One might suggest a resonance phenomenon as the reason for this unexpected situation. It is felt that this is ruled out by the regularities observed in the second and third differences in Table III. Even a small resonance interaction would introduce serious irregularities. It is possible that $2\nu_1$ may be displaced due to some local resonance interaction, but the other resonating level is not obvious. If the transition involving the other level is normally too weak to be seen, one would expect it to borrow intensity enough from $2\nu_1$ to be seen, for $2\nu_1$ is a rather strong band.

Using levels in which no normal mode is excited by more than one quantum of energy, it is possible to evaluate, in several ways, what appear to be constants in a quadratic energy expression. In the light of the information in Table III this is fortuitous. Since no level was excited by $v > 1$, the resulting constants are probably combinations of X_{ij}'s and Y_{ijk}'s. Constants which can be evaluated in this way are given in Table IV where the designation used is that appropriate to a quadratic equation.

A final piece of information which can be deduced is the band center of ν_4^1. This can be determined three different ways: ν_3 and $\nu_3 - \nu_4^0$, $\nu_2 + \nu_3 + \nu_4^1$ and $\nu_2 + \nu_3 + \nu_4^1 - \nu_4^1$, and $\nu_3 + \nu_4^1$ and $\nu_3 + \nu_4^1 - \nu_4$. The values obtained for ν_4^1 are 518.40, 518.25 and 518.32 cm.$^{-1}$. Since there is no reason to prefer any one of these values, the average 518.31 cm.$^{-1}$ should represent the band center satisfactorily. The poor agreement can be explained by the fact that these values were deduced from hot bands which were badly overlapped by a strong C_2HD band. Hence the band centers may be in error as much as 0.1 cm.$^{-1}$.

Acknowledgments.—The authors wish to thank Dr. M. Hellman for preparing the sample and Mr. Joseph M. Cameron for performing the least squares reduction on SEAC.

WASHINGTON 25, D. C.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, AND THE RESEARCH LABORATORIES, EASTMAN KODAK COMPANY ROCHESTER, N. Y.]

Dipole Moments and Structures of Two Heteropolar Cyanine Dye Molecules[1,2]

BY ANTHONY J. PETRO, CHARLES P. SMYTH AND LESLIE G. S. BROOKER

RECEIVED DECEMBER 29, 1955

The molecular dipole moments of two cyanine dyes have been measured in very dilute solutions in dioxane. Comparison of the observed moment values 9.8 and 13.3 × 10^{-18} with those calculated for the possible resonating structures indicates that a full, or nearly full, electronic charge is carried by the acidic radical of the molecule, while an equal positive charge is equally divided between the nitrogens of the two basic nuclei.

Dipole moment measurements carried out in the Frick Laboratory have been used,[3,4] in conjunction with absorption data in the visible region, to help clarify the resonance conditions in various non-ionized dyes. A long series of papers by Brooker and colleagues dealing with these molecules is listed in reference 4. Two new dyes are of particular interest because of their possibly large polarities. The two compounds are 1,3-bis-(2-methoxyethyl)-5-[bis-1,3-(3-ethyl-2-benzothiazolinylidene)-2-propylidene]-barbituric acid and 1,3-diethyl-5-[bis-1,3-(3-ethyl-2-benzothiazolinylidene)-2-propylidene]-2-thiobarbituric acid, both belonging to the group of dyes known as the holopolar cyanines.[5] They will hereafter be referred to as I and II, respectively.

Experimental

The dipole moments were measured in dioxane solutions at 30°. "Practical" 1,4-dioxane from the Carbide and Carbon Chemicals Corporation was refluxed overnight with sodium and then fractionally distilled as needed. The fraction used boiled at 101.2–101.3° at 758.0 mm. and had a dielectric constant of 2.2005 ± 0.0002 at 30°. Dioxane was chosen as solvent because of the greater solubility of the dyes in this medium than in benzene.

Because of the very slow rate of solution of the dyes, heat was used to dissolve the solids. In the more concentrated solutions, which were evidently supersaturated, the solids recrystallized after two days, so that measurements were carried out as soon as possible after the solutions were prepared.

