H
If: X=2 - Cl, Y=2′-CH_3
Ig: X=2-CH_3, Y=H
Ih: X=H, Y=2′, 4′, 6′-CH_3



Ia-h

Also, the electron-impact induced fragmentation of these compounds is compared to their known thermal decomposition behaviour. The influence of electron beam energy (13-70 eV) is also examined.

Results and Discussion

a. Major electron-impact fragmentation pathways.

The mass spectra of compounds *Ia-g* are given in tabular form in Table I and those of *Ih* at various conditions in bar-graph form in Figures 1 and 2. A general schematic representation including the main fragmentation processes, without

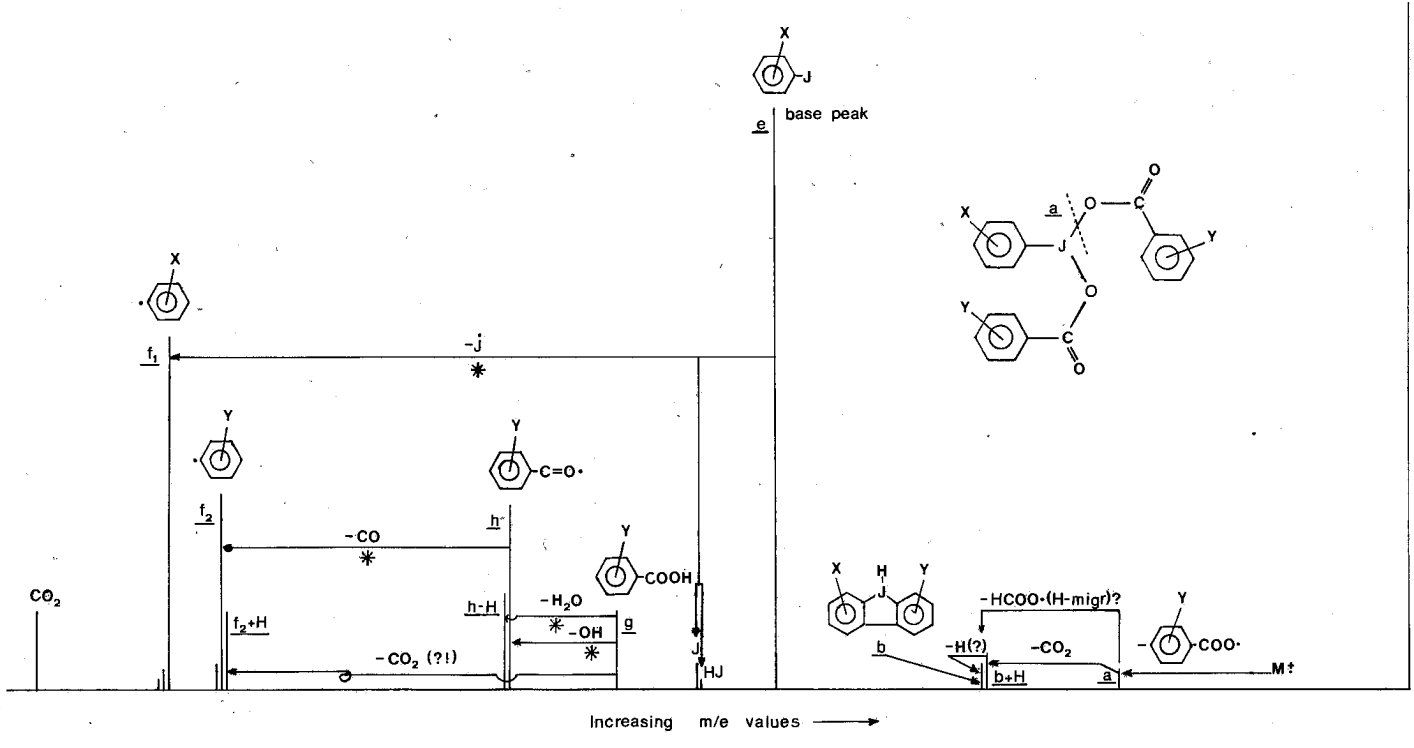
TABLE I.: *Mass spectra of aryliodine dibenzoates.*[a]

Compound	
Ia	m/e 44(23), 51(25), 52(4), 74(6), 75(4), 76(5), 77(83), 78(15), 94(1), 102(3), 102,5(1), 105(35), 106(3), 122(36), 123(2), 127(2), 154(1), 198(0,8), 204(100), 205(7), 223(0,2), 226(0,5), 280(0,2), 281(0,3), 293(0,3), 308(0,1), 325(1).
Ib	m/e 44(5), 50(10), 51(16), 63(4), 65(8), 74(5), 75(3), 76(5), 77(60), 78(6), 91(50), 92(22), 102(4), 102,5(4), 105(2), 119(32), 120(3), 127(2), 136(21), 137(3), 168(1,2), 204(100), 205(7), 212(1,5) 218(1,5), 254(0,2), 294(0,3), 295(0,7), 339(1).
Ic	m/e 44(23), 45(2), 50(11), 51(20), 59(3), 63(4), 65(7), 76(5), 77(75), 78(7), 89(4), 90(8), 91(38), 92(17), 102(4), 105(5), 118(22), 119(11), 122(2), 127(4), 135(3), 136(24), 137(3), 168(0,8), 204(100), 205(7), 212(0,3), 218(1), 294(0,2), 295(0,4), 321(0,2), 339(0,6).
Id	m/e 44(40), 50(18), 51(26), 75(10), 76(7), 77(87), 102(5), 111(13), 112(19), 113(5), 114(7), 127(3), 139(28), 140(2), 141(10), 156(24), 158(8), 188(0,9), 204(100), 205(7), 222(0.2), 232(0,9), 238(1), 294(0,2), 314(0,3), 315(0,1), 359(0,8).
Ie	m/e 44(22), 50(16), 51(14), 74(7), 75(22), 76(7), 77(24), 78(16), 105(42), 106(3), 111(38), 112(5), 113(13), 119(5), 122(26), 123(3), 127(5), 154(0.4), 188(0,7), 204(2), 232(2), 234(0,7), 238(100), 254(0,4), 314(0,3), 315(0,3), 316(0,1), 317(0,1), 359(1,5), 361(0,5).
If	m/e 44(30), 50(11), 51(6), 65(6), 74(6), 75(19), 76(11), 77(10), 89(1), 90(11), 91(36), 105(3), 111(40), 112(4), 113(13), 118(21), 119(11), 127(4), 128(1), 135(3), 136(27), 137(3), 167(0,5), 202(0.2), 204(0.3), 218(0.6), 238(100), 239(7), 240(33), 246(0.2), 254(0.1), 328(0.4), 329(0.5), 355(0.1), 373(1), 375(0.3).
Ig	m/e 44(46), 50(15), 51(22), 52(9), 63(10), 65(23), 74(5), 75(3), 76(5), 77(36), 78(35), 89(10), 90(11), 92(7), 94(1), 105(43), 106(4), 109(1), 127(2,5), 128(1,5), 154(0,8), 168(0,8), 204(2), 212(3), 218(100), 219(8), 254(0,4), 294(0,2), 295(0,3), 339(2,5), 340(0,3).

