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A MODIFIED CLASSIFICATION OF THE ELEMENTS. II. THE BONDING IN I_3^-

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(Received June 25, 1987)

SUMMARY

Spectrophotometric studies of potassium triiodide, in correlation with the corresponding electronic transitions presented in this work, resolve the problem posed by the bond in I_3^- . The LCAO-MO model used as the basis for the interpretation was constructed from *f*-orbitals, assuming the validity of a modified classification of the elements, by which iodine becomes an inner transition element.

Key words: Spectroscopy of I_3^- . Iodine as an *f*-orbital element.

INTRODUCTION

The system KI_3 has attracted much study, from the earliest investigation (cf. literature review in (1)) to quite recent research (2), (3). Many comprehensive works have included already typical properties of KI_3 in the text, but the following citation from (4) indicate that the problems concerning such a system are by no means resolved yet:

p. 1554 "The problems posed by the bonding in I_3^- illustrate well the sort of impasse that has been reached at the theoretical level, arising partly from limitations of calculated wave functions and partly from the difficulty of correlating molecular with atomic properties".

Therefore a spectroscopic investigation of $KI + I_2$ solutions has been undertaken in this work, with the aim to apply and confirm a hypothesis which has proved applicable and useful for the solution of structure problems of other compounds as well. The hypothesis rests upon the obvious possibility of classifying the heavier elements differently i.e. by filling up the higher energy levels in accordance with the regular sequence of *s*, *p*, *d* and *f*-orbitals, for instance for iodine $4s^2 4p^6 4d^{10} 4f^7$. Through such an assumption for iodine the RUSSEL-SAUNDERS multiplet term $^2S_{1/2}$ results instead of $^2P_{1/2}$. Iodine becomes thereby an inner transition element, with 7 electrons in the *f*-orbitals. The small energy difference between 4*f* and 5*s* orbitals is causing limitations

in the literature interpretations of the experimentally established values, which can be attributed to several configurations. All literature data maintain that inner orbitals must be involved in the bonding in KI_3 in a certain way, and thereby indicate the plausibility of the aforementioned hypothesis, which is consistent also with the significant differences of the physical and chemical properties of iodine and the halogen group.

Iodine reveals a distinct electrical conductivity, which is increased at higher temperatures as with semiconductors, and decreases with temperature in molten iodine as with metals.

EXPERIMENTAL

The synthesis of KI_3 and NaI_3 was carried out in water solutions. For comparisons sake the NaI_3 was also investigated. In the literature the assumption prevails that the triiodide ion is formed, but the experimental results were inconclusive (1). Numerous investigators maintain that they have proved the existence of KI_3 , but there are also numerous those who maintain that they have experimentally proved that KI does not exist but instead a mixture of KI and I_2 . By the advent of modern experimental techniques, the study of the bond between KI and I_2 began, but even the results of such experiments did not bring about the solution of the problem posed by the enhanced solubility of iodine in KI solutions.

The synthesis of the triiodide in this work was performed as recommended in (5). Into a hot, saturated solution of KI , an equimolar amount of I_2 was added. A homogenous solution resulted in the case of KI , whereas in the saturated solution of NaI , an equimolar amount of I_2 was not soluble. Therefore it might be supposed that NaI_3 is a more labile compound.

When the solutions were cooled to $0^\circ C$, crystallization resulted, but differences were observed between KI_3 and NaI_3 . From the $(KI + I_2)$ mixture a compact crystallized mass was separated, with a small rest of water, whereas from the $(NaI + I_2)$ mixture a small amount of loose crystals was formed. The influence of the counterion was observed by other investigators also (6).

When these crystals were kept at room temperature, they melted. The crystals decomposed on desiccation, and partially on dilution. When the solutions of KI_3 and NaI_3 were diluted, the separation of dark iodine crystals was observed.

The clear solutions of KI_3 and NaI_3 above the iodine crystals were used for spectroscopic measurements which have included a saturated water solution of elemental iodine also, in order to make perceptible the effects of bonding between $KI + I_2$, or $NaI + I_2$ respectively.

The water used for the preparation of solutions was triply distilled. All chemicals were of p.a. purity, and were used without further purification.

The measurements were performed with a V S U - 1 Zeiss Spectrophotometer in the ultraviolet and visible region of the spectrum.

RESULTS AND DISCUSSION

The fundamental diagram was recorded with a saturated solution of I_2 (Fig.1.). The transmission versus wave length plot has three minima of transmission. The first at 287 nm and the second at 350 nm, i.e. in the ultraviolet region, and the third minimum of transmission at 465 nm in the visible region of the spectrum. The second spectrogram was recorded in KI_3 and NaI_3 solutions (Fig. 2.). From such a spectrogram it is visible that the transmission is unaltered in the ultraviolet region, whereas the minimum at 465 nm is significantly shallower.

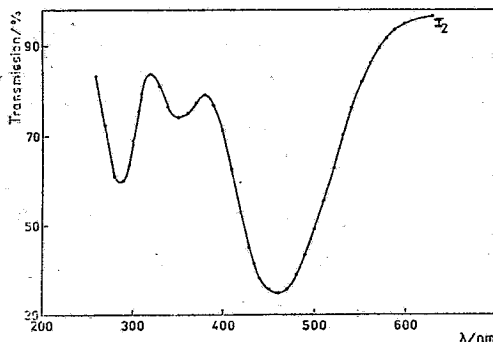


Figure 1. Spectrogram recorded in a saturated water solution of elemental I_2 .

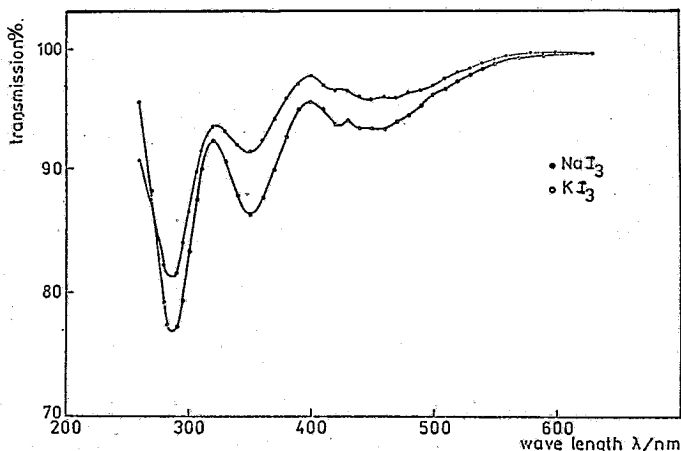
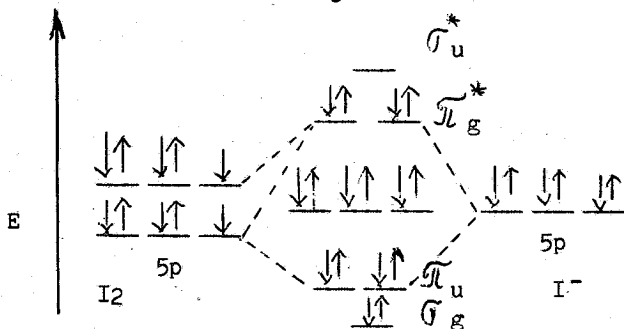


Figure 2. Spectrogram recorded in a water solution of KI_3 ($10^{-4} \text{ mol.dm}^{-3}$)
 (— o —)
 Spectrogram recorded in a water solution of NaI_3 ($10^{-4} \text{ mol.dm}^{-3}$)
 (— ● —)

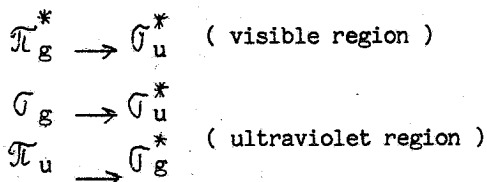
Such experimental results are indicating the formation of a sort of bond, by which the absorption of photons with small energies, corresponding to the visible region of the spectrum, is hindered. Consequently a participation of orbitals in the bond can be surmised, which previously have been available for electron transitions.

The LCAO-MO diagrams used as the basis for interpretations were constructed in two ways i.e. by supposing the valence electrons of iodine to be in the orbitals $5s^2 5p^5$, or in $4f^7$ orbitals respectively, consistent with the modified classification.

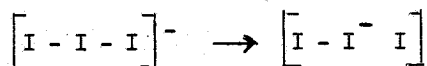
The p-orbital diagram of I_3^-



Based upon such a p-orbital diagram, the correlation of the spectra with the electron transitions is not conclusive. Pimentel (7) and Hach and Rundle (8) are supposing the following transitions to occur:



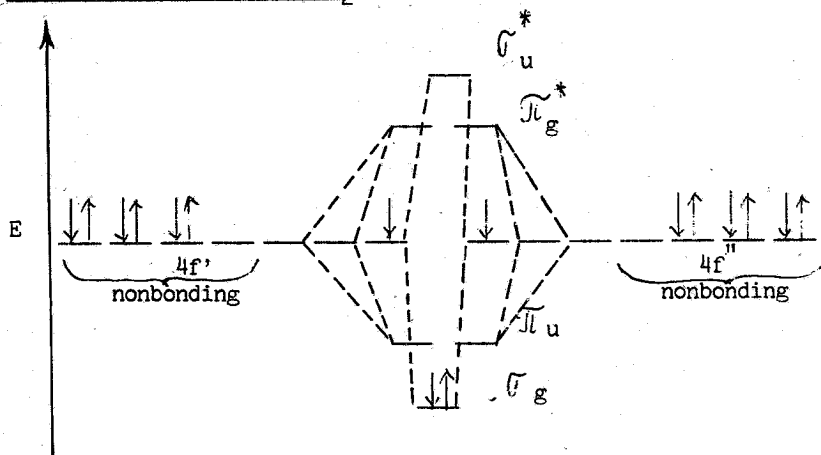
The transition $\pi_u \rightarrow \sigma_g^*$ it is supposed to occur within the p-shell of the central atom, and the transition $\sigma_g \rightarrow \sigma_u^*$ to entail electron transfer from the terminal atom to the central iodine atom



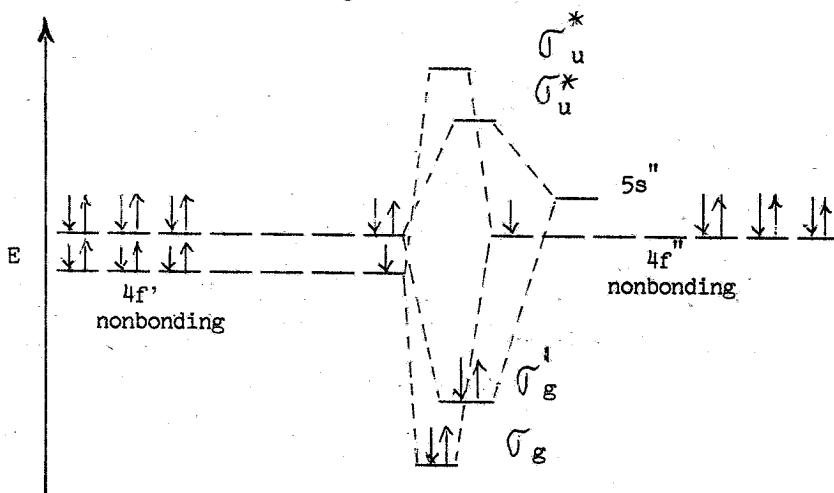
It is presumed a spin-orbit splitting to account for the absorption, to which the aqueous I_3^- anion owes its red colour.

The drawbacks of such a scheme are obvious. The bond order in the triiodide ion is not 1, as resulting from the p-orbital scheme, and all electron transfers into an antibonding σ_u^* orbital are not probable. Even the supposition of spin-orbit splitting, would have to include the d or f orbitals. Instead the f-orbital diagrams enable acceptable interpretations:

The f-orbital diagram of I_2



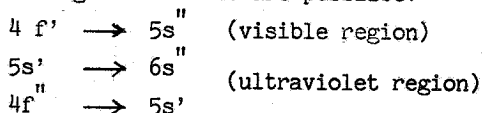
The f-orbital diagram of I_3^-



By the pairing of electrons in f -orbitals, an enhanced overlap of bonding orbitals is enabled, with greater symmetry, resulting in greater stability. Despite the widely accepted Mulliken's charge transfer theory of the donor-acceptor bond, the nonsymmetrical structure with the electron pair in the σ_g' orbital seems in accordance with the RAMAN spectra (9) and solvation energies (10).

The assumption of f -orbitals as valence orbitals, results in a bond order 2, in accordance with the structural formula of the compound. The bonds are not of equal energy, but a σ_g and σ_g' bond, consistent with the instability of I_3^- , subject to easy decomposition resulting in a I_2 molecule and the I^- anion. The scheme complies also with the almost linear structure of I_3^- , with bond angles between $170-180^\circ$, established by crystallographic studies (10), (11) and MO calculations (6), (12), (13).

From such a ground state the transitions of bonding electrons are not possible, but instead the nonbonding electrons are engaged in light absorption. The following transitions are possible:



The iodine molecule contains in the ground state $5s''$ orbitals which are empty. When the triiodide ion is formed, a partial filling of the $5s''$ orbitals occurs, which means that the availability of such orbitals for electron transfer is diminished. As a consequence the intensity of light absorbance in the visible region is decreased, and the minimum at 465 nm becomes shallower, as confirmed by experiment (Fig.2.). The other transitions, i.e. $5s' \rightarrow 6s''$ and the transition into the $5s'$ orbital of the left atom of the iodine molecule are unhindered. The corresponding wave length can be calculated by the application of SLATER's shielding constants.

Such calculations make evident that the spectra shown in this work can not be caused by promotion of $4f$ electrons in the $5s$ orbitals of the same iodine atom. The calculation of the promotion energy $4s^2 4p^6 4d^{10} 4f^7 \rightarrow 4s^2 4p^6 4d^{10} 4f^6 5s^1$ by applying SLATER's coefficients, with a screening factor $s = 48,1$, gives a value of 217 nm.

In his original work (14) SLATER has not elaborated the coefficients and rules for molecules, but he is stating that his principal criterion in setting up the rules for the shielding constants was the energy check with experiment. The very precise spectroscopic measurement of the iodine spectra presented in this work, have served as a check for setting up the rules for molecular shielding constants, which shall be presented in a separate work.

In this work however the shielding constants shall be applied to show the accordance between the experimental and calculated wave length of 465 nm. The maximum of absorption at such a wave length is causing the transition of electrons from the $4f'$ orbital of the left iodine atom into the $5s''$ orbital of the right atom of iodine in the iodine molecule. The additional electron from the covalent bond is included for calculating the effective nuclear charge ($Z-s$).

$$(Z-s) = 53 - 2 - 8 - 18 - 25.0,85 - 0,8 = 2,95$$

By inserting of such effective nuclear charge into the formula for the wave number:

$$\frac{1}{\lambda} = R \cdot (Z-s)^2 \cdot \left[\frac{1}{n'^2} - \frac{1}{n''^2} \right]$$

$$\frac{1}{\lambda} = 1,097 : 10^7 \cdot (2,95)^2 \cdot \left[\frac{1}{16} - \frac{1}{25} \right]$$

$$\frac{1}{\lambda} = 0,217 \cdot 10^7 \text{ m}^{-1}$$

$$\lambda = \underline{\underline{465 \text{ nm}}} \quad (\text{measured } 465 \text{ nm})$$

By the correspondence of the measured and calculated wave length it becomes evident that transitions of the nonbonding electrons are accompanying light absorption. The diminution of the intensity of absorption at 465 nm (Fig.2.) enables unambiguous conclusions about the sort of bond between I_2 and I^- . It is a covalent bond, but formed by the use of an outer orbital upon the iodine molecule. The f -orbital approach applied thereby for the electronic configuration of iodine, has removed the impasse at the theoretical level, which was mentioned in the literature (4).

ΠΕΡΙΛΗΨΗ

ΜΙΑ ΤΡΟΠΟΠΟΙΗΜΕΝΗ ΤΑΞΙΝΟΜΗΣΗ ΤΩΝ ΣΤΟΙΧΕΙΩΝ ΙΙ. ΔΕΣΜΟΙ ΣΤΟ J_3^-
Φασματοσκοπικές μελέτες του KJ_3 συνδισσόμενες με συσχετίσεις των αντιστοίχων ηλεκτρονικών μεταπτώσεων, λύουν το πρόβλημα που θέτουν οι δεσμοί στο J_3^- . Το μοντέλο LCAO-MO, που χρησιμοποιήθηκε σαν βάση για την ερμηνεία που δίδεται, συντίθεται από f -τροχιακά

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ACRIDONES. A NOVEL SYNTHESIS OF 3-SUBSTITUTED-9-(1OH)ACRIDONE-5-CARBOXYLIC ACIDS AND THEIR DERIVATIVES

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(Received 20 April 1988)

Summary

The syntheses of 3-substituted-9(1OH)acridone-5-carboxylic acids *5a-d* by a new process are reported. The process involves conversion of the 5-substituted diphenylamine-2,2'-dicarboxylic acids *4a-d* to the corresponding dipiperidides *8a-d*, ring closure of the latter with phosphorous oxychloride to 9-choloacridines *9a-d* followed by acid hydrolysis. 3-Bromo, 3-nitro, 3-chloro, and 3-methyl-9(1OH)acridone-5-carboxylic acids (*5a-d*) which were prepared by the novel process were free of the 1-substituted-9(1OH)acridone-4-carboxylic acid isomers *6a-d*.

Using known methodology for the syntheses of *5a-d*, which involves direct cyclization of the diphenylamine dicarboxylic acids *4a-d* with phosphorous oxychloride or with sulfuric acid, mixtures of the isomeric acids *5a-d* and *6a-d* were obtained which contained mainly the undesired isomers *6a-d*. The separation of the isomers from their mixtures by common laboratory procedures was a difficult task due their low solubility in common solvents. The mechanism of the cyclization of the dipiperidides *8a-d* is discussed.