The dielectric constants of the solutions were measured with a heterodyne-beat apparatus as described elsewhere.[3,6] The dielectric cell was similar to that previously described[7] with one modification. Filaments of lead glass (Corning No. 8871) instead of mica strips were used as spacing material between the concentric condenser plates, the glass being fused to the platinum in a high temperature oven.[8] This construction gave added stability to the cell and thus an invariable cell constant.

Because of the low solubilities of the dyes (range of mole fractions used: I, (0.5–1.5) × 10^{-4}; II, (1.2–4.4) × 10^{-5}), it was considered unprofitable to measure the densities of the more dilute solutions. Consequently, the density of only the most concentrated solution was measured in each case, with an Ostwald–Sprengel pycnometer, and a linear dependence of specific volume v_{12} on the mole fraction c_2 was assumed. The values of the slopes β' in the equation

$$v_{12} = v_1 + \beta' c_2$$

were then calculated from the specific volumes of the pure solvent and the most concentrated solution. The effect of

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[1] This research was supported by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

[2] This paper represents a part of the work to be submitted by Mr. A. J. Petro to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] L. M. Kushner and C. P. Smyth, THIS JOURNAL, **71**, 1401 (1949).

[4] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, pp. 347–354.

[5] L. G. S. Brooker and F. L. White, U. S. Patent 2,739,964 (1956).

[6] G. L. Lewis and C. P. Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

[7] C. P. Smyth and S. O. Morgan, THIS JOURNAL, **50**, 1547 (1928).

[8] The cell was constructed by Mr. B. B. Howard of the Frick Laboratory.

entirely omitting the variation of density with concentration from the calculations would be merely to increase the dipole moment value by about 0.2×10^{-18}, so that any error incurred in the above approximation is well within the experimental error. The dielectric constants, ϵ_{12}, were found to be linear functions of the mole fractions of the solutes according to the equation

$$\epsilon_{12} = \epsilon_1 + \alpha' c_2$$

The values of α', the slopes of the lines, were calculated by the method of least squares and were used to calculate the polarizations of the solutes at infinite dilution by the method of Halverstadt and Kumler[9] and the dipole moments. The molar refractions of the D-sodium line, which could not be measured directly because of the color of the solutions, were calculated from bond refractions.[10] A small correction of 2 cc. was added to the calculated values as a rough estimate of the exaltation arising from the conjugated systems of the molecules. The errors resulting from the calculation and the use of R_D instead of the true sum of the atomic and electronic polarizations are negligible in comparison with experimental errors.

The experimental results are listed in Table I.

TABLE I

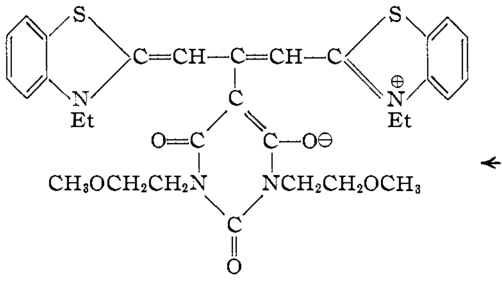
EMPIRICAL CONSTANTS AND POLARIZATIONS AT 30°, REFRACTIONS AND DIPOLE MOMENTS

(ϵ_1 = 2.2005; v_1 = 0.97814)

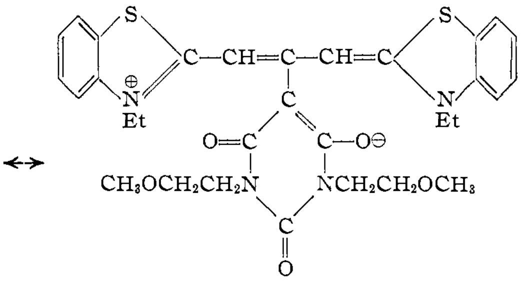
	M_2	α'	β'	P_∞	R_D (calcd.)	μ ($\times 10^{18}$)
I	606.72	136	−2.70	2094.4	167	9.8 ± 0.18
II	562.76	246	−6.04	3609.6	162	13.3 ± 0.40

Discussion of Results

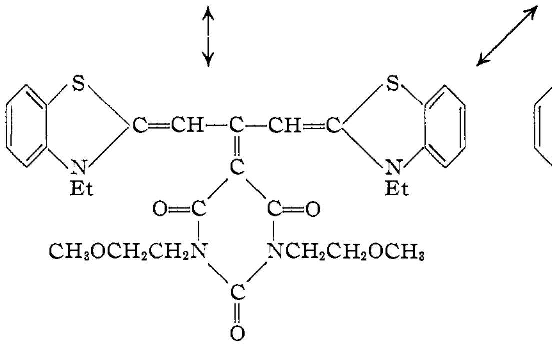
Each dye molecule is made up of two identical basic nuclei and one acidic radical linked to the basic nuclei, as in the merocyanines.