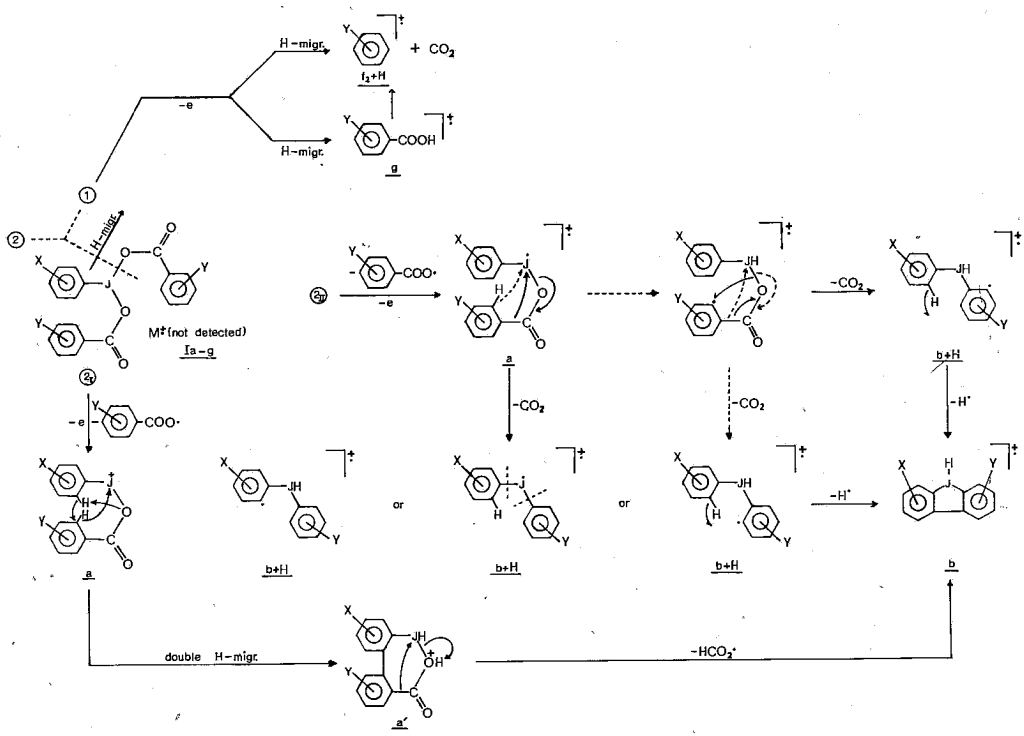
[a]See experimental part for conditions. Numbers in parenthesis represent relative intensities.

specific reference to absolute m/e values and their relative abundances, is given in bar-graph form in Scheme 1. This novel type of schematic representation was adopted because in some cases the detailed fragmentation mechanisms can not be confirmed without accurate mass measurements of the corresponding ions and / or extended deuterium labelling. With these reservations, a mechanistic approach of the observed main fragment ions of the spectrum is attempted in Scheme 2.

In all mass spectra recorded, with the exception of the mesitoyl derivative *Ih*, the molecular ion peaks ($M^{+\cdot}$) were not detected, in accordance with the known enhanced thermal lability of these compounds.[1-4]



SCHEME 1: *Schematic representation of general fragmentation of substituted phenyliodine dibenzoates (charges are ommitted). The molecular ion is observed only in compound Ih.*



SCHEME 2: *The mechanisms of the main fragmentation pathways of substituted phenyliodine dibenzoates (certain cations are depicted as both radicals and radical cations in order to avoid charge localisation).*

The most important higher mass number ions are a and b (Scheme 1). Their formation can be accounted for by either pathway 2_I or 2_{II} (Scheme 2). A distinction between these mechanisms should be possible if a metastable ion was observed for the elimination of H from the iodonium ion *b+H* (pathway 2_{II}):

$$b{+}H \xrightarrow[*?]{-H\cdot} b$$

Such a metastable transition was not detected, however, in all mass spectra studied, although much sought after, so that the occurence of pathway 2_{II} could not be established with certainty. In spite of this lack of evidence, it should be noted that this mechanism can not be ruled out, because only a double focusing mass spectrometer, by use of the appropriate defocusing technique, could definitely prove (or disprove) the existence of this metastable transition. The alternative mechanism of pathway 2_I, which includes double hydrogen migration, is therefore also possible. It is of interest to note that the mesitoyl derivative *Ih* under normal conditions shows a weak *b+H* ion and not at all ion *b*, but at elevated temperatures *b* appears in traces.