Key words: 3-substituted-9(1OH)acridone-5-carboxylic acids, Ring closure of 5-substituted diphenylamine-2,2'-dicarboxylic acids dipiperidides.

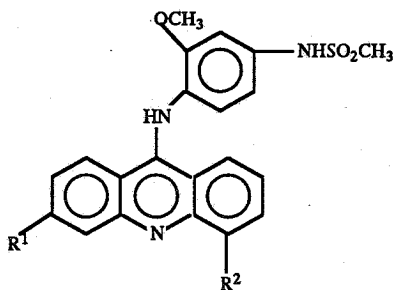
Introduction

4'-(9-Acridinylamino)methanesulfon-m-anisidide (m-AMSA), (1, R¹=R²=H) is a compound with a broad spectrum of experimental antitumor activity and has being clinically evaluated in the treatment of a number of human

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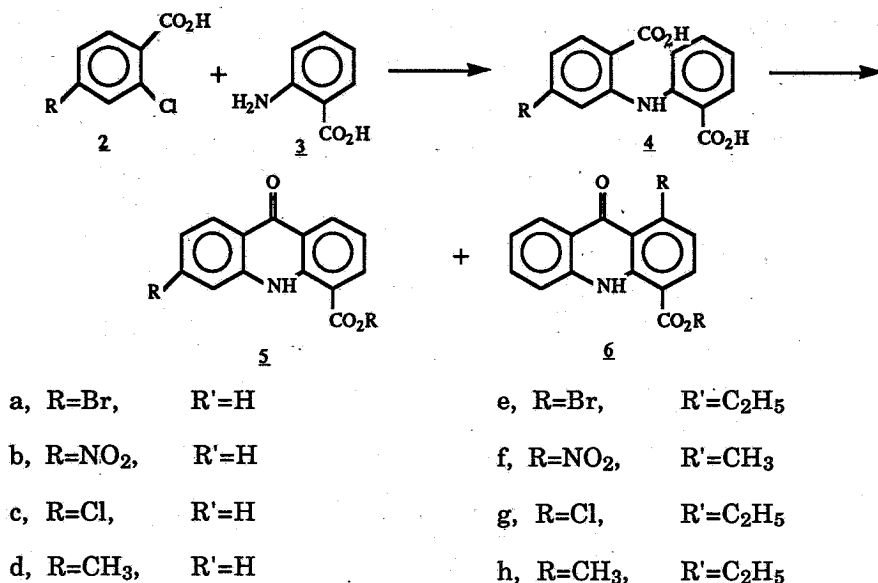
tumors¹. A large number of m-AMSA derivatives have been prepared and portions of the molecule were identified where substituents can be added to increase selectivity and/or antitumor activity^{2a-h}. Of the derivatives of m-AMSA which have been studied, 3,5-disubstituted m-AMSA were of most importance since these products were shown to possess higher activity and potency as well as low mutagenicity (i.e., 1, R¹=CH₃, R²=CONHCH₃)³.



In our research program directed towards the syntheses of various 3,5-disubstituted m-AMSA analogs, 3-substituted-9(1OH)acridone-5-carboxylic acids (*5a-d*) and their esters were required as intermediates. In this paper, the syntheses of the above products by new methodology are described.

Results and discussion

Initially we adopted known methodology for the syntheses of *5a-d* which involves cyclization of the diphenylamine dicarboxylic acids *4a-d*, a general process most often used in the preparation of acridones and their substituted derivatives⁴ (Scheme 1).



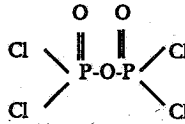
Scheme 1

The required diphenylaminedicarboxylic acids *4a-d* were prepared by the Ullmann reaction of *2a-d* with anthranilic acid⁴. Sulfuric acid, phosphorous oxychloride and dichlorophosphoric acid anhydride were used as the acidic reagents for the cyclization reaction and the results are summarized in Table 1.

Inspection of Table 1 shows, that cyclization of *4* produced mixtures of the isomeric acids *5* and *6* by ring closure in the two possible directions. The ratio *5:6* varied with the substituent in *4* and the condensing agent. Thus, ring closure of the bromodicarboxylic acid *4a* with either sulfuric acid or dichlorophosphoric anhydride gave mixtures of *5a* and *6a*, but the required isomer *5a* was produced in lower yield. The ratio of *5a:6a* in both cases was 34:66.

TABLE I

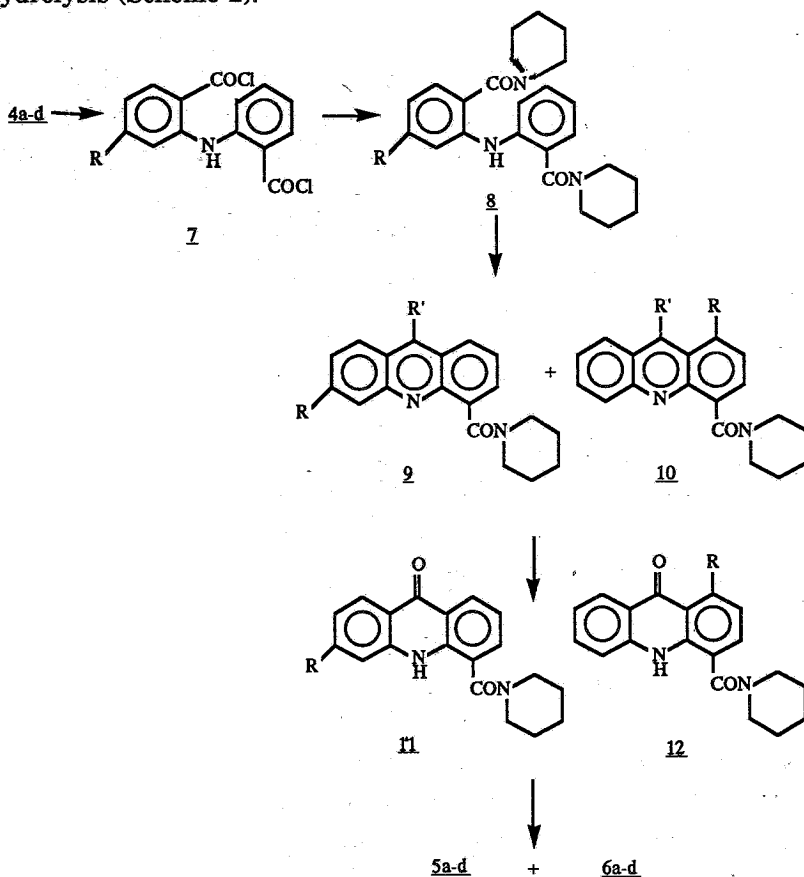
TABLE I: Ratios of 5:6 from the Cyclization of 4 with Various Condensing Reagents

Dicarboxylic acid	R in 4 - 6	Condensing Reagent and Ratio of 5:6		
		H ₂ SO ₄	POCl ₃	
4a	Br	34:66		33:67
4b	NO ₂	15:85	60:40	
4c	Cl	33:67	34:66	
4d	CH ₃	65:35	Decomposition	

Similarly, the chlorodicarboxylic acid *4c* upon cyclization with sulfuric acid or phosphorous oxychloride produced mixtures of *5c* and *6c* in which the desired *5c* was also the minor isomer; in both instances the ratio of *5c*:*6c* was 34:66. Cyclization of the nitrocarboxylic acid *4b* yielded a mixture of *5b* and *6b* in ratios that varied with the nature of the acidic reagent. Thus, treatment of *4b* with sulfuric acid gave predominantly the 1-isomer *6b* in accordance with previously published results⁵; the ratio of *5b*:*6b* in this case was 15:85. Treatment of *4b* with phosphorous oxychloride gave a mixture of *5b* and *6b* in a ratio of 60:40. Cyclization of the methyl dicarboxylic acid *4d* with sulfuric acid gave a mixture of *5d* and *6d* in a ratio of 65:35, while cyclization of the same acid with phosphorous oxychloride yielded decomposition products.

The separation of *5a-d* from mixtures with their isomers *6a-d* was found to be difficult and in some cases could not be accomplished by common laboratory techniques. Repeated recrystallizations were inefficacious to provide pure materials mainly because of the low solubilities of both isomers in common organic solvents. Furthermore, compounds *5a-d* melted above 360 °C and therefore melting points could not be used as a criterion of their purity.

It is apparent from the above results that new methodology for the syntheses of the acids *5a-d* was most desirable. A most promising potential route for the preparations of the above acids involves the cyclization of the dipiperidides *8a-d* with phosphorous oxychloride followed by acidic hydrolysis (Scheme 2).



5-8 and 11, 12
 a, R = Br
 b, R = NO₂
 c, R = Cl
 d, R = CH₃

9, 10
 a, R = Br R' = Cl
 b, R = NO₂ R' = Cl

c, R = Cl R' = Cl
 d, R = CH₃ R' = Cl
 e, R = Br R' = -NC₅H₁₀.HCl
 f, R = NO₂ R' = -NC₅H₁₀.HCl
 g, R = Cl R' = -NC₅H₁₀.HCl
 h, R = CH₃ R' = -NC₅H₁₀.HCl

Scheme 2

It was anticipated that cyclization of **8** would proceed in that direction as to provide piperidide **9** rather than the isomer **10** and that **9** could readily be converted to **5** by acid hydrolysis. These expectations were based on the following arguments: a) Alkylamides of *N*-phenylanthranilic acid are known to cyclize in a similar fashion as the corresponding acids and provide the corresponding 9-alkylaminoacridines^{6a-g,7}, which readily cleave to 9(10H)acridones. b) On ring closure of the dipiperidide **8**, the steric interaction between the substituent *R* and the piperidine ring of the carbonyl function would prevent reaction on the aromatic ring carrying the substituent *R*, thus preventing formation of **10** and favoring formation of **9**. This expectation was further supported by a previous report that cyclization of 2-(3-methylanilino)benzopiperidide afforded exclusively 3-methyl-9(10H)-acridone⁷.

Diphenylaminedicarboxylic acids **4a-d** were converted, via the acyl chloride **7a-d**, to the dipiperides **8a-d** (Scheme 2). Since the purifications of the acids proved to be a difficult task, crude acids were used in these preparations and the products **8a-d** were purified simply by filtration through a silica gel column.

Treatment of the dipiperidides **8a-d** with phosphorous oxychloride affected ring closure and produced predominantly 9-chloroacridines **9a-d** rather than the 9-piperidinoacridines **9e-h** as might have been expected^{6a-g,7}. Thus, treatment of **8b** with phosphorous oxychloride in benzene at the refluxing temperature and crystallization of the product from 95% ethanol gave the 9-chloroacridine **9b** as a crystalline solid. The structure of **9b** was confirmed by elemental analysis, ¹Hmr spectroscopy (one piperidine ring per molecule) and by the fact that it was quantitatively converted to the 9-acridone **11b** when treated with boiling 95% ethanol. Although isolation and further purification of **9a-d** were feasible, they had no practical value in the present syntheses and therefore compounds **9a-d** were prepared and converted to 9-acridones **11a-d** by mild acid hydrolysis in a single flask. The yields of **11a-d** thus prepared, were influenced by the reaction time in the ring closure step. Optimum yields of **11a-d** were afforded when **8a-d** had been treated with phosphorous oxychloride for 45 min.; when this period of time was exceeded, the yields were reduced to 60-63% after a period of 3 h. The 1-isomers **12a-d** were also formed, but in small proportions (5-10%) and were not isolated.

Hydrolysis of **11a-c** was readily accomplished and provided the acids **5a-c** in high yields. Thus, treatment of **11a** with concentrated hydrochloride acid-

acetic acid mixture (1:2) at the refluxing temperature for 24 h gave the acid *5a* in 97% yield. In an analogous manner, *11b* was hydrolyzed to provide *5b* in 96% yield; under the same conditions, *11c* afforded *5c* in 90% yield.

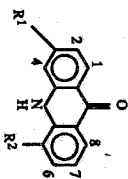
Conveniently, all steps involved in the conversion of *8a-d* to the acids *5a-d* could be performed in a single flask. Thus, treatment of *8b* with phosphorous oxychloride under the conditions described above (45 min) followed by acidic hydrolysis of the products (hydrochloric acid-acetic acid, 1:2) gave pure *5b* in 75% yield. Application of this sequence to the methyl analog provided pure *5d* in 50% yield. By the same process *5a* and *5c* were produced in 81% and 73% yields, respectively, but these products were contaminated (5-10%) with the corresponding isomers *6a* and *6c*.

Ethyl and methyl esters *5e-h* were best prepared and in high yields by reaction of the corresponding acid with diethyl and dimethyl sulfate respectively, in the presence of diisopropylethylamine using a modified literature procedure⁸.

The structures of the acids *5a-d* and their derivatives *5e-h* and *11a-d* were established on the basis of ¹Hmr spectroscopy. There are conflicting reports in the literature regarding the structure of the acid produced by cyclization of the diphenylaminedicarboxylic acid *4b* with phosphorous oxychloride; Lehmstedt^{9,10} has claimed this product to be 3-nitro-9(1OH)acridone-5-carboxylic acid (*5b*) whereas Matsumura^{11,12} has assigned the 1-nitro-9(1OH)acridone-4-carboxylic acid structure (*6b*) to this product. Structures *5b* and *6b* can now be readily recognized on the basis of their ¹Hmr spectra. The spectral data for *5a-d*, *5e-h* and *11a-d* are recorded in Table 2. Identification of the aromatic protons was based on values reported for the chemical shifts in 9(1OH)acridone¹³ and on the effect of substituents on the resonance frequency of aromatic protons¹⁴. The ¹Hmr spectrum of *5b* exhibited a triplet at δ 7.47 ($J_{6,7}=J_{7,8}=8$ Hz) assigned to H-7 proton. It also showed a double doublet at δ 8.0 ($J_{1,2}=9$, $J_{2,4}=2$ Hz) due to H-2 proton and a doublet at δ 8.92 ($J_{2,4}=2$ Hz) due to

H-4 proton. These spectral characteristics are in complete accord with the structure assigned to *5b*. On the other hand, the ¹Hmr spectrum of *6b* showed a doublet at δ 8.16 ($J_{1,2}=8$ Hz) and a doublet at δ 8.53 ($J_{1,2}=8$ Hz) due to H-2 (adjacent to NO₂) and H-3 (adjacent to CO₂H) protons, respectively. The ¹Hmr spectra of *5a*, *5c* and *5d* showed similar patterns as that of *5b*. Thus, a triplet at δ 7.33-7.38 ($J_{6,7}=J_{7,8}=8$ Hz), a double doublet in the region δ 7.15-7.44 ($J_{1,2}=9$, $J_{2,4}=2$ Hz) and a doublet in the region δ 7.54-8.18 ($J_{2,4}=2$ Hz) were

TABLE II: Nuclear Magnetic Resonance data of

3-substituted-9(1H)-acridone-carboxylic acids and Derivates^a.