The main fragmentation pathways, which serve to identify the components of the molecular ions, consist in their splitting under formation of both ions of the corresponding benzoic acids and iodobenzenes, which are the most intensive peaks

of each spectrum. All iodobenzenes are also detected as doubly charged ions, ArJ^{++}, with relatively high abundances (3-5%).

$$ArJ(OCOAr')_2 \xrightarrow{-e} \begin{cases} ArJ^{\rceil +\cdot} \\ Ar'COOH^{\rceil +\cdot} \end{cases}$$

These main daughter ions are further fragmented in all mass spectra studied following well-known pathways, i.e.

$$\underset{g}{YC_6H_4COOH^{\rceil +\cdot}} \xrightarrow[*]{-\dot{O}H} \underset{h}{YC_6H_4CO^+} \xrightarrow[*]{-CO} \underset{f_2}{YC_6H_4^+} \xrightarrow[*]{-C_2H_2} YC_4H_2^+$$

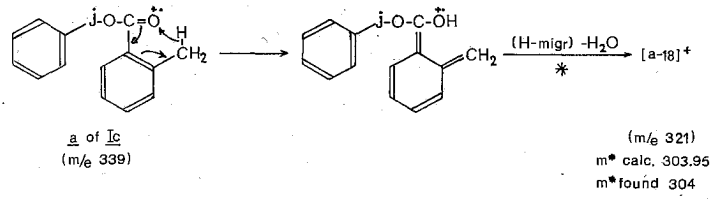
$$J^+; HJ^{\rceil +\cdot} \longleftarrow \underset{e}{XC_6H_4J^{\rceil +\cdot}} \xrightarrow[*]{-\dot{J}} \underset{f_1}{XC_6H_4^+} \xrightarrow[*]{-C_2H_2} XC_4H_2^+$$

A common feature of all spectra is ion f_2+H (Scheme 1). Its unusually high value of relative intensity in relation to ion f_2, $YC_6H_4^+$, makes it difficult to attribute its formation to CO_2 elimination from a substituted ionic fragment of the acid, i.e.:

$$YC_6H_4COOH^{\rceil +\cdot} \xrightarrow[?]{-CO_2} YC_6H_5^{\rceil +\cdot}$$

Thus, it is suggested that at least partially ion f_2+H is formed from the fragmentation of the whole molecule immediately after its ionisation (path I, Scheme 2), without excluding the possibility that there is also some CO_2 elimination due to thermal decomposition and/or an electron-impact fragmentation process of the acid.

A characteristic ortho-effect has been detected in the mass spectra of compounds *Ic, If* and *Ih,* in which the acid component bears one or two methyl groups in ortho-position. It is known generally that benzoic acids with an ortho-substituent containing an α-hydrogen udergo loss of water, through the operation of an ortho-effect.[5] In the mass spectra of compounds *Ic, If* and *Ih* this ortho-effect is observed not only in the corresponding acid fragments but also in fragment ions of type *a,* where an ion of m/e *a-18* results. This process has been confirmed in *Ic* with the observed appropriate metastable ion, while in *If* and *Ih* the corresponding metastable transitions have not been confirmed with certainty. The process is attributed in its first stage to a McLafferty type of rearrangement (six-membered transition with charge localisation on carbonyl oxygen) followed by hydrogen migration, as follows:

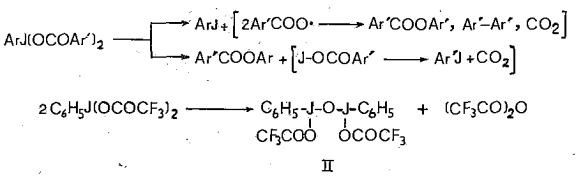


It should be noted that compound *Ig,* with an o-methyl group at the iodobenzene nucleus does not show this ortho-effect, probably because the six-membered transition can not be achieved.

b. Thermal effects and the influence of electron beam energy.

Aryliodine dicarboxylates are generally thermally labile and they decompose on melting. The thermal behaviour of a number of them has been thoroughly

studied and the following types of decomposition have been established,[2,4] for temperatures not exceeding 140°:

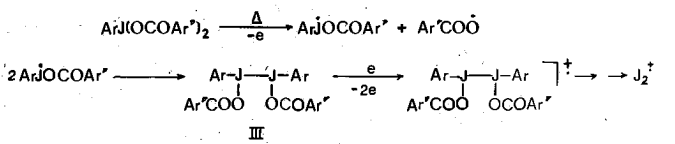


II

In order to investigate the influence of heating on their mass spectral patterns as well as the connection with their decomposition modes, certain of the compounds studied were allowed to remain in the probe of the mass spectrometer for a relatively long period of time (5-10 min) at 150-220°. The influence of the probe temperature on the mass spectrum pattern is rather complicated and it does not allow for any strict correlation with known thermal decomposition data. This may partially be attributed to the irreproducibility of experimental conditions inside the probe. Nevertheless, the following observations are reported.

With the exception of the trivalent iodine compound *II,* formed thermally from phenyliodine ditrifluoroacetate, all other thermolytic products appear with the appropriate mass numbers of their molecular ions, but it is not certain whether all of them are formed thermally, since their relative intensity is not always increased with temperature. The most characteristic temperature effect is reflected in the abundance of ion CO_2 (m/e 44), whose intensity increases with increasing probe temperature. A less well pronounced temperature effect appears in the case of ion m/e 128, which is attributed to HJ. This ion is a normal electron-impact fragment of iodobenzenes but its abundance in relation to ion m/e 127 (J^+) increases with temperature and at 200-230° it becomes more intense than ion 127. So, the formation of HJ is partially due to a thermal decomposition reaction.

In most spectra recorded a low relative intensity peak at m/e 254 is positively influenced by heating. This peak is not accompanied by isotopic peaks and it is attributed to J^+_2. In compounds *Ib, Ic* and *If* there is an m/e mass number overlap with the m/e value of benzoic acid anhydride ion (see also Table II) and the peak of m/e 254 is split into two peaks under conditions of high resolution. Since molecular iodine has not been reported to be formed by thermal decomposition, the formation of J^+_2 may be accounted for by a combination of a homolytic thermal dissociation and a subsequent electron-impact fragmentation, according to the equations:



III

Further fragmentation of *III,* whose molecular ion is not observed, is expected to give the same fragment ions as the corresponding phenyliodine dibenzoates. It should be mentioned that the formation of J^+_2 seems to a certain degree to be in competition with the formation of HJ^+, because in some cases when the relative intesity of m/e 254 is increased, with increasing temperature, the rise of relative intensity of m/e 128 is diminished.

The mass spectra of compound *Ih* at various temperatures are given in bar-graph form in Figure 1. This compound is the most stable among the compounds studied; it is the only one with a weak molecular ion peak and it lacks

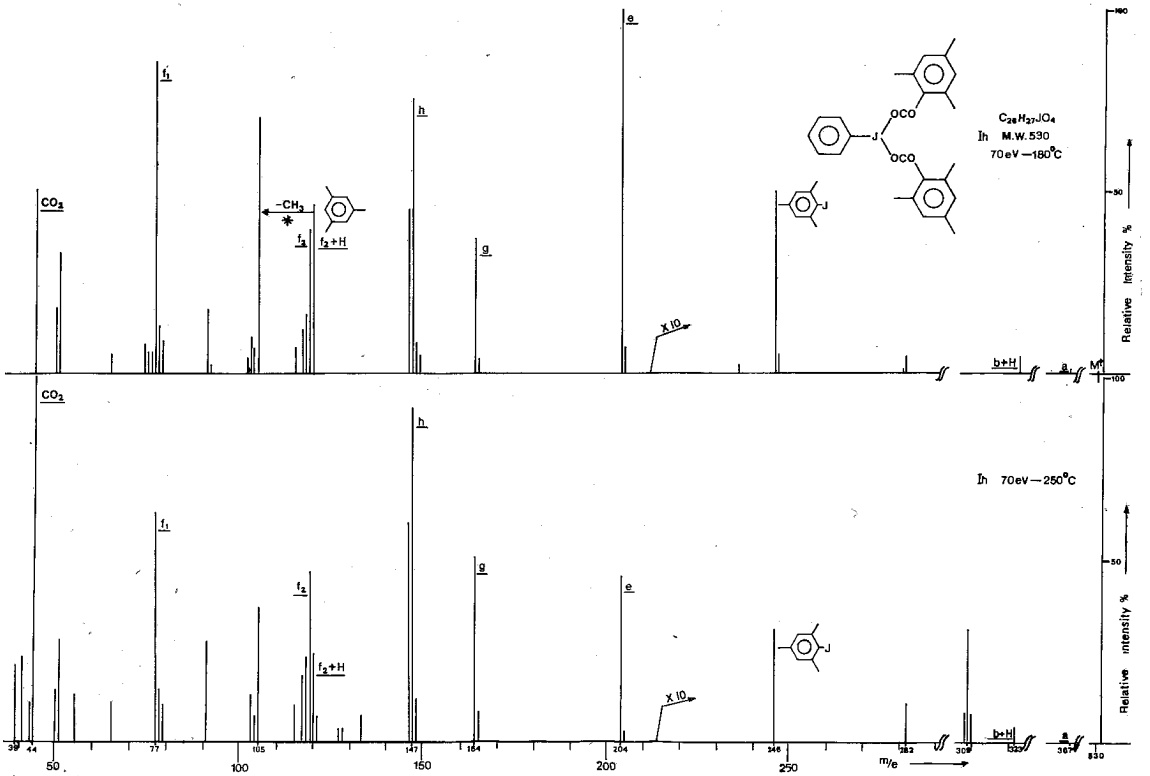


FIG. 1: *Mass spectra of Ih at 180° and 250° (70 eV).*

ion 254 (J^{+}_{2}). Its thermal decomposition begins abruptly at 230°, as it can be seen by the spectacular increase of the intensity of CO_2 peak. This unusual stability must be the result of pronounced stereochemical effects.

In order to complete the examination of the influence of energy on the fragmentation mode of aryliodine dibenzoates, compound *Ih* was also studied at low electron beam energy. Its mass spectra at various energy values are given in Figure 2. As it can be seen, even at 13 eV electron beam energy, the relative intensity of the molecular ion and the fragmentation pattern are not influenced to an appreciable degree. It is noted, that formation of ion *b+H*(m/e 323) is favoured at high energy, while that of ion *a* (m/e 367) is favoured at lower energy. This is a proof of the very low appearance potential of *a* and, consequently, of the weakness of the J-O bond of trivalent iodine.

c. Minor electron-impact and/or thermal fragmentation pathways.

A number of peaks of weak relative intensity which represent odd-electron fragment ions have been observed in all mass spectra obtained. Their formation is mainly attributed to electron-impact degradation reactions, i.e. skeletal rearrangements occuring after the easy rupture of one J-O bond but some of these ions must be the result of thermal reactions. The formulae of these ions along with