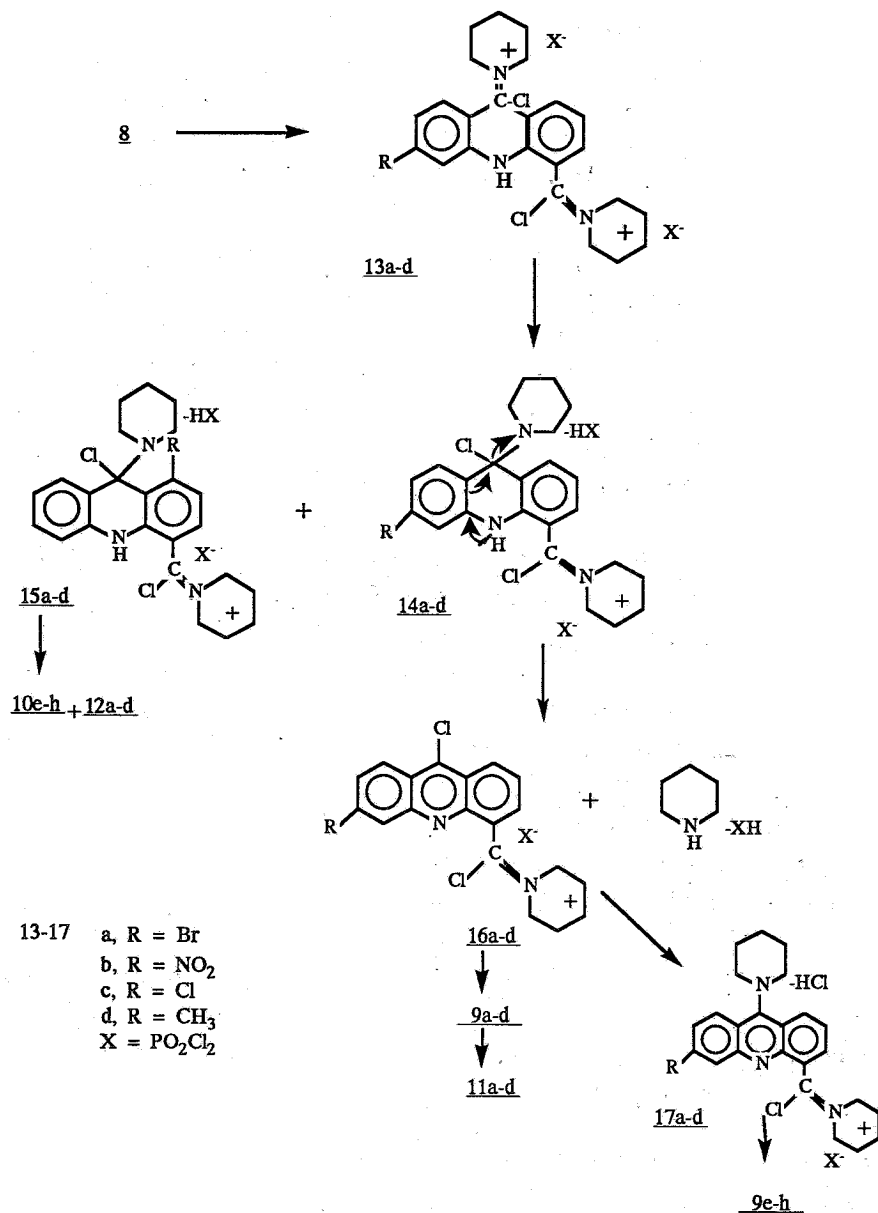
Compound	Chemical shifts (ppm) and coupling constants (Hz) of aromatic protons								Other (ppm)	Solvent
	H-1	H-2	H-4	H-6	H-7	H-8				
5a, R ¹ = Br, R ² = CO ₂ H	8.14 (d) J _{1,2} = 8	7.44 (dd) J _{1,2} = 8, J _{2,4} = 2	8.18 (d) J _{2,4} = 2	8.52 (dd) J _{6,7} = 8, J _{6,8} = 2	7.38 (t) J _{6,7} = J _{7,8} = 8	8.45 (dd) J _{6,7} = 2, J _{7,8} = 8	3.1 (bs, 1H, CO ₂ H) 11.87 (s, 1H, NH)	DMSO-d ₆		
5b, R ¹ = NO ₂ , R ² = CO ₂ H	8.42 (d) J _{1,2} = 9	8.0 (dd) J _{1,2} = 9, J _{2,4} = 2	8.92 (d) J _{2,4} = 2	8.37 - 8.59 overlapped with H-8	7.47 (t) J _{6,7} = J _{7,8} = 8	8.37 - 8.59 overlapped with H-6	3.4 (bs, 1H, CO ₂ H)	DMSO-d ₆		
5c, R ¹ = Cl, R ² = CO ₂ H	8.21 (d) J _{1,2} = 9	7.32 (dd) J _{1,2} = 9, J _{2,4} = 2	8.05 (d) J _{2,4} = 2	8.51 (dd) J _{6,7} = 8, J _{6,8} = 2	7.38 (t) J _{6,7} = J _{7,8} = 8	8.45 (dd) J _{6,7} = 2, J _{7,8} = 8	3.0 (bs, 1H, CO ₂ H) 11.81 (s, 1H, NH)	DMSO-d ₆		
5d, R ¹ = CH ₃ , R ² = CO ₂ H	8.12 (d) J _{1,2} = 8	7.15 (dd) J _{1,2} = 8, J _{2,4} = 2	7.54 (d) J _{2,4} = 2	8.51 (dd) J _{6,7} = 8, J _{6,8} = 2	7.33 (t) J _{6,7} = J _{7,8} = 8	8.43 (dd) J _{6,7} = 2, J _{7,8} = 8	2.47 (s, 3H, CH ₃ -C) 11.74 (s, 1H, NH) 3.2 (bs, 1H, CO ₂ H)	DMSO-d ₆		
5e, R ¹ = Br, R ² = CO ₂ H	8.29 (d) J _{1,2} = 9	7.37 (dd) J _{1,2} = 9, J _{2,4} = 2	7.59 (d) J _{2,4} = 2	8.70 (dd) J _{6,7} = 8, J _{6,8} = 2	7.27 (t) J _{6,7} = 2, J _{7,8} = 8	8.44 (dd) J _{6,7} = 2, J _{7,8} = 8	1.48 (t, 3H, CH ₃) 4.49 (q, 2H, CH ₂) 11.40 (bs, 1H, NH)	CDCl ₃		
5f, R ¹ = NO ₂ , R ² = CO ₂ CH ₃	8.61 (d) J _{1,2} = 9	8.04 (dd) J _{1,2} = 9, J _{2,4} = 2	8.33 (d) J _{2,4} = 2	8.72 (dd) J _{6,7} = 8, J _{6,8} = 2	7.35 (t) J _{6,7} = J _{7,8} = 8	8.50 (dd) J _{6,7} = 2, J _{7,8} = 8	4.06 (s, 3H, OCH ₃)	CDCl ₃		
5g, R ¹ = Cl, R ² = CO ₂ H	8.38 (d) J _{1,2} = 9	7.23 (dd) J _{1,2} = 9, J _{2,4} = 2	7.42 (d) J _{2,4} = 2	8.71 (dd) J _{6,7} = 8, J _{6,8} = 2	7.28 (t) J _{6,7} = J _{7,8} = 8	8.47 (dd) J _{6,7} = 2, J _{7,8} = 8	1.47 (t, 3H, CH ₃) 4.48 (q, 2H, CH ₂) 11.35 (bs, 1H, NH)	CDCl ₃		
5h, R ¹ = CH ₃ , R ² = CO ₂ H	8.34 (d) J _{1,2} = 8	7.12 (dd) J _{1,2} = 8, J _{2,4} = 2	7.25 (d) J _{2,4} = 2	8.73 (dd) J _{6,7} = 8, J _{6,8} = 2	7.24 (t) J _{6,7} = J _{7,8} = 8	8.43 (dd) J _{6,7} = 2, J _{7,8} = 8	1.47 (t, 3H, CH ₃) 2.49 (s, 3H, CH ₃ -C)	CDCl ₃		
9a, R ¹ = Br, R ² = CONH ₂	8.28 (d) J _{1,2} = 9	7.35 (dd) J _{1,2} = 9, J _{2,4} = 2	7.53 (d) J _{2,4} = 2	7.62 (dd) J _{6,7} = 8, J _{6,8} = 2	7.23 (t) J _{6,7} = J _{7,8} = 8	8.50 (dd) J _{6,7} = 2, J _{7,8} = 8	9.97 (bs, 1H, NH)	CDCl ₃		
9b, R ¹ = NO ₂ , R ² = CONH ₂	8.56 (d) J _{1,2} = 9	7.97 (dd) J _{1,2} = 9, J _{2,4} = 2	8.25 (d) J _{2,4} = 2	7.69 (dd) J _{6,7} = 8, J _{6,8} = 2	7.26 (t) J _{6,7} = 7, J _{7,8} = 8	8.50 (dd) J _{6,7} = 2, J _{7,8} = 8	10.42 (bs, 1H, NH)	CDCl ₃		
9c, R ¹ = Cl, R ² = CONH ₂	8.36 (d) J _{1,2} = 9	7.20 (dd) J _{1,2} = 9, J _{2,4} = 2	7.36 (d) J _{2,4} = 2	7.63 (dd) J _{6,7} = 8, J _{6,8} = 2	7.24 (t) J _{6,7} = J _{7,8} = 8	8.53 (dd) J _{6,7} = 2, J _{7,8} = 8.0	10.0 (bs, 1H, NH)	CDCl ₃		

^a Spectra were recorded at 80 MHz

assigned to H-7, H-2 and H-4 protons, respectively and were taken as evidence for the structures assigned to these products.

Formation of 9-alkylaminoacridines by cyclization of alkylamides of N-phenylanthranilic acid with phosphorous oxychloride is well documented^{6a-g,7}. It was also reported that cyclization of 3-(3-methylanilino) benzopiperidide produced 3-methyl-9-piperidinoacridine, which was readily converted to 3-methyl-9-acridone by mild acid hydrolysis⁷.

From the above evidence, it was expected that ring closure of *8a-d* would proceed in an analogous manner and produce the 9-piperidinoacridines *9e-h* and *10e-h* which by hydrolytic cleavage of the piperidine moiety should yield the corresponding 9-acridones. Our results however, were not in accord with these expectations and merit further discussion since they shed light on the mechanism of the cyclization reaction. As previously mentioned above, 9-chloroacridines *9a-d* (contaminated with *10a-d*) were the major products of the cyclization of *8a-d* with phosphorous oxychloride. 9-Piperidinoacridines *9e-h* (contaminated with *10e-h*) were also produced and were present as by products in all preparations of *11a-d* and of the acids *5a-d* (in the one pot process). Formation of *9e-h* and *10e-h* is best explained in terms of a bimolecular reaction between the initially formed 9-chloroacridines *9a-d* and *10a-d* and the liberated piperidine hydrochloride. Evidence for the bimolecular process is provided by the fact that the yields of *9e-h* and isomers *10e-h* were increased as the reaction time in the cyclization step was increased. The yields of *9e-h* (and *10e-h*) were also increased when piperidine hydrochloride was added in the cyclization step; in this way *9e* was produced in 72% yield. Compounds *9e-h* were remarkably stable to acidic hydrolysis and therefore cannot be regarded as precursors of *11a-d* or *5a-d* in the present syntheses. For example, *9e* was recovered quantitatively when subjected to acidic hydrolysis under the conditions employed in the preparation of the acids *5a-d*. The above results are best rationalized in terms of a mechanism as presented in Scheme 3.



Scheme 3

Ring closure of the Vilsmeier complexes *13a-d*¹⁵ proceeds readily in that direction to provide intermediates *14a-d* as the major isomers. Intermediates

15a-d are also formed but in small proportions. Elimination of one molecule of piperidine from *14a-d* and formation of *16a-d* is the major route for the decomposition of these intermediates. On the other hand, elimination of hydrogen chloride from *14a-d* and formation of *17a-d* is of secondary importance.

Imidoyl chlorides *16a-d* readily react with water to form *9a-d* which on hydrolysis are converted to *11a-d*.

Alternatively, imidoyl chlorides *16a-d* slowly react with piperidine salt and form *17a-d* which in the presence of water are converted to 9-piperidinoacridines *9e-f*. Minor products *10e-h* and *12a-d* are produced from intermediates *15a-d* by a similar mechanism.

Experimental

The infrared spectra were recorded on a Perkin-Elmer 267 grating infrared spectrophotometer. The ^1H NMR spectra were determined on Varian CFT-20 spectrometer using tetramethylsilane as internal standard. Melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Thin layer chromatography (tlc) was carried out on pre-coated silica gel plates 5 cm (E. Merck F-254). Preparative liquid chromatography was performed on Waters Associates Prep 500 L.C system using PrepPak-500/silica column. The analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

All compounds were analysed for C, H, N or halogen; analytical results were within $\pm 0.4\%$ of the theoretical value.

2-[(2-Hydroxycarbonyl)anilino]-4-bromobenzoic acid (4a)

This product was prepared according to the procedure described below for the preparation of the nitro analog *4b*. Thus, 4-bromo-2-chlorobenzoic acid (100 g, 0.425 mol) was reacted with anthranilic acid (85.2 g, 0.616 mol) in *n*-amyl alcohol (600 mL) in the presence of anhydrous potassium carbonate (176.7 g, 1.28 mol) and copper powder (3 g). After refluxing for 1 h a heavy precipitate was formed. An additional 400 mL of *n*-amyl alcohol was added to facilitate stirring and after refluxing for 10 h, the product was isolated to yield 121 g (85%) of crude product *4a*. This material was used in the next reaction without further purification.

2-[(2-Hydroxycarbonyl)anilino]-4-nitrobenzoic acid (4b)

This product was prepared according to a modified procedure described in literature¹¹ as follows: Into a 3 L 3-neck-flask fitted with condenser and mechanical stirrer was added 2-chloro-4-nitrobenzoic acid (100.8 g, 0.5 mol) and n-amyl alcohol (600 mL) and the mixture stirred at room temperature until the solids dissolved. To the resultant solution was added potassium carbonate (208 g, 1.5 mol), the mixture stirred for 10 min and then anthranilic acid (100 g, 0.73 mol) and copper powder (4 g) were added and the mixture heated under reflux with vigorous stirring. Rapid evolution of gases occurred and after 10-15 min of refluxing a heavy precipitate was formed. An additional 200 mL of n-amyl alcohol was added to facilitate stirring and the mixture refluxed for 8 h. After cooling to room temperature, the solids were collected by filtration, washed with ether and dried. This product (sodium salt of *4b*) was dissolved in water (600 mL) and the solution was filtered. The filtrate was acidified with concentrated hydrochloric acid (~120 mL) and the precipitate was collected, washed with water and dried. Recrystallization from DMF-water mixture (1:1, 600 mL) gave 110 g (70.5%) of *4b*, m.p. 315-320°C. This material was used in the next experiment. An analytical sample was obtained by recrystallization from DMF (3 mL/g) - ether (1.5 mL/g), m.p. 323-324°C (lit.¹¹ m.p. 324-325°C).

2-[(2-Hydroxycarbonyl)anilino]-4-chlorobenzoic acid (4c)

Employing the procedure described above for the preparation of the nitro analog *4b*, 2,4-dichlorobenzoic acid (95.5 g, 0.5 mol) was treated with anhydrous potassium carbonate (207.3 g, 1.5 mol) in n-amyl alcohol (0.5 L) and the resulting potassium salt reacted with anthranilic acid (102.86 g, 0.75 mol) in the presence of copper powder (4 g) to provide 127 g (87.6%) of the title compound. This product was used in the next reaction without further purification.

A sample of *4c* was converted to the diethyl ester, and the latter product purified by chromatography of silica gel. Hydrolysis of the diester with sodium hydroxide in ethanol followed by acid treatment provided the acid *4c*, m.p. 280-282°C. Anal. calcd for C₁₄H₉ClNO₄: C 57.84, H 3.12, Cl 12.20, N 4.82. Found: C 57.35, H 3.12, Cl 13.81, N 4.70.

2-[(2-Hydroxycarbonyl)anilino]-4-methylbenzoic acid (4d)

Using the procedure described above for the syntheses of **4b**, 2-chloro-3-methylbenzoic acid (8.53 g, 50 mmol) was reacted with anthranilic acid (10.3 g, 75 mmol) in presence of anhydrous potassium carbonate (20.7 g, 150 mmol) and copper powder (0.4 g) in *n*-amyl alcohol (50 mL) to yield 9.5 g (70%) of crude **4d**. This product was used in the next reaction without further purification

Cyclization of diphenylaminebicarboxylic acids 4 to mixtures of 5 and 6*A. Cyclization with sulfuric acid*

A mixture of **4** (1 g) and 98% sulfuric acid (5 mL) was heated in an oil bath at 100°C for 1 h. The reaction solution was poured into water (60 mL). The solids were collected, washed with water and dried at 100°C/0.1 Torr to provide a mixture of the isomeric acids **5** and **6**, in 80-90% yield.

B. Cyclization with phosphorous oxychloride

A mixture of **4** (1 g) and phosphorous oxychloride (5 mL) was refluxed with stirring for 1.5 h. After removal of phosphorous oxychloride under reduced pressure, water (25 mL) was added and the mixture was heated under reflux with stirring for 1 h. The solids were collected, washed with water and dried (100°C/0.1 Torr) to give a mixture of **5** and **6** in 85-90% yield.

C. Cyclization with dichlorophosphoric acid anhydride

The general procedure described by Effenberger¹⁶ and coworkers was used as follows: A stirred mixture of **4a** (1.4 g, 4.17 mmol) and dichlorophosphoric acid anhydride (3.77 g, 15 mmol) in dry and ethanol-free chloroform (15 mL) was heated under reflux conditions until homogeneous, then 1.5 h longer. The solvent was removed *in vacuo* and the residue was cooled at 0°C. Water (50 mL) was cautiously added, then the mixture was heated under reflux with stirring for 15 min. The solids were collected, washed with water and dried to give 1 g (75%) of a mixture of **5a** and **6a**.

D. Analysis of mixtures of 5 and 6

The proportions of isomers in mixtures of 5 and 6 were determined by ^1Hmr spectroscopy. The ^1Hmr spectra of mixtures of 5a and 6a, 5c and 6c and 5d and 6d showed absorption signals in the region δ 8.40-8.58 due to H-6 and H-8 protons of 5a, c, d which were well separated from the other bands in the aromatic region. The ^1Hmr spectrum of a mixture of 5b and 6b showed a band (d, J=2) at lowest field (δ 8.92) due to H-4 proton of 5b. Calculations of percentages of 5a-d in mixtures with their isomers 6a-d were based on the integrals of the above mentioned bands in relation to the total integrals of the aromatic region.

Preparation of the acyl chlorides 7a-d

General procedure

Method A

Hydrogen chloride was bubbled for 10 min. into a stirred suspension of the dicarboxylic acid 4 (100 mmol) in chloroform (200 mL).

After removal of the solvent *in vacuo*, thionyl chloride (150 mL) and dimethylformamide (3 drops) were added and the mixture was heated under reflux until all solids had dissolved and gas evolution had ceased (30-40 min). The reaction mixture was evaporated under reduced pressure, benzene was added and the mixture again evaporated to remove traces of thionyl chloride. The acyl chloride thus obtained was used in the next reaction without delay.

Method B

To a stirred suspension of the acid 4 (15 mmol) in methylene chloride (50 mL) and dimethylformamide (0.53 g, 7.3 mmol) was slowly added oxalyl chloride (7.64 g, 60 mmol) and the mixture stirred at room temperature until all solids had dissolved and evolution of gases had ceased (2-3 h). Removal of the solvent and excess of oxalyl chloride *in vacuo* afforded the acyl chloride which was used in the next reaction without delay.

N-[2-((2-Piperidonocarbonyl)anilino)-4-bromobenzoyl]piperidine (8a)

The acid chloride 7a [prepared from the acid 4a (67.23 g, 200 mmol) by method A above] was dissolved in methylene chloride (400 mL) and the solution cooled in an ice-bath while stirring. To this solution was added a solution of piperidine (102.8 g, 1.2 mol) in methylene chloride (100 mL) in a dropwise manner at such a rate as to keep the inside temperature below 15°C. After the addition was completed, the reaction mixture was stirred at room temperature overnight. The reaction solution was washed successively with water, 5% hydrochloric acid, 5% sodium hydroxide and finally with water, dried and filtered. The filtrate was evaporated under reduced pressure and the residue was filtered through a silica gel column. The column was washed first with chloroform and then with 1% methanol in chloroform to give 86 g of 8a as a syrup. This product was crystallized from hexane (300 mL)-methylene chloride (35 mL) solvent mixture to provide 78 g (83%) of 8a, mp 129-132°C which on tlc (4% MeOH-CH₂Cl₂) showed a single spot of Rf 0.47. An analytical sample was obtained by recrystallization from ethyl acetate-hexane mixture, mp 133-135°C; ir (CHCl₃) : 3350, 1630, 1580 cm⁻¹. Anal. calcd for C₂₄H₂₈N₃BrO₂: C 61.28, H 6.00, N 8.93. Found: C 61.24, H 5.94, N 8.87.