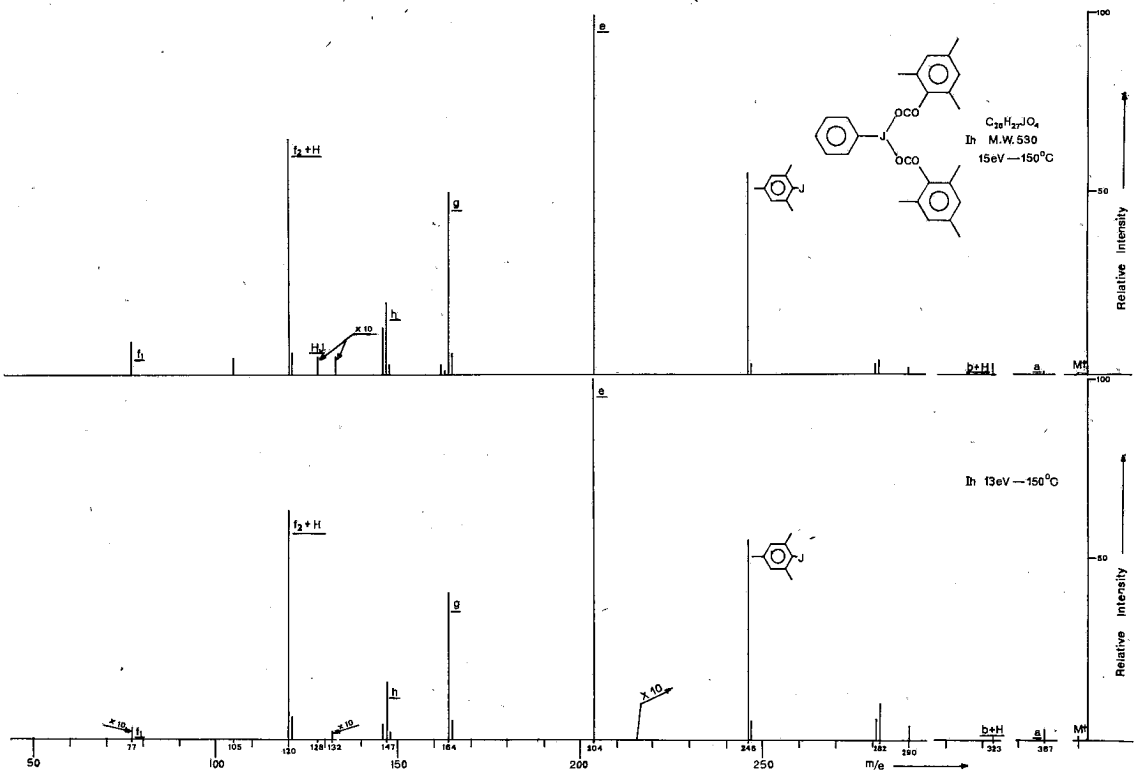


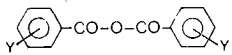
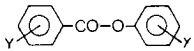
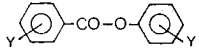
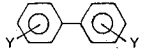
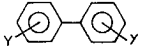
FIG. 2: *Mass spectra of Ih at 15 and 13 eV (150°).*

their m/e values and their relative intensities are collected in Table II. It is noted that the constitution of the ions bearing one or two chlorine atoms has been verified from their isotopic clusters.

It is evident that ions of type *a* (Scheme 2) are prone to rearrangements, under expulsion of carbon dioxide or iodine or both, because of the general tendency of polyvalent iodine to acquire the more stable electronic configuration in its outer shell, with eight instead of ten electrons. Thus, elimination of carbon dioxide leads to the iodonium compounds XC_6H_4-J^+-C_6H_4Y (ions *b+H* of Scheme 2) from which the "reversed" iodobenzenes, $YC_6H_4J^+$, are easily formed by rupture of one J-C bond. Elimination of iodine from ion *a*, possibly by way of a three membered ring intermediate, leads to the formation of "mixed" esters $XC_6H_4OCOC_6H_4Y^+$, while the "mixed" biphenyls XC_6H_4-$C_6H_4Y^+$ are probably formed either as a result of simultaneous ejection of carbon dioxide and iodine from ion *a* or from the "mixed" esters by loss of carbon dioxide.

The formation of the other ions is more difficult to be explained as a result of electron-impact reactions and it is suggested that they are the products of minor thermal reactions. It should be noted, however, that although thermal decomposition of ArJ $(OCOAr')_2$ produces both Ar'COOAr' and Ar'-Ar'[2] only in one case the corresponding ester is observed (from compound *Ih*) in the mass spectra, while all biphenyls of type Ar'-Ar' are present, but in lower relative abundances than the "mixed" biphenyls of type Ar-Ar'.

TABLE II: *Fragment ions generated through rearrangements from compounds Ia-h.*

Formula of fragment ion	*Ia* m/e (RI)	*Ib* m/e (RI)	*Ic* m/e (RI)	*Id* m/e(RI)	*Ie* m/e (RI)	*If* m/e (RI)	*Ig* m/e (RI)	*Ih* m/e (RI)
	226(0.5)	254[a]	254[a]	294[c](0.2)	226[b]	254[a]	226(0.2)	310[b]
	198(0.7)	212(1.5)	212(0.2)	232[c](0.8)	232(2.0)	246[c](0.9)	212(3.0)	240[b]
	-	-	-	-	-	-	-	288(0.5)
	154(1.0)	182(0.2)	182[b]	222[c](0.2)	154(0.5)	-	154(0.6)	-
	-	168(1.2)	168(0.8)	188[c](0.8)	188[c](0.7)	202[c](0.6)	168(0.5)	196(0.4)
	204(100)	218(1.5)	218(1.5)	238(1.0)	204(2.0)	218(5.0)	204(2.0)	246(5.0)

[a]Relative intensity uncertain because of overlap with J^{+}_{2}.
[b]In trace amount (< 0.1%).
[c]Confirmed isotopically.

It is concluded that the distinction between electron-impact and thermal reactions responsible for the formation of the ions in Table II is difficult to be effected with certainty.

Experimental

All mass spectra were run at 70 eV, except for compound *Ih* which was also run at 13 and 15 eV, on a RMU-6L Hitachi-Perkin Elmer single focusing mass spectrometer, using the direct probe insertion for the samples. Probe temperature was in the range of 140-180° except when otherwise indicated and chamber temperature between 100 and 110°. The ion source used was a T-2p model. Molecular weights were determined with a Hewlett-Packard model 301A Vapour Pressure Osmometer, using toluene as solvent.

The compounds studied were prepared according to one of the three following methods:

Method a. The aryliodide was converted first to its dichloride and then to the

TABLE III: *Characteristics of Aryliodine Dibenzoates.*

Compound	Method of Preparation	M. p.	Molecular Formula (Mol. Weight)	Molecular Weight (found)	IR (nujol) νCO (cm^{-1})
Ia	a	158-160° [a]	$C_{20}H_{15}JO_4$ (446.2)	-	1650
Ib	b	160-161°	$C_{22}H_{19}JO_4$ (474.2)	460[b]	1640
Ic	b	126-128°	$C_{22}H_{19}JO_4$ (474.2)	b	1633
Id	b	163-165°	$C_{20}H_{13}Cl_2JO_4$ (515.1)	507[b]	1665
Ie	a	149-153°	$C_{20}H_{14}ClJO_4$ (480.7)	464[b]	1625
If	b	146-149°	$C_{22}H_{18}ClJO_4$ (508.7)	498[b]	1635
Ig	a	144-147°	$C_{21}H_{17}JO_4$ (460.2)	449	1640
Ih	c	93-96°	$C_{26}H_{27}JO_4$ (530.3)	530[c, b]	1630

[a]Literature value[1] 159-160°.
[b]These compounds gave satisfactory elemental analyses.
[c]Molecular ion of the mass spectrum.

corresponding iodosocompound.[6] This was suspended in chloroform and a doubly equimolecular amount of the acid was added. The mixture was stirred for 12 hr in the presence of anhydrous calcium sulphate, then filtered, evaporated to dryness and the crude product obtained was recrystallised from chloroform-petroleum ether.

Method b. The aryliodides were converted directly to their diacetates[7] and the dibenzoates were obtained by exchange[8] with the appropriate benzoic acids. They were recrystallised from chloroform-petroleum ether.

Method c. This method[4] was applied for *Ih,* where the other methods fail. Phenyliodine dichloride in chloroform was stirred for 12 hr with doubly equimolecular amount of silver mesitoate, in the dark. Silver chloride formed was filtered off and the residue obtained after evaporation of the solvent was recrystallised from ether-petroleum ether.

The characteristics of the compounds studied are shown in Table III. It should be mentioned that generally these compounds are not very stable and they decompose slowly upon standing.

Περίληψη

Μελέτη φασμάτων μαζῶν ὑποκατεστημένων διβενζοϋλοξυ-ιωδοβενζολίων.

Στὴν ἐργασία αὐτὴ γίνεται μελέτη τῶν φασμάτων μαζῶν ὀκτὼ ὑποκατεστημένων διβενζοϋλοξυ-ιωδοβενζολίων *(Ia-Ih),* τοῦ γενικοῦ τύπου ArJ(OCO-Ar′)$_2$. Κοινὸ χαρακτηριστικὸ αὐτῶν τῶν ἑνώσεων εἶναι ἡ ἔλλειψη μοριακοῦ ἰόντος, μὲ ἐξαίρεση τὸ σχετικὰ σταθερότερο παράγωγο τοῦ μεσιτοϊκοῦ ὀξέος, *Ih,* τὸ ὁποῖο παρουσιάζει καὶ μερικὲς ἄλλες ἀποκλίσεις στὴ συμπεριφορά του σὲ σχέση μὲ τὰ ὑπόλοιπα παράγωγα.

Ὁ κύριος μηχανισμὸς θραυσματοποιήσεως κατὰ τὸ βομβαρδισμὸ μὲ δέσμη ἠλεκτρονίων 70 eV, ποὺ ὁδηγεῖ καὶ στὴν ταυτοποίηση τῶν δομικῶν συστατικῶν τῶν ἑνώσεων ποὺ ἐξετάζονται, συνίσταται στὴ διάσπαση τοῦ μοριακοῦ ἰόντος μὲ ταυτόχρονο σχηματισμὸ τῶν ἰόντων τοῦ βενζοϊκοῦ ὀξέος *(g)* καὶ τοῦ ἰωδοβενζολίου *(e)* (Σχῆμα 1).

Σὲ ὅλα τὰ φάσματα μαζῶν παρατηροῦνται ἰόντα μικρῆς σχετικῆς ἐντάσεως, ποὺ προέρχονται ἀπὸ μεταθέσεις μετὰ τὸ βομβαρδισμὸ μὲ ἠλεκτρόνια. Τὸ πιὸ ἐνδιαφέρον ὡς πρὸς τὴν δομὴ εἶναι τὸ ἰὸν *b* (Σχῆμα 2), ποὺ σχηματίζεται μετὰ ἀπὸ ἀπόσπαση μιᾶς ρίζας ὀξέος ἀπὸ τὸ ἀρχικὸ μόριο, ποὺ δίνει πρῶτα τὸ ἰὸν *a*· ἀπὸ αὐτὸ μὲ ἀπόσπαση διοξειδίου τοῦ ἄνθρακα καὶ ὑδρογόνου προκύπτει τὸ *b.* Οἱ πολυάριθμες μεταθέσεις ἀποδίδονται στὴν ἀστάθεια τοῦ δεσμοῦ J-O καὶ στὴν τάση τοῦ ἰωδίου νὰ ἀποκτήσει ἐξωτερικὴ στιβάδα μὲ ὀκτὼ ἠλεκτρόνια.

Ἀρκετὰ ἰονικὰ θραύσματα εἶναι προϊόντα θερμολυτικῆς διασπάσεως καὶ μάλιστα ὁρισμένα ἀπὸ αὐτὰ δὲν ἔχουν παρατηρηθεῖ σὲ προηγούμενες μελέτες θερμικῆς διασπάσεως.

Τέλος, ἐξετάζονται ἡ ἐπίδραση τῆς θερμοκρασίας καὶ τῆς ἐνεργείας τῆς ἠλεκτρονικῆς δέσμης στὴ μορφὴ τῶν φασμάτων μαζῶν.

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Short Papers

Chimika Chronika, New Series, 6, 505-509 (1977)

UBER DEN ANELLIERUNGSEFFEKT BEI FLAVYLIUMSALZEN I. 2 - [(1′ - Naphthyl) -und 5,6-Benzo-2 (1′-naphthyl-)] -flavyliumsalze.

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(Erhalten am 8 Dezember 1976)

Zusammenfassung

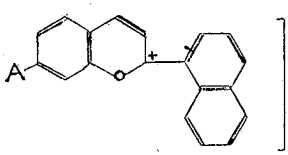
2-(1′-Naphthyl-) benzopyryliumsalz bei längeren Wellen absorbiert als das Flavyliumsalz selbst. Der Anellierungseffekt des Ringes in 2′, 3′- Stellung, sinkt mit der Einführung von Auxochromen in die 7-Stellung. Einführung von Benzolringen in die 2′, 3′-5, 6-und in 2′, 3′, 5, 6-Stellungen hat einen Anellierungseffekt entsprechend, von rund 50 nm, 54 nm und 75 nm zur Folge.

Key Words: Flavyliusmalze, Anthocyane, Farbstoffe, Laser-farbstoffe.