Similar yields of 8a were obtained when the acid chloride 7a was prepared by method B.

N-[2-((2-Piperidinocarbonyl)anilino)-4-nitrobenzoyl]piperidine (8b)

This product was prepared according to the procedure described above for the preparation of the bromo analog 8a. Thus a solution of the acyl chloride 7b [prepared from acid 4b (90.6 g, 0.3 mol) by method A] in methylene chloride (500 mL) was treated with piperidine (170 g, 2 mol) and the product was isolated as above. This product was dissolved in methylene chloride (200 mL) and filtered through silica gel column (13cmx7cm ID) and the column washed with 2% MeOH-CH₂Cl₂ to provide 109 g (84%) of 8b as a syrup which crystallized on standing. An analytical sample was obtained by recrystallization from ethyl acetate, mp 90-92°C; ir (Nujol); 3350, 1630, 1605, 1580, 1530, 1500 cm⁻¹; ¹Hmr (CDCl₃) δ: 1.65 (m, 12H, CH₂), 3.57 (m, 8H, NCH₂), 7.1-8.2 (m, 7H, ArH). Anal. calcd. for C₂₄H₂₈N₄O₄: C 66.03, H 6.46,

N 12.84. Found: C 66.10, H 6.94, N 11.67. A similar yield of *8b* was obtained when acyl chloride *7b* was prepared by method B.

N-[2-((2-Piperidinocarbonyl)anilino)-4-chlorobenzoyl]piperidine (*8c*)

Employing the procedure described above for the preparation of *8a*, the acyl chloride *7c* [prepared from the acid *4c* (4.35 g, 15 mmol) by the method B] in methylene chloride (50 mL) was treated with a solution of piperidine (7.45 g, 87.5 mmol) in methylene chloride (10 mL) and the product was isolated as above to yield 6.39 g (100%) of the title compound as a syrup. Thin-layer chromatography (4% MeOH-CH₂Cl₂) showed one major spot of R_f 0.48 (*8c*) and a minor impurity of R_f 0.35. A sample was purified by column chromatography on silica gel using 1% methanol in chloroform as eluent. The purified material was crystallized from methylene chloride-hexane solvent mixture to afford the analytical sample, mp 135-137°C; ir (CHCl₃): 3350, 1630, 1580 cm⁻¹. Anal. calcd. for C₂₄H₂₇N₃ClO₂: C 67.83, H 6.40, N 9.89, Cl 8.37. Found: C 67.63, H 6.58, N 9.85, Cl 8.33.

A similar yield of *8c* was obtained when the acyl chloride *7c* was prepared by method A.

N-[2-((2-Piperidinocarbonyl)anilino)-4-methylbenzoyl]piperidine (*8d*)

Employing the procedure described above for the preparation of *8a*, the acid chloride *7d* [prepared from 6.5 g (24 mmol) of the acid *4d* by method B with the exception that benzene was used instead of methylene chloride as the solvent] in methylene chloride (60 mL) was treated with piperidine (12 g, 140 mmol) and the product was isolated as described above. The crude dipiperidide *8d* was purified by column chromatography on silica gel using first chloroform and then 2% methanol in chloroform as eluent to give 9.4 g (97%) of *8d* as syrup. Crystallization from methylene chloride-hexane solvent mixture afforded the analytical sample, mp 154-155°C; ir (CHCl₃): 3350, 1630, 1580 cm⁻¹. Anal. calcd. for C₂₅H₃₀N₃O₂: C 74.23, H 7.47, N 10.39. Found: C 73.98, H 7.53, N 10.36.

3-Bromo-5-piperidinocarbonyl-9(1OH)acridone (11a)

To a stirred solution of *8a* (47 g, 100 mmol) in dry benzene (250 mL) was added phosphorous oxychloride (60 mL) and the solution was heated under

reflux for 45 min. The solvent and excess of phosphorous oxychloride were removed by evaporation under reduced pressure; toluene was added to the residue and the mixture again evaporated to remove traces of phosphorous oxychloride. To residue was dissolved in dioxane (250 mL) - water (50 mL) solvent mixture and the solution was evaporated *in vacuo* to give a partly solidified residue¹⁷. To this product was added 95% ethanol (250 mL) and the mixture heated under reflux with mechanical stirring for 20 min. The solids were collected by filtration of the warm reaction mixture, washed first with water and then ethanol (50 mL) and dried to give 32 g (83%) of *11a*, mp 270-273°C. This product showed on tlc (4% MeOH-CH₂Cl₂) one major spot of R_f 0.53 (*11a*) and traces of another component with R_f 0 (presumably corresponding acid) and was used in the next preparation. A sample was purified by chromatography (silica gel, 1% MeOH-CHCl₃) and recrystallized from chloroform-hexane (1:1) solvent mixture to afford an analytical sample of *11a*, mp 274-276°C; ir (CHCl₃): 3350, 1630, 1610, 1570 cm⁻¹. Anal. calcd. for C₁₉H₁₇N₂BrO₂: C 59.23, H 4.45, N 7.27, Br 20.74. Found: C 59.11, H 4.50, N 7.32, Br 20.53.

In another experiment, a solution of *8a* (7 g) and phosphorous oxychloride (9 mL) in benzene (37 mL) was heated under reflux for 3 h and the product isolated as described above to yield 3.5 g (61%) of *11a*. The mother liquor was evaporated *in vacuo* and the residue was chromatographed on a wet silica gel column using 2% methanol in chloroform as eluent to give 2.0 g (27.5%) of a mixture of 9-piperidino-acridine hydrochlorides *9e* and *10e*.

3-Nitro-5-piperidinocarbonyl-9(1OH)acridone (*11b*)

A solution of *8b* (8.73 g, 20 mmol) and phosphorous oxychloride (12 mL) in dry benzene (50 mL) was heated under reflux for 45 min. The reaction solution was evaporated under reduced pressure, toluene was added and the mixture again evaporated. The residue was dissolved in 90% dioxane-water mixture (80 mL) and the solution stirred at room temperature for 15 min¹⁷. The solvent was removed *in vacuo*, 95% ethanol (50 mL) was added and the mixture stirred and heated under reflux for 30 min. After cooling to room temperature the solids were collected, washed with water and dried to give 5.96 g (85%) of *11b*, mp 224-226°C. Recrystallization from acetonitrile afforded the analytical sample, mp 227-228°C; ir (CHCl₃): 3300, 1650, 1620, 1580, 1520 cm⁻¹. Anal. calcd. for C₁₉H₁₇N₃O₄: C 64.95, H 4.88, N 11.96. Found: C 64.80,

H 4.88, N 12.05.

The yield of *11b* was reduced to 65% when the solution of *8b* and phosphorous oxychloride in benzene was heated under reflux for 3 h.

*3-Chloro-5-piperidinocarbonyl-9(10H)acridone (11c) and
1-(3-Chloro-5-piperidinocarbonylacridine-9-yl)piperidine hydrochloride (9g)*

To a stirred solution of *8c* (5.93 g, 13.89 mmol) in dry benzene (35 mL), phosphorous oxychloride (8.3 mL) was added and the solution was heated under reflux for 45 min. The solvent and excess phosphorous oxychloride were removed under reduced pressure; toluene was added and the mixture evaporated. The residue was dissolved in dioxane (40 mL) and water (5 mL) and the resulting solution was stirred at room temperature for 10 min and then evaporated under reduced pressure¹⁷. The residue was dissolved in 95% ethanol (40 mL) and the solution heated under reflux with stirring for 45 min. The solid precipitate was collected by filtration of the warm reaction mixture, washed first with water then with ethanol (15 mL) and dried to give 3.5 g (74%) of *11c*, as yellow crystals, mp 264-265°C. This product showed on tlc (5% MeOH-CH₂Cl₃) a single spot of R_f 0.59. An analytical sample was obtained by recrystallization from dimethylformamide-ethanol (1:3) solvent mixture, mp 264-265°C; ir (CHCl₃): 3350, 1630, 1610 cm⁻¹. Anal. calcd for C₁₉H₁₇N₂ClO₂: C 66.96, H 5.03, N 8.23 Found: C 66.71, H 5.10, N 8.27.

The yield of *11c* was decreased to 60% when the refluxing time of *8c* with phosphorus oxychloride in benzene was extended to 3 h.

The mother liquor, after removal of the solvent *in vacuo*, was chromatographed on a wet silica column using first 2% and then 4% methanol in methylene chloride as eluent. The fractions containing *9g* were combined and evaporated and the residue recrystallized from ethanol-ether (5:1) mixture to provide an analytical sample of *9g* monohydrate, mp 293-297°C (dec.). Anal. calcd. for C₂₄H₂₆N₃ClO.HCl.H₂O: C 62.74, H 5.70, Cl 15.43. Found: C 62.06, H 5.76, N 8.84, Cl 15.78.

*3-Bromo-9(1OH)acridone-5-carboxylic acid (5a)**(A) Preparation from 3-Bromo-5-piperidinocarbonyl-9(1OH)acridone by Acid Hydrolysis*

A stirred suspension of *11a* (31.6 g, 82 mmol) in glacial acetic acid-concentrated hydrochloric acid mixture (2:1, 180 mL) was heated in an oil bath at 140°C. Soon after reflux commenced, all solids had dissolved and 15 min later crystalline *5a* started to precipitate. After refluxing for 24 h, the reaction mixture was allowed to cool to room temperature. The solids were collected, washed with water and dried to give 25.3 g (97%) of *5a*, mp > 360°C. Thin-layer chromatography (20% MeOH-CH₂Cl₂) showed a single spot of Rf 0.40 well distinguished from isomer *6a* (Rf 0.32). Anal. calcd for C₁₄H₈NBrO₃: C 52.85, H 2.53, N 4.40, Br 25.12. Found: C 52.60, H 2.56, N 4.31, Br 25.12.

The homogeneity of this product was further established by conversion to the ethyl ester and analysis of the latter by tlc and ¹Hmr spectroscopy. The ester *5e* found to be free of isomer *6e*.

B) Preparation from the Dipeperidide 8b by Ring Closure and Hydrolysis in a Single Flask.

A solution of *8a* (16.29 g, 34.6 mmol) and phosphorous oxychloride (21 mL) in dry benzene (80 mL) was stirred and heated under reflux for 45 min. The solvent and excess phosphorous oxychloride were removed by evaporation under reduced pressure. Toluene was added and the mixture was again evaporated. The residue was dissolved in glacial acetic acid-concentrated hydrochloric acid (2:1, 140 mL) mixture and the resulting solution was heated under reflux with stirring for 24 h. After cooling to room temperature, the solids were collected, washed with water and dried to give 8.93 g (81.2%) of *5a*, mp > 360°C. This product contained approximately 5% of the isomer *6a* as was shown by conversion to the ethyl ester and separation of the two isomers *5e* and *6e* by preparative liquid chromatography.

3-Nitro-9(1OH)acridone-5-carboxylic acid (5b)

(A) Preparation from 3-Nitro-5-piperidinocarbonyl-9(1OH)acridone (11b) by Acid Hydrolysis.

Compound *11b* (5.46 g, 15.6 mmol) was hydrolyzed with an acetic acid-concentrated hydrochloric acid mixture (2:1, 60 mL) as in the procedure given for the hydrolysis of *11a* to yield 4.26 g (96%) of *5b*, mp >360°C. Anal. calcd. for C₁₄H₈N₂O₅: C 59.16, H 2.84, N 9.86. Found: C 58.96, H 2.97, N 9.78.

This product was free of isomer *6b* as was shown by conversion to the methyl ester and analysis of the latter product by tlc and ¹Hmr spectroscopy. This ester showed on tlc (2% ethyl acetate in methylene chloride) a single spot of R_f 0.32 (*5f*) well distinguished from isomer *6f* which had R_f 0.40.

B) Preparation from Dipiperidide 8b

Employing the procedure described above for the preparation of *5a* from *8a*, compound *8b* (8.73 g, 20 mmol) was treated with phosphorous oxychloride (12 mL) in benzene (50 mL) and the product was hydrolyzed with acetic acid-concentrated hydrochloric acid mixture (2:1, 60 mL) to provide 4.26 g (75%) of *5b* free of isomer *6b*.

3-Chloro-9(1OH)acridone-5-carboxylic acid (5c)

A) Preparation from 3-Chloro-5-piperidinocarbonyl-9(1OH)acridone (11c) by Acid Hydrolysis.

To a solution of *11c* (17.3 g, 50.7 mmol) in hot glacial acetic acid (80 mL) was added concentrated hydrochloric acid (40 mL) and the resulting solution was heated under reflux with stirring. After 2 h refluxing, a heavy precipitate was formed. An additional 60 mL of 2:1 acetic acid-concentrated hydrochloric acid mixture was added to facilitate stirring and the mixture was refluxed for 19 h more. After cooling to room temperature, the solids were collected, washed with water and dried to give 12.5 g (90.1%) of the acid *5c*, mp > 360°C. This product was free of the 1-chloro isomer as evidenced by tlc and ¹Hmr spectrum of its ethyl ester. Anal. calcd. for C₁₄H₈NC₂O₃: C 61.43, H 2.95, Cl 12.95, N 5.12. Found: C 60.95, H 3.16, Cl 13.14, N 4.99.

B) Preparation from Dipiperidide 8c.

In a manner analogous to that given in the preparation of 5a from 8a, compound 8c (6.39 g, 15 mmol) was treated with phosphorous oxychloride (9 mL) in benzene (35 mL) and the product was hydrolyzed with acetic acid-concentrated hydrochloric acid mixture (2:1, 60 mL) to give (73%) of 5c, mp > 360°C. This product was contaminated with 5-10% of an impurity (presumably isomer 6c) as was evidenced by the ¹Hmr spectrum of its ethyl ester.

3-Methyl-9(1OH)acridone-5-carboxylic acid (5d)

A solution of the dipiperidide 8d (12.4 g, 30.6 mmol) and phosphorous oxychloride (18 mL) in dry benzene (70 mL) was heated under reflux for 45 min and then evaporated under reduced pressure. Toluene was added and the mixture again evaporated to remove traces of phosphorous oxychloride. The residue was dissolved in glacial acetic-concentrated hydrochloric acid mixture (2:1, 90 mL) and the resulting solution was heated under reflux with stirring for 24 h. The solids were collected, washed first with acetic acid-water mixture (1:2, 30 mL) then with water and dried to give 3.87 g (50%) of 5d, mp 332-335°C (lit.³ mp 337-338°C). This product showed on tlc (15% MeOH-CH₂Cl₂, two immersions) a single spot of Rf 0.39 well distinguished from isomer 6d which had Rf 0.49.

3-Nitro-9-chloro-5-piperidinocarbonylacridine (9b)

A solution of dipiperidide 8b (4.36 g, 10 mmol) and phosphorous oxychloride (6.5 mL) in dry benzene (24 mL) was heated under reflux for 3 h. After removal of the solvent and excess of phosphorous oxychloride under reduced pressure, toluene was added and the mixture evaporated *in vacuo* to remove traces of phosphorous oxychloride. The syrupy residue was dissolved in 95% ethanol and the solution was allowed to crystallize at room temperature. The yellow crystalline product was collected and recrystallized from methylene chloride (10 mL) - ethanol (60 mL) mixture to give 1.84 g (50%) of 9b, mp 258-259°C. Anal. calcd. for C₁₉H₁₆ClN₃O₃: C 61.71, H 4.36, N 11.36, Cl 9.59. Found: C 61.64, H 4.40, N 11.44, Cl 9.64.

When a solution of *9b* in 95% ethanol was heated under reflux for 30 min, 3-nitro-5-piperidinocarbonyl-9(1OH)acridone (*11b*) was obtained in quantitative yield.

1-(3-Bromo-5-piperidinocarbonylacridine-9-yl)piperidine hydrochloride (9e)

A solution of *8a* (3.76 g, 8 mmol) and phosphorous oxychloride (4.8 mL) in dry benzene (20 mL) was heated under reflux for 45 min. Piperidine hydrochloride (2.2 g, 18 mmol) was added and refluxing continued for an additional 30 min. After removal of the solvent and excess of phosphorous oxychloride *in vacuo*, the residue was dissolved in dry toluene (16 mL) and the solution was refluxed for 2.5 h. The reaction mixture was concentrated under reduced pressure and the residue was dissolved in 95% ethanol (50 mL). The resulting solution was heated under reflux for 30 min and then was concentrated under reduced pressure. The residue was dissolved in methylene chloride (150 mL) and the solution was washed with water (4 x 35 mL), dried and evaporated under reduced pressure. The residue was chromatographed on a wet silica column (33 cm x 2.8 cm I.D) using first 2% and then 5% methanol in chloroform as eluent to give 2.75 g (72%) of *9e* (contaminated with the isomer *10e*) as a yellow solid. Recrystallization from ethanol-ether mixture (2:1) afforded the analytical sample of *9e* as the monohydrate, mp 297-298°C; ¹Hmr (CDCl₃) δ: 1.74 (m, 12H, CH₂), 3.67-3.76 (m, 8H, NCH₂), 7.26-7.53 (m, 3H, H-2, H-6, H-7), 8.24 (d, 1H, H-1, J_{1,2}= 8 Hz), 8.60 (d, 1H, H-4, J_{2,4}=2 Hz), 8.72 (dd, 1H, H-8, J_{7,8}=8, J_{6,8}=2 Hz). Anal. calcd for C₂₄H₂₆N₃BrO.HCl.H₂O: C 56.87, H 5.77, N 8.29. Found: C 57.05, H 5.40, N 8.28.

Stability of 9e to Acidic Hydrolysis

A solution of *9e* (0.7 g) in a mixture of acetic acid-concentrated hydrochloric acid (2:1, 15 mL) was heated under reflux for 22 h. After removal of the solvent *in vacuo* the residue was dissolved in methylene chloride (100 mL). The solution was washed with water (12 mL), dried and evaporated to give 0.65 g (93% recovery) of a yellow solid identical (tlc, ¹Hmr) with the starting material *9e*.

Ethyl 3-bromo-9(1OH)acridone-5-carboxylate (5e)

This product was prepared according to a general procedure described in the literature⁸ which was modified as follows. To a suspension of a 3-bromo-9(1OH)acridone-5-carboxylic acid (20 g, 63 mmol) in acetone (63 mL) was added diisopropylethylamine (8.9 g, 69.3 mmol) and diethyl sulfate (18.8 g, 122 mmol) and the mixture was heated in an oil bath at 90°C. After refluxing for 30 min, the condenser was removed and heating continued until the solvent had evaporated. The residue was cooled to room temperature and treated with 5% hydrochloric acid. The solids were collected, washed with water and dried to give 19.6 g (90%) of *5e*. An analytical sample was obtained by recrystallization from ethyl acetate, mp 214-216°C; ir (CHCl₃): 3680, 3620, 1680, 1640, 1600, 1550 cm⁻¹. Anal. calcd. for C₁₆H₁₂NO₃Br: C 55.50, H 3.49, N 4.05, Br 23.08. Found: C 55.72, H 3.47, N 3.97, Br 22.90.

Methyl 3-nitro-9(1OH)acridone-5-carboxylate (5f)

To a suspension of 3-nitro-9(1OH)acridone-5-carboxylic acid (0.852 g, 3 mmol), in dry acetone (5 mL) was added diisopropylethylamine (0.43 g, 3.3 mmol) and dimethylsulfate (0.416 g, 3.3 mmol) and the mixture heated in an oil bath at 90°C while stirring. A heavy precipitate was soon formed. An additional 5 mL of acetone was added to facilitate stirring and the mixture heated under reflux for 30 min and then the solvent was allowed to evaporate at atmospheric pressure while heating was maintained. The residue was treated with 5% hydrochloric acid; the solids were collected washed with water and dried to give 0.89 g (100%) of *5f* which on tlc (2% ethylacetate in CH₂Cl₂) showed a single spot of R_f 0.32. An analytical sample was obtained by recrystallization from chloroform, mp 249-250°C; ir (CHCl₃): 1690, 1640, 1620, 1600, 1520 cm⁻¹. Anal. calcd. for C₁₅H₁₀N₂O₅: C 60.40, H 3.38, N 9.39. Found: C 60.32, H 3.43, N 9.63.

Ethyl 3-chloro-9(1OH)acridone-5-carboxylate (5g)

In a manner analogous to that given for the preparation of *5e*, 3-chloro-9(1OH)acridone-5-carboxylic acid (5 g, 18.3 mmol) was reacted with diethylsulfate (5.47 g, 35.5 mmol) in acetone (18 mL) in the presence of diisopropylethylamine (2.6 g, 20 mmol) and the product purified by preparative liquid

chromatography to provide 4.97 g (90%) of *5g*. The analytical sample was obtained by recrystallization from ethylacetate, mp 197-199°C; ir (CHCl₃): 3680, 3620, 1680, 1640, 1600, 1550 cm⁻¹. Anal. calcd. for C₁₆H₁₂NO₃Cl: C 63.69, H 4.01, N 4.64, Cl 11.75. Found: C 63.62, H 4.04, N 4.54, Cl 11.57.

Ethyl 3-methyl-9(1OH)acridone-5-carboxylate (5h)

Employing the procedure described above for the preparation of *5e*, 3-methyl-9(1OH)acridone-5-carboxylic acid (3.12 g) was treated with diethylsulfate and the product purified by preparative liquid chromatography to provide 3.3 g (95.4%) of the ester *5h*. The analytical sample was obtained by recrystallization from ethanol, mp 158-159°C; ir (CHCl₃): 3300, 1680, 1650, 1600, 1550 cm⁻¹. Anal. calcd for C₁₇H₁₅NO₃: C 72.58, H 5.37, N 4.98. Found: C 71.83, H 5.34, N 4.88.

Methyl 1-nitro-9(1OH)acridone-4-carboxylate (6f)

In a manner analogous to that given for the preparation of *5f*, 1-nitro-9(1OH)acridone-4-carboxylic acid⁵ was reacted with dimethylsulfate to provide a 90% yield of *6f*, mp 274-276°C. On tlc (silica, 2% ethylacetate in methylene chloride) this product showed a spot of R_f 0.40; ir (Nujol): 1690, 1640, 1620, 1600, 1540, 1520 cm⁻¹. Anal. calcd. for C₁₅H₁₀N₂O₅: C 60.40, H 3.38, N 9.39. Found: C 60.12, H 3.43, N 9.44.

Περίληψη

Μια βελτιωμένη σύνθεση των 3-υποκαταστημένων-9(1OH)-ακριδον-5-καρβοξυλικών οξέων και παραγώγων τους.

Στο παρόν άρθρο περιγράφεται μια βελτιωμένη πορεία σύνθεσης των 3-υποκαταστημένων-9(1OH)-ακριδον-5-καρβοξυλικών οξέων *5a-d*. Η μέθοδος εμπεριέχει την μετατροπή των υποκαταστημένων διφαινυλαμιν-2,2-δικαρβοξυλικών οξέων *4a-d* στα αντίστοιχα διπιπεριδίδια *8a-d*, η κυκλοποίηση των οποίων με οξυγλωριούχο φωσφόρο αποδίδει 9-γλωρο ακριδίνες *9a-d*, που με όξινη υδρόλυση παρέχουν τα αντίστοιχα οξέα *5a-d*.

Τα 3-βρωμο-, 3-νιτρο-, 3-χλωρο- και 3-μεθυλ-, παράγωγα του 9(10H)ακριδον-5-καρβοξυλικού οξέος (5*a-d*), που παρασκευάστηκε με τη νέα αυτή μέθοδο, ήταν ελεύθερα των 1-υποκαταστημένων ισομερών 6*a-d* σαν παραπροϊόντα. Είναι άξιο να σημειωθεί ότι η κατ' ευθείαν κυκλοποίηση του διφαινυλαμινο-δικαρβοξυλικών οξέων 4*a-d* με οξυχλωριούχο φωσφόρο ή με θειικό οξύ δίνει μίγμα ισομερών προϊόντων 5*a-d* και 6*a-d* τα οποία είναι δύσκολο να διαχωριστούν.

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 17. When treatment with aqueous dioxane prior to treatment with aqueous ethanol was omitted, the yield of title product was reduced due to formation of ethyl ester.

SHORT PAPER

Dilute solution behavior of Star-Branched Polymers

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Abstract

In the present work the predictions of the Zimm-Kilb, Stockmayer-Fixman are compared with a new relationship for g and with experimental data ($g = [\eta]_{\text{branched}} / [\eta]_{\text{linear}}$, where $[\eta]$ is the intrinsic viscosity). It is found that the new relationship is in good agreement with experimental data.

Keywords: Dilute solution, star polymers.

Introduction:

Zimm and Stockmayer were the first to analyze the configurational properties of star-branched macromolecules. They related the average square of the radius of gyration (\bar{S}^2) with the effective number of segments and their effective length. These parameters can be eliminated by comparing the star to a linear polymer molecule by using the parameter g , defined as:

$$g = (\bar{S}^2)_{\text{branched}} / (\bar{S}^2)_{\text{linear}}$$

for a constant molecular weight molecule.

By proposing that chains ends follow the distribution of Gauss it is found the relationship¹:

$$g' = (3f - 2) / f^2 \quad (1)$$

where f is the number of arms.

In the star system, the end to end distance is no longer a meaningful parameter because there are more than two ends. Flory² states that the radius of gyration should be substantiated for the end - to - end distance because it is defined for all types of polymer architecture. This gives:

$$g' = g^{3/2} \quad (2)$$

where $g = [\eta]_{\text{branched}} / [\eta]_{\text{linear}}$, ($[\eta]$ is the intrinsic viscosity) for a constant molecular weight molecule.

So from equations (1) and (2)

$$g' = [(3f - 2) / f^2]^{3/2} \quad (3)$$

Stockmayer and Fixman³ calculated using Kirkwood and Riesman's method⁴ that:

$$g' = f^{3/2} \cdot (2 - f + 2^{1/2} \cdot (f-1))^{-3} \quad (4)$$

This predicts that the intrinsic viscosity of a branched polymer molecule is a less sensitive function of branching. Zimm and Kilb⁵ using the model developed by Zimm⁶ for linear polymers calculated g . The mathematics is complex and exact values of g were only calculated for f equal to 4 and 8.

An approximation can be made that the even numbered eigenvalues of the branched

polymer are equal to the values calculated in the linear case. The error involved is slight and decreases with the increasing f . So

$$g' = (2/f)^3 [0.390(f-1) + 0.196] / 0.586 \quad (5)$$

this relation may be used when calculating g for star polymers. For more complicated branching Zimm and Kilb proposed the empirical relationship⁵.

$$g' \approx g^{1/2} \quad (6)$$

but this approximation is less accurate when dealing with model star polymers. Here must be noted that, for large f there is the relationship⁷:

$$[\eta]_b / [\eta]_l = 1.88f^{1/2} \quad (7)$$

New Relationship for g :

As it is known the solubility parameter is related the intrinsic viscosity of solution $[\eta]$ by the following expression⁸:

$$[\eta] = n_0 \exp [-v (d-d_0)]^2 \quad (8)$$

where: d is the solubility parameter of polymer solution, d_0 is the solubility parameter of solvent, n_0 is the viscosity of solvent, V is the molar volume ($V = M/D$), D is the density and M the molecular weight of polymer. For branched and linear polymers the relationship (8) has the following expression

$$[n]_b = n_o \exp(-M_b/D_b(d_b-d_o)^2) \text{ for branched}$$

$$[n]_l = n_o \exp(M_l/D_l(d_l-d_o)^2) \text{ for linear}$$

But $M_b = f M_a$, $M_l = 2M_a$

where M_a is arm molecular weight. So

$$g' = \exp(-M_a (f/D_b \cdot (d_b-d_o)^2 - 2/D_l (d_l-d_o)^2)) \quad (9)$$

With no mistake⁹⁻¹¹ can be considered that:

$$D_b \approx D_l \approx D = 1 \text{ gr/cm}^3 \quad (10)$$

Using Small's equation for solubility parameter (8)

$$d = \frac{D(\Sigma G)}{M_m}$$

Where D is the density of polymer, G the molar attraction constants and M_m the monomer weight of polymer

So

$$d_l = \frac{D_l(\Sigma G)_l}{M_{ml}} \quad \text{for linear} \quad (11)$$

and

$$d_b = \frac{D_b(\Sigma G)_b}{M_{mb}} \quad \text{for branched} \quad (12)$$

But: $M_{mb} = M_{ml}$ and $(\Sigma G)_1 = (\Sigma G)_b$ (13)

So from equations (10), (11) and (12)

$$d_1 = d_b = d$$

Also, from equations (10), and (14), the relationship (9) has the following expression:

$$g' = \exp(-M_a / D (d-d_0)^2 \cdot (f-2))$$

or

$$\ln g' = -M_a / D (d-d_0)^2 \cdot (f-2) \quad (15)$$

The magnitude $M_a / D (d-d_0)^2$ is characteristic for polymer and solvent. The plot of $\ln g'$ as function of $(f-2)$ is a straight line with slope $M_a / D (d-d_0)^2$.

Hence, star polymers, with the same molecular weight of arms, the same monomer and the same solvent have the same slope and all the values must be on the same line.

Results and discussion:

Experimental data are all from bibliography (Table I). From the plot of $\ln g$ as a function of $(f-2)$ of experimental data (Fig. 1) one can see that all the points lie on straight lines with different slopes. The higher value of the slope is about -0.11 and the lower value is about -0.17. Intermediate values are: -0.141, -0.155. We believe that, value -0.11 may be used for all star-branched polymers and solvents.

The main factor that define differences in slope is the molecular weight of arms.

Table I: Theoretical and Experimental values of g for star-branched polymers.

No. of arms	Experimental values of g' for star-branched polymers					Theoretical values of g' for star-branched polymers					
	Polystyrenes					Polyiso- nrenes	Copolymers of Styrene- Isonrene		Stockma- yer	New re- lation- ship	
	Cyclohexane		THF	Benzene		Dioxane	Benzene- n Heptane	Kilb	Fixman		
	g'	Mean Value g'	g'	g'	Mean Value g'	g'	g'	g'	g'	g'	
3	0.851 (13)	0.869						0.906	0.850	0.896	
3	0.94 (17)										
3	0.835 (14, 15)										
3	0.85 (16)	0.766	0.76 (16)								
4	0.75 (16)						0.722 (26)	0.803 (24)	0.814	0.709	0.803
4	0.77 (17)										
4	0.82 (12)										
4	0.76 (18, 19)										
4	0.736 (20)										
4	0.76 (21)										
6	0.5 (17)	0.59		0.543 (17)		0.625 (26)		0.705	0.507	0.644	
6	0.57 (17-18)										
6	0.63 (22)										
6	0.588 (23)										
7	0.554 (23)	0.534		0.50 (23)	0.478			0.661	0.437	0.577	
7	0.514 (13)			0.456 (13)							
8	--			--	--	0.517 (25)					
8.7	0.451 (23)			0.442 (23)				0.602	0.349	0.479	
10.5	0.426 (23)			0.395 (23)				0.553	0.283		
10.7	0.388 (23)			0.398 (23)				0.549	0.277		
11.6	0.433 (14)			0.352 (14)				0.529	0.252		
12	--			--		0.330 (25)	0.330 (24)			0.333	
12.3	0.359 (23)			0.360 (23)				0.515	0.236		
13.5	0.547 (23)			0.306 (23)				0.493	0.211		
13.9	0.386 (23)			0.308 (23)				0.487	0.203	0.270	

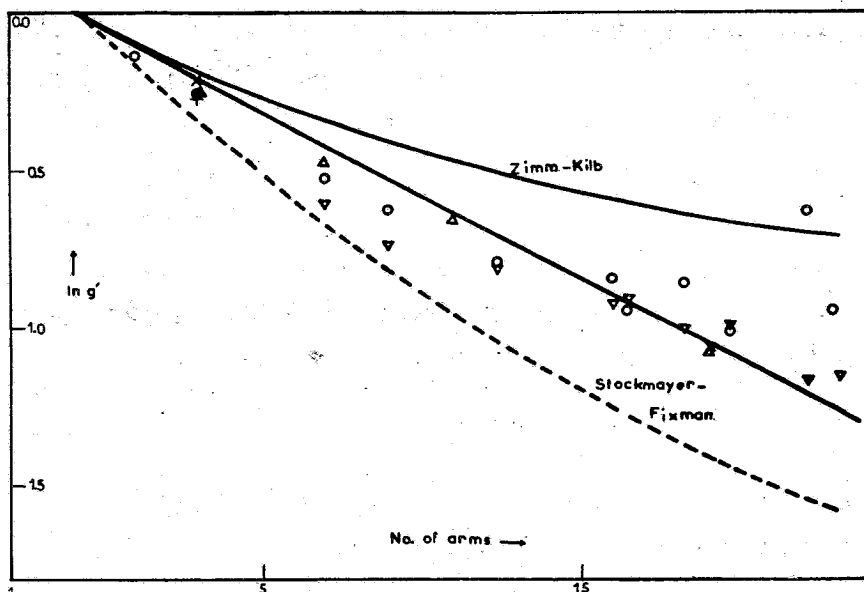


Figure 1.

Plot of $\ln g'$ v.s. f (\circ Cyclohexane, ∇ Benzene, $+$ THF, \triangle Dioxane, \times Benzene - n Heptane, 9:1).

Figure 1 presents $\ln g' - f$ data for the star - branched polystyrenes listed in Table I. Differences in values of g for the same f and solvent were due to experimental errors. For example Morton and coworkers¹² have presented data on the dilute solution properties of three and four branched materials Orofino and Wegner¹³ also undertook the characterization of the three branched polystyrene stars under theta conditions and in good solvents. Disagreement as to detail on several important points between the revised data of Morton and coworkers and those of Orofino and Wegner is evident e.g. Morton's g is larger in cyclohexane than in toluene,

whereas the opposite was found by Orofino and Wegner.

As it can be seen from Figure 1 the predictions of the Zimm - Kilb and Stockmayer - Fixman theories for g are in relations poor agreement with experiment results. In opposite the new relationship for g' is in good agreement with experiment results.

Conclusions:

The new relationship for g , **a)** is exponentially related with solubility parameter of polyre, solubility parameter of solvent, density and arm molecular weight of polymer and the number of arms. and **b)** is in good agreement with experimental data.

Περίληψη:

Η συμπεριφορά σε διάλυμα των αστεροειδών πολυμερών

Στην εργασία αυτή γίνεται σύγκριση των σχέσεων Zimm - Kilb και Stockmayer-Fixman με μια προτεινόμενη για το g με τα πειραματικά δεδομένα ($g =$ λόγος των εσωτερικών ξωδών διακλαδισμένου και γραμμικού μακρομορίου ίδιου μοριακού βάρους).

Από τη σύγκριση αυτή προκύπτει ότι η νέα προτεινόμενη σχέση προσεγγίζει καλύτερα τα πειραματικά δεδομένα από τις άλλες δύο.