Einleitung

Bei Flavyliumion bestehen Möglichkeiten zur Anellierung eines isocyclischen Sechsringes in 2′, 3′ - 3′, 4′ - 5, 6 - 6, 7 - 7, 8 - Stellung.

Naphthyl- und substituierte Naphthylbenzopyrylium-salze sind schon bekannt,[1] doch umfassende Regeln über den Anellierungseffekt sind bisher nicht ermittelt worden. Wir haben nun mit der einigermassen systematischen Bearbeitung dieses umfangreichen Gebietes begonnen. Als erstes wählen wir die Untersuchung der Anellierung in der 2′, 3′ - Stellung, also der Verbindung des Typus.



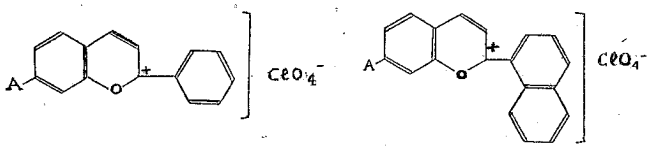
ClO_4^- **1**

Zur Verfügung standen uns Flavyliumsalzen mit

$$A = H, -OH, -N\begin{matrix}CH_3\\CH_3\end{matrix}$$

Diese Flavyliumsalze haben wir nach der besonders von Robinson[2,3] ausgebauten Methode dargestellt, nämlich durch Kondensation von Salicylaldehyd, Resorcylaldehyd, und 4-Dimethylamino-salicylaldehyd mit a-Naphthymethylketon, in stark saurer Lösung.

Zum Vergleich stellen wir nun diese Flavyliumsalze den analogen Grundkörper **2** gegenüber.

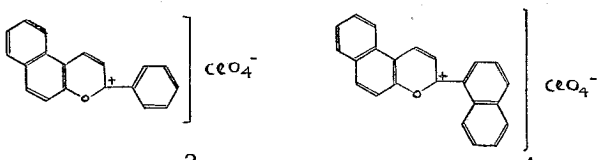


2 1

Tabelle I.: Zeigt unter a und a′ die Absorptionsmaxima (in nm) der Lösungen in Eisessig angegeben unter b und b′ die bathochrome Wirkung der Auxochrome und unter c′ (Δa′ - a) die Anellierungseffekte der Farbsalze **1** und **2**.

	A=	a	b	Farbe	a′	b′	Farbe	c′ (Δa′ - a)
2a	H.	397	—	blassgelb	1a 447	—	gelborange	50
2b	HO-	435	38	gelb	1b 478	31	rotorange	43
2c	$(CH_3)_2$ N-	518	121	karminrot	1c 560	113	rotviolett	42

Zur Ergänzung betrachten wir nunmehr die Verhältnisse bei der Anellierung in 5, 6- und 5, 6-2′, 3′-Stellungen, also bei Verbindungen folgenden Typus.



3 4

Tabelle II. Zeigt unter a′ die Absorptionsmaxima (in nm) der Lösungen in Eisessig angegeben, unter b′ die bathochrome Wirkung der Auxochrome und unter c′ (Δa′ - a) die Anellierungseffekte der Farbsalze **3** und **4**.

a′	b′	Farbe	c′ (Δa′-a)	a′	b′	Farbe	c′ (Δa′-a)
3 451	—	grünlich-gelb	54	4 472	—	rot-braun	75

Diskussion

Über die Farbsalze **2a** wurde schon von Baid und Shriner[4], über Farbsalze **2b**, **2c** und **3** von Kokkinos und Wizinger[5,6,7] berichtet. Farbsalz **4** haben wir dargestellt analog durch Kondensation von 2-Hydroxy-naphthaldehyd mit a-Naphthylmethylketon, in saurer Lösung. Farbsalze **1a**, **1b**, **1c** und **4** wurden neu dargestellt.

Der Vergleich der Grundkörper **2a** mit **1a** zeight, dass bei Einführung eines Benzolringes in die 2′, 3′ - Stellung von den Phenyl-zu den entsprechenden Naphthylbenzopyrylium-salzen der Anellierungseffekt rund 50 nm beträgt. Er sinkt bei Einführung von Auxochromen in die 7-Stellung ab. Beim Farbsalz **1c** mit

der Dimethylaminogruppe in der 7-Stellung ist der Wert von nur 42 nm. Dieser Fall bedarf noch einer Aufklärung. Wie nun der Vergleich der Verbindungen **2a** und **3** zeigt, (Benzolring in 5, 6-Stellung), beträgt der Anellierungseffekt 54 nm.

Die Einführung von Benzolringen in die 5, 6- und 2′, 3′-Stellungen (Farbsalz 4), ergibt den Wert von 75 nm.

Es wäre verfrüht, beim gegenwärtigen Stand der Erkenntnis aus diesem doch noch sehr knappen Material schon bestimmte theoretische Aussagen ableiten zu wollen. Zuvor müsste die Untersuchung auf eine viel breitere Basis gestellt und vor allem ermittelt werden, in wieweit ausser dem Anellierungseffekt noch andere Momente, insbesondere solche sterischer Art mitwirken.

Hier seien nur folgende Zusammenhänge kurz hervorgehoben. a) Der Anellierungseffekt des Ringes in 2′, 3′ - Stellung (a′-a) sinkt mit der Einführung von Auxochromen in die 7-Stellung. b) Einführung von Benzolring in die 2′, 3′ in 5, 6 und in 2′, 3′, 5, 6-Stellungen entsprechend hat einen Anellierungseffekt von rund 50 nm, 54 nm und 75 nm zur Folge, wie der Vergleich der Verbindungen **2a** und **1a**, **2a** und **3** und **2a**, **4** zeigt. c) Das Flavylium-Ion spricht auf 7-ständige Auxochrome stärker an, als das 1′ - Naphthyl-benzopyryliumsalz. So beträgt der bathochrome Effekt der Dimethylaminogruppe in der Flavyliumreihe 121 nm (**2a** und **2c**), in dem 1′-Naphthylbenzopyryliumsalz 113 nm (**1a** und **1c**).

Die Spektren aller Verbindungen in Eisessig, wurden mit dem Cary-14-spektrophotometer aufgenommen.