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REVIEW

ΕΠΙΔΡΑΣΗ ΤΗΣ ΔΟΜΗΣ ΚΑΙ ΤΗΣ ΠΑΡΑΣΚΕΥΑΣΤΙΚΗΣ ΔΙΑΔΙΚΑΣΙΑΣ ΣΠΙΝΕΛΛΙΚΩΝ ΦΕΡΡΙΤΩΝ ΣΤΗ ΔΙΑΜΟΡΦΩΣΗ ΤΩΝ ΦΥΣΙΚΟΧΗΜΙΚΩΝ ΤΟΥΣ ΙΔΙΟΤΗΤΩΝ. ΙΙ. ΜΑΓΝΗΤΙΚΕΣ, ΗΛΕΚΤΡΙΚΕΣ ΚΑΙ ΚΑΤΑΛΥΤΙΚΕΣ ΙΔΙΟΤΗΤΕΣ ΣΠΙΝΕΛΛΙΚΩΝ ΦΕΡΡΙΤΩΝ.

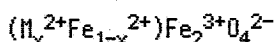
Ζ. ΛΟΪΖΟΣ, Ν. ΣΠΥΡΕΛΛΗΣ & Π. ΣΑΚΕΛΛΑΡΙΔΗΣ

Τμήμα Χημικών Μηχανικών, Τομέας Χημικών Επιστημών, Εργαστήριο Γενικής Χημείας Εθνικού Μετσόβιου Πολυτεχνείου, Πολυτεχνειούπολη Ζωγράφου, Ελλάδα.

(Ελήφθη στις 10 Μαρτίου 1987)

ΠΕΡΙΛΗΨΗ

Οι σπινελλικοί φερρίτες είναι μικτά οξειδία σιδήρου και ενός άλλου μετάλλου (M), τα οποία είναι δυνατό να περιγραφούν από το γενικό τύπο:



όπου το x παίρνει τιμές μεταξύ 0 και 1, και κρυσταλλώνονται στο κυβικό σύστημα, ακολουθώντας τη δομή του ορυκτού *σπινελλίου* ($MgAl_2O_4$).

Οι σπινελλικοί φερρίτες χαρακτηρίζονται από ενδιαφέρουσες μαγνητικές και ηλεκτρικές ιδιότητες. Έτσι, ανήκουν στην κατηγορία των *σιδηριμαγνητικών υλικών* με αποτέλεσμα να εμφανίζουν υψηλές γενικά τιμές μαγνητικής επιδεκτικότητας, οι οποίες μάλιστα εξαρτώνται από τον τρόπο κατανομής των μαγνητικών μεταλλοκατιόντων τους στις *τετραεδρικές (A)* και στις *οκταεδρικές (B)* θέσεις του σπινελλικού πλέγματος.

Όσον αφορά στις ηλεκτρικές τους ιδιότητες, οι σπινελλικοί φερρίτες παρουσιάζουν αυξημένες τιμές ειδικής ηλεκτρικής αγωγιμότητας, σε σύγκριση με άλλα στερεά ιοντικής κατασκευής, οι οποίες μάλιστα τείνουν να αυξάνονται με την αύξηση της θερμοκρασίας. Έτσι, ανήκουν στην κατηγορία των ημιαγωγών και, ανάλογα με τις συνθήκες παρασκευής τους, είναι δυνατό να συμπεριφέρονται ως ημιαγωγοί τύπου *n* ή τύπου *p*.

Ως αποτέλεσμα των ημιαγωγικών τους ιδιοτήτων, οι σπινελλικοί φερρίτες εμφανίζουν αξιόλογη καταλυτική δράση σε μεγάλο αριθμό αντιδράσεων της Ανοργάνου και της Οργανικής Χημείας. Εμφανίζουν ακόμη και αξιόλογες ροφητικές ιδιότητες.

Λέξεις κλειδιά: Φερρίτες, σπινελλίοι, οξειδία νικελίου-σιδήρου, τρεβορίτης.

ΜΑΓΝΗΤΙΚΕΣ ΙΔΙΟΤΗΤΕΣ

Γενικά

Οι σπινελλικοί φερρίτες ανήκουν στην κατηγορία των *σιδηριμαγνητικών υλικών*¹⁻⁴. Πράγματι, όπως προκύπτει από τη μελέτη της κρυσταλλικής δομής τους, τα μεταλλοκατιόντα τους συνιστούν δύο διαφορετικά υ-

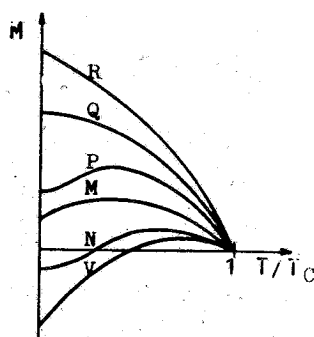
ποπλήγματα, αντιστοιχούντα στις *τετραεδρικές* (A) και στις *οκταεδρικές* (B) θέσεις του σπινελθικού πλέγματος. Οι μαγνητικές περιοχές τους (domains) αποτελούνται από μια ομάδα στοιχειωδών κυττάρων ή ακόμη και από μέρος ενός μόνο στοιχειώδους κυττάρου. Αποτέλεσμα είναι η εμφάνιση κάποιας μη μηδενικής μαγνήτισης μέσα στις περιοχές αυτές, ακόμη και όταν το σιδηριμαγνητικό υλικό δεν βρίσκεται υπό την επίδραση εξωτερικού μαγνητικού πεδίου, που είναι χυσατή ως *αυθόρμητη μαγνήτιση*.

Μεταβολή της αυθόρμητης μαγνήτισης και της μαγνητικής επιδεκτικότητας των φερριτών με τη θερμοκρασία

Τα σιδηριμαγνητικά υλικά και επομένως και οι σιδηριμαγνητικοί φερρίτες για θερμοκρασίες μεγαλύτερες του σημείου Curie (T_c) συμπεριφέρονται ως παραμαγνητικά υλικά. Το φαινόμενο αυτό ερμηνεύεται με την εξαφάνιση του αυθόρμητου παραλληλισμού των μαγνητικών ροπών των περιοχών μ με συνέπεια το μηδενισμό της αυθόρμητης μαγνήτισης μέσα σε κάθε τέτοια περιοχή.

Εξάλλου, ο αυθόρμητος παραλληλισμός των μαγνητικών ροπών των περιοχών μ ενός φερρίτη οφείλεται στη δράση του εσωτερικού μαγνητικού πεδίου, η οποία με τη σειρά της εξαρτάται από τη θερμοκρασία του υλικού. Πράγματι, όσο μεγαλώνει η θερμοκρασία του φερρίτη, τόσο αυξάνεται η θερμική κίνηση των δομικών του μονάδων, χεχονός που τείνει να αποπροσανατολίσει τις μαγνητικές ροπές από τη διάταξη, την οποία προσπαθεί να επιβάλει το εσωτερικό μαγνητικό πεδίο, με αποτέλεσμα τη μείωση της αυθόρμητης μαγνήτισης. Σε θερμοκρασίες μεγαλύτερες του σημείου Curie, επομένως, αίρεται πλήρως ο παραλληλισμός των μαγνητικών ροπών με αποτέλεσμα οι φερρίτες να μετατρέπονται σε απλά παραμαγνητικά υλικά (μηδενισμός της αυθόρμητης μαγνήτισης).

Το Σχήμα 1 παρουσιάζει τον τρόπο μεταβολής της αυθόρμητης μαγνήτισης διαφόρων φερριτών συναρτήσει της αυξημένης στο σημείο Curie θερμοκρασίας τους (T/T_c). Η συνηθισμένη τιμή μιας τέτοιας μεταβολής για τους σπινελθικούς φερρίτες είναι αυτή της καμπύλης Q του Σχήματος 1, η μορφή της οποίας ταυτίζεται με την μορφή της καμπύλης, που παρέχει την μεταβολή της αυθόρμητης μαγνήτισης των σιδηρομαγνητικών υλικών συναρτήσει της αυξημένης στο σημείο Curie θερμοκρασίας τους. Σύμφωνα με την καμπύλη αυτή, υφίσταται μηδενισμός της αυθόρμητης μαγνήτισης μ στο σημείο Curie ($T/T_c=1$), ενώ για θερμοκρασίες μικρότερες του σημείου Curie η αυθόρμητη μαγνήτιση αυξάνεται όσο μικραίνει η θερμοκρασία. Η αύξηση αυτή ολοκληρώνεται σε θερμοκρασίες πολύ κοντά



ΣΧΗΜΑ 1: Μεταβολή της αυθόρμητης μαγνήτισης φερριτών με τη θερμοκρασία.

στο απόλυτο μηδέν, γεγονός που φαίνεται και από την μηδενική κλίση της καμπύλης Q σ' αυτήν την περιοχή.

Διάταξη των μαγνητικών ροπών των μεταλλοκατιόντων στις θέσεις Α και Β του σπινελλικού πλέγματος.

Ο τρόπος διάταξης των μαγνητικών ροπών των μεταλλοκατιόντων, που καταλαμβάνουν τις Α και Β θέσεις του σπινελλικού πλέγματος, οι οποίες υπάρχουν σε μια μαγνητική περιοχή, καθορίζεται από τον τρόπο προσανατολισμού των μαγνητικών ροπών, τον οποίο τείνουν να επιβάλλουν τα εσωτερικά μαγνητικά πεδία ή, με άλλα λόγια, οι αλληλεπιδράσεις ανάμεσα στα διάφορα μαγνητικά ιόντα.

Στα τυπικά μόρια των ευθέων και αντιστρόφων φερριτών δομής σπινελλίου η θεωρητική τιμή της μαγνητικής ροπής κόρου, εκφρασμένη σε μαγνητόνια του Bohr, προκύπτει με τον τρόπο, που παρουσιάζεται στον Πίνακα 1³, δηλαδή λαμβανομένου υπόψη του αριθμού των ασυζεύκτων ηλεκτρονίων των μεταλλοκατιόντων τους. Στον ίδιο Πίνακα είναι ακόμη σημειωμένες οι αντίστοιχες για κάθε φερρίτη τιμές, που προσδιορίζονται πειραματικά, καθώς επίσης και το αντίστοιχο σημείο Curie.

Όπως διαπιστώνεται από τον Πίνακα 1, οι θεωρητικές τιμές των μαγνητικών ροπών κόρου των τυπικών μορίων των ευθέων και αντιστρόφων σπινελλικών φερριτών ταυτίζονται με τον αριθμό των ασυζεύκτων ηλεκτρονίων του μεταλλοκατιόντος M^{2+} . Προκύπτει ακόμη ότι υφίσταται, ανάλογα με το φερρίτη, μια μικρή ή μεγάλη διαφορά μεταξύ των θεωρητικών και των πειραματικών τιμών της μαγνητικής ροπής κόρου. Η διαφορά αυτή οφείλεται σε ποικίλους παράγοντες, όπως:

ΠΙΝΑΚΑΣ 1

	Φερρίτες Δομής Σπινελίου								
	Ευθείς				Αντίστροφοι				
	MnFe ₂ O ₄	ZnFe ₂ O ₄	CdFe ₂ O ₄	Fe ₃ O ₄	CoFe ₂ O ₄	NiFe ₂ O ₄	CuFe ₂ O ₄	MgFe ₂ O ₄	
T _c (°C)	300	-	-	575	520	585	455	440	
Αριθμός Αυξεκτόνων Ηλεκτρονίων	Fe ³⁺ :5	Fe ³⁺ :5	Fe ³⁺ :5	Fe ³⁺ :5, Fe ²⁺ :5	Fe ³⁺ :5, Fe ²⁺ :3	Fe ³⁺ :5	Fe ³⁺ :5	Fe ³⁺ :5	
Μαγνητική Ροπή (μ) (μ _B)	A B B'	Mn ²⁺ :5 Zn ²⁺ :0 Fe ³⁺ :5	Zn ²⁺ :0 Cd ²⁺ :0 Fe ³⁺ :5	Mn ²⁺ :5 Fe ²⁺ :4 Fe ³⁺ :5	Zn ²⁺ :0 Fe ³⁺ :5 Fe ²⁺ :4	Cd ²⁺ :0 Fe ³⁺ :5 Co ²⁺ :3	Ni ²⁺ :2 Fe ³⁺ :5 Ni ²⁺ :2	Cu ²⁺ :1 Fe ³⁺ :5 Cu ²⁺ :1	Mg ²⁺ :0 Fe ³⁺ :5 Mg ²⁺ :0
Μόρτου (θεωρ.) (μ _B)* (πειρ.)	5 4,6	0 †	0 †	4 4,1	3 3,7	2 2,3	1 1,3	0 1,1	

* Μαγνητική ροπή κόρου ανά τυπικό μόριο φερρίτη.

† Παραμαγνητικό υλικό.

α. Δεν ισχύει πάντοτε απόλυτα ότι στην κατάσταση του κόρου οι μαγνητικές ροπές είναι μεταξύ τους παράλληλες. Έτσι, είναι πιθανό το σύνολο των μαγνητικών ρομών των μεταλλοκατιόντων των θέσεων **A** να χωρίζονται σε δύο ομάδες **A'** και **A''**, η καθεμία από τις οποίες αποτελείται από παράλληλες μαγνητικές ροπές, ενώ οι ροπές της ομάδας **A'** να σχηματίζουν ορισμένη γωνία ως προς τις ροπές της ομάδας **A''**. Η διάκριση αυτή των μαγνητικών ρομών σε δύο ομάδες είναι πιθανό να ισχύει (και) για τις μαγνητικές ροπές των δύο υποπλέγματων των θέσεων **B**.

β. Οι σπινελιτικοί φερρίτες γενικά δεν είναι ιδανικά ευθείς ή αντίστροφοι αλλά μάλλον μικτοί. Σ' αυτές τις περιπτώσεις έχει θεωρηθεί ότι ο συντελεστής x του τύπου των μικτών φερριτών είναι πρακτικά ίσος με 1 ή με 0 αντίστοιχα, υπόθεση περιέχουσα οπωσδήποτε κάποιο σφάλμα.

Μικτοί κρυσταλλικοί φερριτών δομής σπινελίου.

Τρόποι δημιουργίας μικτών κρυστάλλινων. Στην περίπτωση των σπινελιτικών φερριτών είναι δυνατό να παρασκευασθούν μικτοί κρυσταλλικοί, δηλαδή στερεά διαλύματά τους, κατά τους ακόλουθους τρόπους:

α. *Με απλή υποκατάσταση.* Συνίσταται στην υποκατάσταση μερικών μεταλλοκατιόντων του κρυσταλλικού πλέγματος των φερριτών από άλλα μεταλλοκατιόντα με τον ίδιο αριθμό οξειδωσης με τα υποκαθιστώμενα. Απλή

υποκατάσταση είναι δυνατό να συμβεί τόσο για τα ιόντα M^{2+} , όσο και για τα ιόντα Fe^{3+} των φερριτών. Σχετικό παράδειγμα αποτελεί η υποκατάσταση των ιόντων Fe^{3+} από Cr^{3+} ή Al^{3+} .

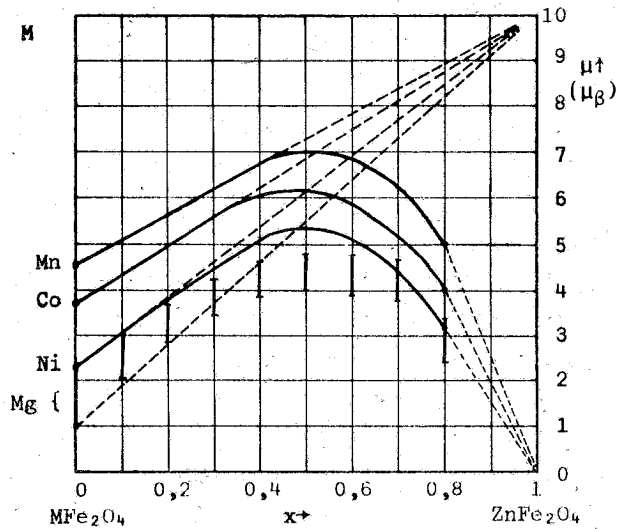
β. Με διπλή υποκατάσταση. Μερικά όμοια μεταξύ τους μεταλλοκατιόντα του πλέγματος των φερριτών υποκαθίστανται από ίσο αριθμό άλλων μεταλλοκατιόντων διαφορετικού αριθμού οξειδωσης και φύσης, τόσο σε σχέση με τα υποκαθιστώμενα όσο και μεταξύ τους. Π.χ. διπλή υποκατάσταση υφίσταται, όταν δύο ιόντα Fe^{2+} του *μαγνητίτη* ($Fe^{2+}Fe_2^{3+}O_4$) υποκαθίστανται από ένα ιόν Fe^{3+} και ένα ιόν M^+ ή ακόμη όταν δύο ιόντα Fe^{3+} υποκαθίστανται από ένα ιόν Fe^{2+} και ένα ιόν M^{4+} .

γ. Με δημιουργία κενών πλέγματικών θέσεων. Στις δύο προηγούμενες περιπτώσεις στο κρυσταλλικό πλέγμα των φερριτών τη θέση του υποκαθιστώμενου ιόντος πήρε το ιόν, που τό υποκατέστησε. Είναι δυνατό, όμως, κατά τις υποκαταστάσεις των ιόντων να παραμένουν και κενές θέσεις στο πλέγμα του φερρίτη.

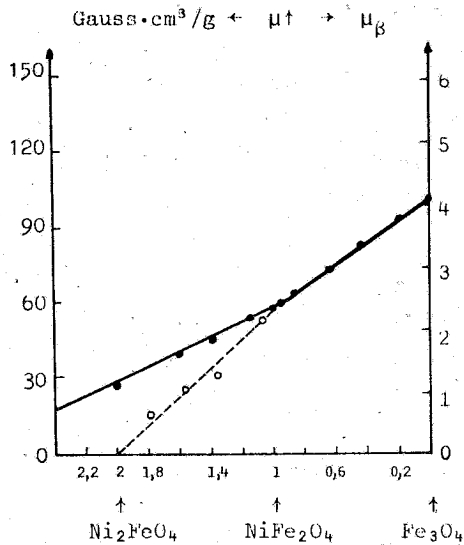
Συνέπειες της δημιουργίας μικτών κρυστάλλινων στις μαγνητικές ιδιότητες των φερριτών. Η δημιουργία μικτών κρυστάλλινων στους σπινελλικούς φερρίτες είναι δυνατό να οδηγήσει σε διαφορετική μαγνητική συμπεριφορά τους, επειδή το νέο μεταλλοκατιόν, το εισαχόμενο στο κρυσταλλικό τους πλέγμα, πιθανόν να προτιμά διαφορετικού είδους θέση απ' αυτήν, την οποία είχε καταλάβει το υποκαθιστώμενο ιόν.

Στο Σχήμα 2^β φαίνονται οι μεταβολές της μαγνητικής ροής κόρου για τους σπινελλικούς φερρίτες μαγνανίου, κοβαλτίου και νικελίου, όταν λαμβάνει χώρα υποκατάσταση αυτών των μετάλλων από ψευδάργυρο. Όπως διαπιστώνεται, η μαγνητική ροπή κόρου αυξάνεται, περίπου μέχρις ότου γίνει: $x = 0,4$ για όλους τους φερρίτες, και στη συνέχεια μειώνεται για να αποκτήσει τελικά την μηδενική τιμή την χαρακτηριστική για τον φερρίτη ψευδαργύρου.

Ένα άλλο χαρακτηριστικό παράδειγμα είναι η περίπτωση των πλουσίων σε νικέλιο σπινελλικών φερριτών, δηλαδή σ' εκείνους τους οποίους έχει πραγματοποιηθεί μερική υποκατάσταση ιόντων Fe^{3+} από Ni^{3+} . Στο Σχήμα 3^β φαίνεται η μεταβολή της μαγνητικής ροής ως συνάρτησης της περιεκτικότητας του φερρίτη σε νικέλιο. Το διακεκομμένο τμήμα της καμπύλης αντιστοιχεί στις θεωρητικές τιμές της μαγνητικής ροής, όπως αυτές υπολογίζονται με βάση την κατανομή: $Fe^{3+}[Ni^{2+}Ni^{3+}]O_4$ και ταυτίζεται απόλυτα με τις πειραματικές τιμές, οι οποίες έχουν προσδιορισθεί σε δείγματα, που παρασκευάστηκαν σε υψηλές πιέσεις O_2 . Η συνεχής



ΣΧΗΜΑ 2: Μεταβολή της μαγνητικής ροπής κόρου με τη σύσταση των συνθετικών σπινελιτικών φερριτών.



ΣΧΗΜΑ 3: Μεταβολή της μαγνητικής ροπής κόρου στους φερρίτες νικελίου.

γραμμή αντιστοιχεί σε δείγματα, τα οποία παρασκευάστηκαν στον αέρα υπό ατμοσφαιρική πίεση και σε υψηλές θερμοκρασίες. Επειδή, όμως, κάτω από τέτοιες συνθήκες αυτό που συμβαίνει στην πραγματικότητα είναι α-

πλήως αραίωση του NiFe_2O_4 με παραμαγνητικό NiO , μετρήθηκαν σαφώς μεγαλύτερες τιμές μαγνητικής ροπής κόρου (που αντιστοιχούν δηλαδή σε μίγματα NiFe_2O_4 και NiO). Επιβεβαιώνεται ακόμη και το γεγονός ότι τα ιόντα Ni^{3+} προτιμούν να τοποθετούνται στις οκταεδρικές θέσεις (B) του σπινελλικού πλέγματος.

Η δημιουργία επομένως των μικτών κρυστάλλινων φαίνεται να έχει σε πολλές περιπτώσεις ευνοϊκή επίδραση στη διαμόρφωση των μαγνητικών ιδιοτήτων ενός σπινελλικού φερρίτη. Πράγματι, καθώς π.χ. η προσθήκη ψευδαργύρου έχει ως αποτέλεσμα την ταπείνωση του σημείου Curie των αντιστρόφων φερριτών, η μαγνητική επιδεκτικότητά τους στη συνήθη θερμοκρασία εμφανίζεται να είναι αρκετά μεγάλη, γεγονός πολύ σημαντικό για ορισμένες εφαρμογές.

ΗΛΕΚΤΡΙΚΕΣ ΙΔΙΟΤΗΤΕΣ

Γενικό

Όπως ήδη έχει αναφερθεί, ένα από τα σημαντικότερα γνωρίσματα των φερριτών είναι το γεγονός ότι, ενώ οι περισσότεροι απ' αυτούς έχουν πολύ μεγάλες τιμές μαγνητικής επιδεκτικότητας, συγκρίσιμες μ' αυτές των σιδηρομαγνητικών μετάλλων, παρουσιάζουν σε σύγκριση με τα τελευταία σαφώς μικρότερη ηλεκτρική αγωγιμότητα. Πράγματι, όλοι σχεδόν οι φερρίτες χαρακτηρίζονται από ημιαγωγικές ιδιότητες και συγκεκριμένα διακρίνονται σε ημιαγωγούς τύπου **n** και τύπου **p**.

Ο μηχανισμός της ηλεκτρικής αγωγιμότητας στους σπινελλικούς φερρίτες.

Ο μηχανισμός, σύμφωνα με τον οποίο οι φερρίτες και γενικότερα τα οξειδία των στοιχείων μετάπτωσης άχουν το ηλεκτρικό ρεύμα, αναπτύχθηκε κατά βάση από τον Verwey και τους συνεργάτες του⁶⁻⁸ και έγινε αποδεκτός από άλλους ερευνητές⁹⁻¹⁴. Έτσι, θεωρείται ότι η ηλεκτρική αγωγιμότητα αυτών των ενώσεων οφείλεται στην ανταλλαγή ηλεκτρονίων μεταξύ μεταλλοκατιόντων με διαφορετικούς αριθμούς οξειδωσης.

Ένα χαρακτηριστικό παράδειγμα αυτού του μηχανισμού ηλεκτρικής αγωγιμότητας αποτελεί το οξείδιο του νικελίου (NiO). Αν υποθεθεί ότι πρόκειται για τελείως καθαρό από χημικής άποψης και απόλυτα στοιχειομετρικό NiO , τότε όλα τα άτομα του νικελίου θα βρίσκονται στη δεύτερη οξειδωτική βαθμίδα, δηλαδή με τη μορφή των ιόντων Ni^{2+} . Στην περίπτωση αυτή θα ήταν θεωρητικά δυνατή η εκδήλωση μιας πολύ ασθενούς ηλεκτρικής αγωγιμότητας (ευδογενούς ημιαγωγιμότητας), οφειλομένης σε ένα είδος διεγερμένης κατάστασης ιόντων Ni^{2+} , η οποία συνίσταται σε ευδε-

χόμενη μετατροπή δύο ιόντων Ni^{2+} σε ένα ιόν Ni^+ και σε ένα ιόν Ni^{3+} . Όμως, όπως είναι άδηλωστε αναμενόμενο, το ηλεκτρικό ρεύμα, το οφειλόμενο σ' αυτόν τον μηχανισμό, θα είναι εξαιρετικά ασθενές, γιατί, πράγματι, το χημικά καθαρό και απόλυτα στοιχειομετρικό NiO χαρακτηρίζεται από ειδική ηλεκτρική αγωγιμότητα της τάξης των $10^{-8} (\Omega \cdot cm)^{-1}$. Αν, ωστόσο, οι συνθήκες παρασκευής του NiO είναι τέτοιες, ώστε να έχουν επιτρέψει την εισαγωγή κάποιας ποσότητας οξυγόνου στο κρυσταλλικό του πλέγμα, γεγονός που ισοδυναμεί με τη δημιουργία κενών πλεγματικών θέσεων μεταλλοκατιόντων, η ειδική ηλεκτρική αγωγιμότητα εμφανίζεται να είναι σαφώς μεγαλύτερη. Πράγματι στην περιοχή κάθε ιόντος Ni^{2+} , που απουσιάζει από κάποια πλεγματική θέση, δημιουργούνται για λόγους ηλεκτροδευτερότητας δύο ιόντα Ni^{3+} . Δεδομένου, όμως, ότι η δεύτερη οξειδωτική βαθμίδα για το νικέλιο είναι πολύ πιο σταθερή από την τρίτη, τα ιόντα Ni^{3+} εμφανίζουν έντονη την τάση να προσλάβουν ένα ηλεκτρόνιο και να μετατραπούν σε ιόντα Ni^{2+} . Αν, λοιπόν, παρασχεθεί η απαιτούμενη ενέργεια (*ενέργεια ενεργοποίησης ημιαγωγιμότητας*), είναι δυνατό κάποιο ηλεκτρόνιο από ένα γειτονικό ιόν Ni^{2+} να μεταπηδήσει στο ιόν Ni^{3+} , μετατρέποντάς το σε Ni^{2+} , ενώ το πρώτο γίνεται Ni^{3+} . Η διαδικασία αυτή αντιστοιχεί στην μετακίνηση μιας *σηής* ανάμεσα στα ιόντα Ni^{2+} . Με άλλα λόγια, κάθε ιόν Ni^{3+} είναι δυνατό να θεωρηθεί ως ιόν Ni^{2+} , που φέρει μια *σηή* (Ni^{2+*}). Έτσι, πραγματοποιείται άτακτη κίνηση θετικών *σηών* και το υλικό συμπεριφέρεται ως ημιαγωγός τύπου p (*μηχανισμός ημιαγωγιμότητας $Ni^{3+} - Ni^{2+}$*).

Μπορεί γενικά να θεωρηθεί ότι τα οξειδία και ειδικότερα οι φερρίτες, που εμφανίζουν στο κρυσταλλικό πλέγμα τους κενές πλεγματικές θέσεις μεταλλοκατιόντων (*σπάζεις Schottky*), χαρακτηρίζονται δηλαδή από περίσσεια οξυγόνου, έχουν την τάση να συμπεριφέρονται ως ημιαγωγοί τύπου p. Αντίθετα, έλλειμμα οξυγόνου στο κρυσταλλικό πλέγμα του φερρίτη, δηλαδή ύπαρξη κενών πλεγματικών θέσεων ανιόντων ή τοποθέτηση μεταλλοκατιόντων σε διαπλεγματικές θέσεις, συνεπάγεται εκδήλωση ημιαγωγιμότητας τύπου n. Πράγματι, η απουσία ανιόντων O^{2-} συνεπάγεται την ύπαρξη ελευθέρων ηλεκτρονίων, προκειμένου να διατηρηθεί η ηλεκτροδευτερότητα του κρυστάλλου.

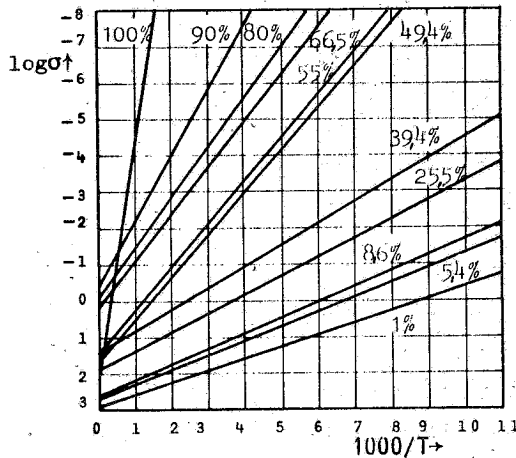
Από όλους τους φερρίτες τις μεγαλύτερες ηλεκτρικές αγωγιμότητες εμφανίζουν οι φερρίτες σιδήρου, δηλαδή οι διάφοροι *μαγνητίτες*, οι οποίοι είναι δυνατό να παρασκευασθούν με κατάλληλες συνθήκες πύρωσης και διαφέρουν μεταξύ τους ως προς το περιεχόμενό τους σε οξυγόνο. Αν-

τό εξηχείται αρκετά απλά σύμφωνα με το πρότυπο, που διατυπώθηκε από του Verwey: Ο *μαγνητίτης* είναι ένας αντίστροφος σπινελλικός φερρίτης ($\text{Fe}^{3+}[\text{Fe}^{2+}\text{Fe}^{3+}]_0_4$), στις Β θέσεις του οποίου υπάρχει ίσος αριθμός ιόντων Fe^{2+} και Fe^{3+} . Όμως, αντίθετα με ό,τι συμβαίνει στο νικέλιο, που περιγράφηκε παραπάνω, η τρίτη οξειδωτική βαθμίδα για τον σίδηρο (Fe^{3+}) είναι σταθερότερη από τη δεύτερη (Fe^{2+}). Έτσι, το επιπλέον ηλεκτρόνιο των ιόντων Fe^{2+} είναι χαλαρότερα συνδεδεμένο. Ακόμη, δεδομένου ότι οι αποστάσεις ανάμεσα στα μεταλλοκατιόντα των οκταεδρικών θέσεων είναι αρκετά μικρές, είναι επιτρεπτή, χωρίς μεγάλες απαιτήσεις σε ενέργεια, η απόσπαση ηλεκτρονίων από τα ιόντα Fe^{2+} , τα οποία περιπλανούνται μέσα στον κρύσταλλο (στο πλέγμα των ιόντων Fe^{3+}) και είναι επομένως ηλεκτρόνια αγωγιμότητας (*μηχανισμός ημιαγωγιμότητας* $\text{Fe}^{2+}-\text{Fe}^{3+}$). Με άλλα λόγια, θα μπορούσε να υποθεθεί ότι στις οκταεδρικές θέσεις του στοιχειομετρικού *μαγνητίτη* υφίσταται πλέγμα μεταλλοκατιόντων Fe^{3+} , ανάμεσα στα οποία κινούνται ελεύθερα ηλεκτρόνια. Έτσι, ο στοιχειομετρικός *μαγνητίτης* είναι ημιαγωγός τύπου n, χαρακτηριζόμενος από πολύ υψηλές τιμές, σε σύγκριση με τους άηθους φερρίτες, ηλεκτρικής αγωγιμότητας (περίπου $200 \Omega \cdot \text{cm}^{-1}$).

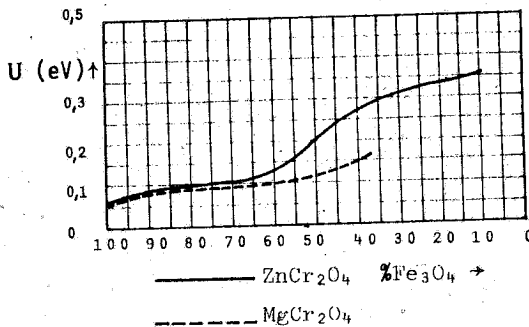
Από τους *μαγνητίτες* με διαφορετικές περιεκτικότητες σε οξυγόνο, την μεγαλύτερη ηλεκτρική αγωγιμότητα εμφανίζει ο στοιχειομετρικός *μαγνητίτης*, ενώ στους μη στοιχειομετρικούς (που περιέχουν περισσότερο οξυγόνο και άρα περιλαμβάνουν κενές θέσεις μεταλλοκατιόντων στο κρυσταλλικό τους πλέγμα), αντίθετα με ό,τι συμβαίνει στο NiO , όσο μεγαλύτερος είναι ο αριθμός των σημειακών αταξιών στο κρυσταλλικό πλέγμα τους, τόσο μικρότερη είναι η ηλεκτρική αγωγιμότητά τους, ενώ αυξάνεται η αντίστοιχη ενέργεια ενεργοποίησης. Πράγματι, η δημιουργία περισσειας ανιόντων O^{2-} συνεπάγεται παχίδευση ελευθέρων ηλεκτρονίων σε ορισμένα σημεία του κρυσταλλικού πλέγματος ή με άλλα λόγια οι κενές πλεγματικές θέσεις επέχουν θέση ηλεκτρωνητικά φορτισμένων κέντρων (*χρωματικών κέντρων*), τα οποία τείνουν να περιβάλλονται οπωσδήποτε από ιόντα Fe^{3+} , γεγονός που διαταράσσει την τυχαία κατανομή των ελευθέρων ηλεκτρονίων γύρω από τα οκταεδρικά μεταλλοκατιόντα. Ακόμη, σε χαμηλές θερμοκρασίες (κάτω από τους -154°C), οπότε πραγματοποιείται "διάταξη" των μεταλλοκατιόντων του *μαγνητίτη* ^{2,3}, η οποία οδηγεί σε ορθορομβική παραμόρφωση του κρυσταλλικού του πλέγματος, παρατηρείται δραστική μείωση της ηλεκτρικής αγωγιμότητας του φερρίτη. Το γεγονός αυτό αποδίδεται ακριβώς στην ομοιόμορφη διάταξη των μεταλλοκατιόντων

του φερρίτη κατά την έννοια $Fe^{2+}-Fe^{3+}$, η οποία περιορίζει σημαντικά την κίνηση (μεταπήδηση) των ηλεκτρονίων από το ένα ιόν στο άλλο.

Οι μικτοί φερρίτες, εξάλλου, χαρακτηρίζονται από μικρότερες ηλεκτρικές αγωγιμότητες σε σύγκριση μ' αυτήν του *μαγνητίτη*. Αυτό οφείλεται στο γεγονός ότι η παρεμβολή ξένων μεταλλοκατιόντων στις Β θέσεις του σπινελλικού πλέγματος, τα οποία συνήθως δεν έχουν την ευχέρεια του σιδήρου εύκολης μεταπήδησης από την δεύτερη στην τρίτη οξειδωτική βαθμίδα και αντίστροφα, προκαλεί αρραίωση - ανάσχεση συνήθως με το πλήθος τους - των ιόντων του σιδήρου και δυσχεραίνει την κίνησή των η-



ΣΧΗΜΑ 4: Μεταβολή της ειδικής ηλεκτρικής αγωγιμότητας στερεών διαλυμάτων $MgCr_2O_4-Fe_3O_4$ με τη θερμοκρασία.