Experimenteller Teil

2-[1′-Naphthyl] - benzopyryliumperchlorat 1a.

In eine Lösung von Je 1/100 mol Salicylaldehyd (1,22g) und a-Napthylmethylketon (1,70g) in 20 ml 85% iger. Ameisensäure bei -5°C 4std. lang Chlorwasserstoff einleiten. Über Nacht stehenlassen. Dann 100 ml Eisessig zugeben und filtrieren. Zu Filtrat 20 ml Überchlorsäure (20% ig) und 100 ml Wasser zusetzen.

Ausgeschiedenes amorphes Perchlorat durch Erhitzen in Lösung bringen. Auskristallisieren lassen, absaugen und aus mit wenig Überchlorsäure versetztem. Eisessig umkristallisieren. Rote Kristalle, Smp. 102°C. Ausbeute 1,0g (81,9% d. Th.). Löslich in Äthylalkohol, Aceton, Eisessig, Pyridin. Farbe der Lösungen in Äthylalkohol hellrot, in Aceton, Pyridin rot, in Eisessig gelb-orange. In Konz. Schwefelsäure blau-rot.

$C_{18}H_{15}O_5Cl$ (356,59) Ber. C:63,99 H:3,64
Gef. C:64,05 H:3,62

2-(1′ Naphthyl)- 7-hydroxy-benzopyryliumperchlorat. 1b.

Analog Präparat **1a.** Aus 1,38g (1/100 mol) Resorcylaldehyd und 1,70g (1/100 mol) a-Naphthylmethylketon. Rote Kristalle. Smp. 180°C. Ausbeute 1,20g (86,9% d.Th.). Löslich in Äthylalkohol, Aceton, Eisessig, Pyridin. Farbe der Lösungen, in Äthylalkohol gelb-orange, in Aceton, Eisessig rot-orange, in Pyridin rot. In Konz. Schwefelsäure rot mit gelbem Ablauf.

$C_{19}H_{13}O_6Cl$ (372,58) Ber. C: 61,24 H:3,48
Gef. C: 61,28 H: 3,45

2-(1′-Naphtyl)- 7-dimethylamino-benzopyryliumperchlorat. 1c.

Analog Präparat **1a.** Aus 1,65g (1/100 mol) p-Dimethylaminosalicylaldehyd

und 1,70g (1/100 mol) a-Naphthylmethylketon. Rot-violette Kristalle. Smp 260°C. Ausbeute 1,2g (72,2% d.Th.). Löslich in Äthylalkohol, Aceton, Eisessig, Pyridin. Farbe der Lösungen rot-violet. In Konz. Schwefelsäure, rot-violet.

$C_{21}H_{18}NO_5Cl$ (399,61) Ber. C: 63,11 H: 4,50 N:3,50
Gef. C: 63,17 H: 4,54 N: 3,46

5,6-Benzo-2-(1'-Naphthyl)-benzopyryliumperchlorat. 4.

Analog Präparat **1a.** Aus 1,72g (1/100 mol) 2-Hydroxy-l-naphtaldehyd und 1,70g (1/100 mol) a-Naphthylmethylketon. Tiefrote Kristalle. Smp. 192°C. Ausbeute 1,30g (75,5% d.Th.). Löslich in Äthylalkohol, Aceton, Eisessig, Pyridin. Farbe der Lösungen, in Äthanol gelb, in Aceton rot, in Eisessig braun-rot, in Pyridin gelb. In Konz. Schwefelsaure rot.

$C_{25}H_{15}O_5Cl$ (406,63) Ber. C: 67,93 H:3,68
Gef. C: 68,05 H: 3,64

Abstract

Ring closure effect in Flavylium salts.

The 2-(1'-Naphtyl)-benzopyrylium perchlorate salt, absorbs at longer wavelenghts than the corresponding benzopyrylium salt. Introduction of auxochromic groups at the 7-position, gives rise to less intense bathochromic effect as compared to that of the Flavylium series.

Ring closure at positions 2', 3' - 5, 6 and 2', 3', 5, 6 results in absorption at even longer wavelengths, versus that of the initial benzopyrylium salt.

Περίληψη

Περὶ τῆς δράσεως τῶν βενζολικῶν δακτυλίων εἰς τὰ ἅλατα τοῦ Φλαβυλίου.

Διὰ συμπυκνώσεως Σαλικυλικῆς-, Ρεζορκιλικῆς-, 4-διμεθυλαμινοσαλικυλικῆς - καὶ 2-ὑδροξυ-1-ναφθαλδεϋδης, μετὰ τῆς α-ναφθυλο-μεθυλοκετόνης, εἰς ὄξινο περιβάλλον, συνετέθη μία σειρὰ ἁλάτων τοῦ Βενζοπυρυλίου.

Τὸ 2-(1'-Ναφθυλο)-βενζοπυρυλιακὸ ὑπερχλωρικὸ ἅλας, ἀπορροφᾶ εἰς μεγαλύτερα μήκη κύματος ἀπὸ τὸ ἀντίστοιχο ἅλας τοῦ Βενζοπυρυλίου. Εἰσαγωγή, εἰς τὴν 7-θέσιν, αὐξοχρώμων ὁμάδων δίδει μικρότερη βαθυχρωμικὴ δρᾶσι ἀπὸ ἐκείνη τῆς σειρᾶς Φλαβυλίου καὶ ἡ ἀπόστασις μεταξὺ τῶν μεγίστων ἀπορροφήσεως (Δα' - α), διὰ τῆς ὑπάρξεως τοῦ δακτυλίου εἰς τὴν 2', 3' θέσιν, ἐλαττοῦται. Ὕπαρξις βενζολικῶν δακτυλίων εἰς τὴν 2', 3' - 5,6 καὶ 2', 3', 5, 6-θέσεις ἔχει ὡς ἀποτέλεσμα ἀπορρόφησιν εἰς μεγαλύτερα εἰσέτι μήκη κύματος, ἀπὸ τὸ ἁπλὸ ἅλας, τοῦ Βενζοπυρυλίου.

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