ΣΧΗΜΑ 5: Μεταβολή της ενέργειας ενεργοποίησης ηλεκτρικής αγωγιμότητας ως προς τη σύσταση των συστημάτων $MgCr_2O_4-Fe_3O_4$ και $ZnCr_2O_4-Fe_3O_4$.

ηλεκτρονίου. Τα φαινόμενα αυτά συνεπάγονται αισθητή μείωση της ηλεκτρικής αγωγιμότητας του υλικού. Ας εξετασθούν π.χ. τα στερεά διαλύματα του σπινελλίτου: $MgCr_2O_4$ σε μαγνητίτη: Fe_3O_4 . Εδώ σημειώνεται ότι ο $MgCr_2O_4$ χαρακτηρίζεται από πολύ μικρή ηλεκτρική αγωγιμότητα [μικρότερη από $10^{-10} (\Omega \cdot cm)^{-1}$], που τόν τοποθετεί στην κατηγορία των μονωτών. Στο Σχήμα 4^B παρέχεται η μεταβολή του δεκαδικού λογαρίθμου της ειδικής ηλεκτρικής αγωγιμότητας ($\log \sigma$) ως προς το αντίστροφο της απόλυτης θερμοκρασίας ($1/T$) στερεών διαλυμάτων $MgCr_2O_4-Fe_3O_4$ για διάφορες περιεκτικότητες του πρώτου μεταξύ 1% και 100%. Διαπιστώνεται ότι η μεταβολή αυτή έχει τη μορφή ευθείας δεδομένου ότι ακολουθείται, όπως θα αναπτυχθεί παρακάτω, κάποιος εκθετικός νόμος. Η ειδική ηλεκτρική αγωγιμότητα μειώνεται θεαματικά σε κάθε θερμοκρασία με την αύξηση της περιεκτικότητας σε $MgCr_2O_4$, ενώ η κλίση των αντιστοιχών ευθειών γίνεται συνεχώς μεγαλύτερη.

Στο Σχήμα 5^B, εξάλλου, απεικονίζεται η μεταβολή της ενέργειας ενεργοποίησης (E) ως συνάρτηση της περιεκτικότητας σε Fe_3O_4 . Διαπιστώνεται ότι στην περιοχή του 50% πραγματοποιείται απότομη αύξησή της, δηλαδή ο μηχανισμός της αγωγιμότητας γίνεται δυσκολότερος. Πράγματι, τα νέα μεταλλοκατιόντα (Mg^{2+} και Cr^{3+}), όταν εισάγονται στο πλέγμα του μαγνητίτη, προτιμούν να τοποθετηθούν (ιδιαίτερα τα μεταλλοκατιόντα Cr^{3+}) στις Β θέσεις του σπινελλικού πλέγματος.

Όπως προκύπτει και από τον Πίνακα 11^B, για περιεκτικότητες σε Fe_3O_4 μεγαλύτερες από 50%, υφίστανται πάντοτε μεταλλοκατιόντα Fe^{3+} και Fe^{2+} στις Β θέσεις του σπινελλικού πλέγματος. Έτσι, η ηλεκτρική αγωγιμότητα εκδηλώνεται καταμήκος κρυσταλλικών επιπέδων, τα οποία περιέχουν και τα δύο αυτά είδη μεταλλοκατιόντων, με τη διαφορά ότι αυτή μειώνεται κατά τρόπο ομαλό, όσο τα ιόντα του σιδήρου αραιώνονται από τα ιόντα Cr^{3+} και Mg^{2+} , που έχουν την τάση να τοποθετούνται στις Β θέσεις. Στην περιεκτικότητα, όμως, των 50% σε Fe_3O_4 η προτίμηση των μεταλλοκατιόντων Fe^{3+} , των οποίων το πλήθος έχει περιοριστεί στο μισό, για τις Α θέσεις, οδηγεί σε πλήρη διαχωρισμό τους από τα μεταλλοκατιόντα Fe^{2+} . Αυτό συνεπάγεται απότομη μείωση της ηλεκτρικής αγωγιμότητας, η οποία εκδηλώνεται με αντιστοιχη αύξηση της ενέργειας ενεργοποίησης. Έτσι, για περιεκτικότητες σε Fe_3O_4 μικρότερες από 50% ο μηχανισμός της ηλεκτρικής αγωγιμότητας γίνεται σημαντικά δυσκολότερος. Αυτή τώρα εκδηλώνεται με ανταλλαγή ηλεκτρονίων ανάμεσα σε μεταλλοκατιόντα Fe^{3+} και Fe^{2+} , που βρίσκονται είτε και τα δύο στις Α θέ-

ΠΙΝΑΚΑΣ II

% Fe ₃ O ₄	θέσεις Α		θέσεις Β	
100	Fe ³⁺		Fe ³⁺ ,	Fe ²⁺
75	Fe ³⁺		1/2Fe ³⁺ ,	1/2Cr ³⁺ , 3/4Fe ²⁺ , 1/4Mg ²⁺
50	Fe ³⁺		Cr ³⁺ , 1/2Fe ²⁺ , 1/2Mg ²⁺	
25	1/2Fe ³⁺ ,	1/2Mg ²⁺	3/2Cr ³⁺ ,	1/4Fe ²⁺ , 1/4Mg ²⁺
25	1/2Fe ³⁺ ,	1/4Fe ²⁺ , 1/4Mg ²⁺	3/2Cr ³⁺ ,	1/2Mg ²⁺
0	Mg ²⁺		2Cr ³⁺	

ΠΙΝΑΚΑΣ III

% Fe ₃ O ₄	θέσεις Α		θέσεις Β	
100	Fe ³⁺		Fe ³⁺ ,	Fe ²⁺
75	3/4Fe ³⁺ ,	1/4Zn ²⁺	3/4Fe ³⁺ ,	1/2Cr ³⁺ , 3/4Fe ²⁺
50	1/2Fe ³⁺ ,	1/2Zn ²⁺	1/2Fe ³⁺ ,	Cr ³⁺ , 1/2Fe ²⁺
25	1/4Fe ³⁺ ,	3/4Zn ²⁺	1/4Fe ³⁺ ,	3/2Cr ³⁺ , 1/4Fe ³⁺ ,
0	Fe ³⁺		2Cr ³⁺	

σεις είτε σε διαφορετικά είδη θέσεων του σπινελλικού πλέγματος. Και οι δύο αυτοί μηχανισμοί είναι αρκετά δύσκοιλοι και περικλείουν αυξημένη ενέργεια ενεργοποίησης: Ο πρώτος, γιατί οι αποστάσεις ανάμεσα στα μεταλλοκατιόντα των θέσεων Α είναι σημαντικά μεγαλύτερες, και ο δεύτερος, γιατί υπάρχει σημαντική διαφορά ανάμεσα στις ενεργειακές στάθμες, που αντιστοιχούν στις Α και στις Β θέσεις.

Αντίθετα, αν χρησιμοποιηθεί αντί του μαγνησίου ψευδάργυρος, αν πρόκειται δηλαδή για στερεά διαλύματα Fe₃O₄ και ZnCr₂O₄, επειδή τα μεταλλοκατιόντα Zn²⁺ προτιμούν τις Α θέσεις και τα μεταλλοκατιόντα Cr³⁺ τις Β θέσεις, υφίστανται, όπως προκύπτει και από τον Πίνακα III⁸, πάντοτε μεταλλοκατιόντα Fe³⁺ και Fe²⁺ στις Β θέσεις, γεγονός που συνεπάγεται συνεχώς ομαλή αύξηση της ενέργειας ενεργοποίησης (Σχήμα 5) με την μείωση της περιεκτικότητας σε Fe₃O₄.

Η μεταβολή της ηλεκτρικής αγωγιμότητας των σπινελλικών φερριτών ως προς το χρόνο.

Έχει διαπιστωθεί ότι οι συνθήκες, που επιλέχονται κατά την παρασκευαστική διαδικασία των φερριτών, παίζει αποφασιστικό ρόλο στη διαμόρφωση των ηλεκτρικών τους ιδιοτήτων' σ' αυτές περιλαμβάνεται και ο ρυθμός, με τον οποίο πραγματοποιείται η ψύξη μετά την πύρωση των φερριτών. Πράγματι, η ηλεκτρική αγωγιμότητα ενός σπινελλικού φερρίτη είναι διαφορετική, αν η ψύξη πραγματοποιήθηκε απότομα ή με βραδύ ρυθμό. Έτσι, διαπιστώθηκε¹² ότι π.χ. φερρίτης νικελίου, ο οποίος πυρώθηκε στον αέρα στους 1250°C εμφανίζει ειδική ηλεκτρική αγωγιμότητα ίση προς $2,8 \cdot 10^{-7} (\Omega \cdot \text{cm})^{-1}$, όταν ψύχεται αρχά, και $7,75 \cdot 10^{-4} (\Omega \cdot \text{cm})^{-1}$, όταν ψύχεται απότομα. Χαρακτηριστική είναι η διαφορά ανάμεσα στις δύο αυτές τιμές. Το απόλυτο μέγεθός τους δεν έχει και πολύ μεγάλη σημασία, αφού καθορίζεται από τις συνθήκες πύρωσης, οι οποίες ακολουθήθηκαν από τους συγκεκριμένους ερευνητές. Η διαφορά αυτή οφείλεται στο γεγονός ότι με την απότομη ψύξη διατηρείται η δομή, που υφίστατο στην υψηλή θερμοκρασία, ενώ με την αρχή ψύξη δίνεται στο υλικό το χρονικό περιθώριο να πραγματοποιήσει κάποια ανακατανομή των μεταλλοκατιόντων του ανάμεσα στις **A** και **B** θέσεις του σπινελλικού πλέγματος.

Ενδιαφέρον είναι επίσης και το γεγονός ότι η ηλεκτρική αγωγιμότητα των φερριτών μεταβάλλεται με την πάροδο του χρόνου ακόμη και στη συνήθη θερμοκρασία¹⁵⁻¹⁷. Διαπιστώθηκε ότι σε ορισμένους απ' αυτούς η αγωγιμότητα αυξάνεται με την πάροδο του χρόνου (MgFe_2O_4 , NiFe_2O_4), ενώ σε άλλους μειώνεται (MnFe_2O_4 , CuFe_2O_4 , CoFe_2O_4). Το φαινόμενο αυτό είναι περισσότερο έντονο σε θερμοκρασίες μεγαλύτερες της συνήθους.

Το παραπάνω φαινόμενο της μεταβολής με το χρόνο της ηλεκτρικής αγωγιμότητας των φερριτών δεν είναι δυνατό να αποδοθεί σε κάποια ενδεχόμενη βαθμιαία συστελούμενη οξείδωση μεταλλοκατιόντων Fe^{2+} προς Fe^{3+} . Στην απόρριψη μιας τέτοιας εξήγησης συνηγορεί και το γεγονός ότι η ηλεκτρική αγωγιμότητα σε άλλους φερρίτες αυξάνεται και σε άλλους μειώνεται με την πάροδο του χρόνου' πράγματι, αν συνέβαινε κάτι τέτοιο, θα έπρεπε σε όλους τους φερρίτες ανεξαιρέτως η ηλεκτρική τους αγωγιμότητα να μειώνεται. Το φαινόμενο αυτό αποδίδεται στο γεγονός ότι κατά την μακροχρόνια παραμονή του φερρίτη πραγματοποιείται προοδευτική ανακατανομή των μεταλλοκατιόντων του στις **A** και **B** θέσεις του σπινελλικού πλέγματος.

ΚΑΤΑΛΥΤΙΚΕΣ ΙΔΙΟΤΗΤΕΣ

Οι φερρίτες, κυρίως λόγω των ημισαγωγικών τους ιδιοτήτων, βρίσκουν σημαντική εφαρμογή ως καταλύτες τόσο στην Ανόργανη, όσο και στην Οργανική Χημεία, και χρησιμοποιούνται για το σκοπό αυτό σε μεγάλη έκταση στη Βιομηχανία¹.

Η κυριότερη εφαρμογή στην Οργανική Χημεία αναφέρεται στην πραγματοποίηση *αφυδραγονώσεων* με σκοπό τη σύνθεση ακορέστων (ή περισσότερο ακορέστων) οργανικών μορίων. Έτσι, είναι π.χ. γνωστή η μετατροπή του *προπιονιτρίλιου* σε *ακρυλονιτρίλιο* παρουσία φερριτικής νικελίου, τοποθετημένου σε υπόστρωμα από αλουμίνα, της *προπανόλης* σε *ακρολεΐνη*, του *κυκλοεξανίου* σε *βενζόλιο*, του *χλωροαιθανίου* σε *βινυλοχλωρίδιο*, του *αιθυλοβενζολίου* σε *στυρόλιο* κ.ά. Αναφέρονται ακόμη η μετατροπή του *βουτανίου* σε *1-βουτένιο* κι αυτού στη συνέχεια σε *1,3-βουταδιένιο*, του *2-μέθυλο-2-βουτενίου* σε *ισοπρένιο* καθώς και άλλες παρόμοιες αντιδράσεις παρουσία φερριτών Co, Ni, Mg, Zn, Cd, Ba, Sr κ.ά.

Οι φερρίτες καταλύουν ακόμη και άλλες οργανικές αντιδράσεις, όπως είναι η *βενζιδινική μετάθεση*, η *διάσπαση* ή η *οξειδωση* του *μυρμηκικού οξέος*, *αφυδραγονώσεις* και *αφυδατώσεις αλκοολών*, *οξειδώσεις υδραξονουθράκων* και *αλκοολών*, *υδροπύσεις εστερών*, *αλκυλίωσεις* και *ακυλίωσεις Friedel-Crafts*, *αντιδράσεις πολυμερισμού*, κ.ά.

Οι φερρίτες χρησιμοποιούνται ακόμη και σε εφαρμογές της Οργανικής Τεχνολογίας, όπως είναι η *υδραγονωτική αποξείωση των ορυκτελαίων*, η *αποξείωση φυσικών αερίων*, *βιομηχανικών αερίων* και *αερίων πάλης* καθώς και *αερίων βιομηχανικών αποβλήτων*, η *αύχυνση* και η *δέσμευση* ή η *διάσπαση προσμίξεων κυρίως οργανικής φύσης (υδραξονουθράκων, αλκοολών, καρβοξυλικών οξέων, αμινών, καρβονυλικών ενώσεων κ.ά.)*, αλλά και *υδραξόνου* και *μονοξειδίου του άνθρακα*, η *εξασπίωση κηραμάτων του πετρελαίου* κ.ά.

Οι φερρίτες βρίσκουν ακόμη σημαντική εφαρμογή στην Πυρηνική Χημεία για την κατάλυση αντιδράσεων *ισοτοπικών ανταλλαγών*, όπως π.χ. ^{12}C μεταξύ CO και CO₂, ^1H και ^2H μεταξύ H₂ και D₂ καθώς και σε βουτυλένια και ^{16}O και ^{18}O σε οξυγονούχες ενώσεις.

Στην Ανόργανη Χημεία και στην Ανόργανη Χημική Τεχνολογία οι φερρίτες μελετήθηκαν ως καταλύτες για τη *σύνθεση της αμμωνίας*, την *οξειδωτική* του CO σε CO₂ και για τη *διάσπαση των οξειδίων του αζώτου*. Έτσι, μπορούν να χρησιμοποιηθούν για τον *καθαρισμό αερίων αποβλήτων* ή *καυσιγέριων*, προερχομένων από τις εξατμίσεις αυτοκινήτων, τα οποία

περιέχουν οξειδία του αζώτου, μονοξείδιο του άνθρακα αλλά και άκαυστους υδρογονάνθρακες. Από φερρίτες καταλύονται και *διασπάσεις ανόργανων ενώσεων*, όπως είναι το *υπεροξείδιο του υδρογόνου*, τα *ανθρακικά*, τα *χλωρικά* και τα *υπερχλωρικά αλάτια*.

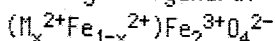
Οι φερρίτες, τέλος, χαρακτηρίζονται και από αξιόλοχες *ροφητικές ικανότητες* στην επιφάνειά τους τόσο αερίων, όσο και ιόντων από υδατικά διαλύματα. Το φαινόμενο αυτό έχει ήδη αρχίσει να αξιοποιείται για τον καθαρισμό βιομηχανικών αποβλήτων από βαρέα μέταλλα.

SUMMARY

Effect of the Structure and the Preparation Procedure of Spinel Ferrites on Their Chemical and Physical Properties. II. Magnetic, Electrical and Catalytic Properties of Spinel Ferrites.

Z. Loizos, N. Spyrellis & P. Sakellariadis

The spinel ferrites are mixed oxides of iron oxide and a metal (M) oxide and may be described by the general formula:



where the value of x may range between 0 and 1 and crystallize in the system with an analogous structure to the mineral spinel ($MgAl_2O_4$).

The spinel ferrites have interesting magnetic and electrical properties. They belong to the category of ferrimagnetic materials and as a consequence they exhibit high magnetic susceptibility values, which actually depend on the distribution of the magnetic metal cations on the tetrahedral (A) and octahedral (B) sites of the spinel crystal lattice.

As far as the electrical properties are concerned, the spinel ferrites exhibit higher values in electrical conductivity with respect to other ionic structured solids, which increase with the increase of the temperature. Thus the spinel ferrites depending on their preparation conditions behave as n- or p- type semiconductors.

As a result of their semiconductivity properties, the spinel ferrites exhibit a considerable catalytic activity for a large number of Inorganic and Organic Chemistry reactions. They also have important absorption properties.

Key words: Ferrites, spinels, nickel-iron oxides, trevorite.

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