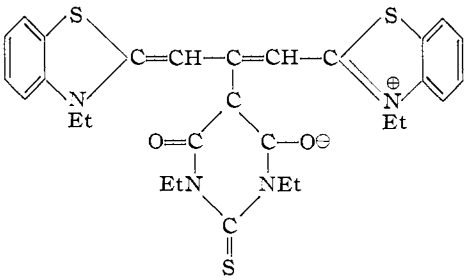
Ia (2 structures)



Ib (2 structures)

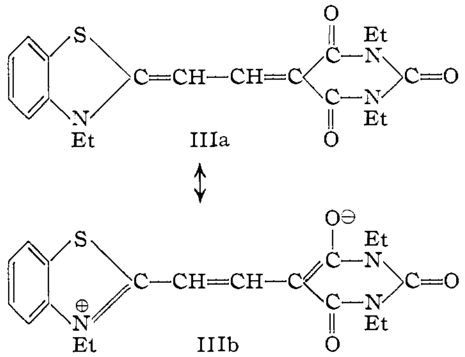


Ic

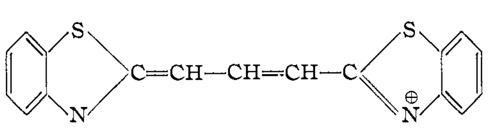


II

The benzothiazole nucleus is strongly "basic," *i.e.*, it has a relatively strong attraction for a positive charge, while the substituted barbituric acid radical is strongly "acidic," *i.e.*, electron-attracting. The combination of one of each of these nuclei in a simple merocyanine (III) gives a strongly polar molecule in which the two resonance structures IIIa and IIIb are not of greatly different energy.



If a second basic nucleus is added to III to give I (or II), the positive charge developed in IIIb is further stabilized by resonance with the second nitrogen through the conjugated system. This added resonance is characteristic of the cation IV. It is



IV

therefore, to be expected that the polarization in I and II should be considerable. However, a scale model of either dye molecule shows that the coplanarity of the three nuclei, which is required for resonance among the non-polar and polar structures, is impossible because of steric hindrance. Each nucleus is, therefore, somewhat twisted with respect to the others, or one of the three is drastically twisted out of the plane of the other two.[11]

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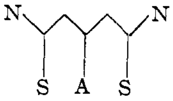
(9) I. F. Halverstadt and W. D. Kumler, THIS JOURNAL, **64**, 2988 (1942).

(10) C. P. Smyth, ref. 4, p. 409.

(11) L. G. S. Brooker, F. L. White, D. W. Heseltine, G. H. Keyes, S. G. Dent, Jr., and E. J. Van Lare, *J. Phot. Sci.*, **1**, 173 (1953).

Twisting the acidic nucleus out of the plane of the two basic nuclei leaves the resonance scheme Ia ↔ Ib in operation, so that light absorption would be expected to be similar to that of the unperturbed cation IV. The schemes Ia ↔ Ic and Ib ↔ Ic no longer apply since they require coplanarity of the two nuclei involved in each. In the scheme Ia ↔ Ib both the structures are dipolar, giving a completely polar molecule which should have a large dipole moment. Light absorption measurements indicate that the acidic nucleus is indeed twisted out of the plane of the two basic nuclei.[11] The maximum observed at about 600 mμ is characteristic of the cation IV. Only when the polarizability of the solvent is reduced below that of anhydrous benzene does a maximum appear at about 520 mμ. This new band corresponds closely to the absorption of the merocyanine III, produced by what has been called "allopolar isomerism."[11] The molecules, therefore, contain permanent dipoles or are actually composed of a cation and an anion in conjugation with one another, yet, because of steric effects, cation and anion are independent as far as electronic interaction through the conjugated system is concerned. This condition allows the *a priori* calculation of the molecular dipole moment, without resorting to quantum-mechanical methods.[3]

Calculation of the molecular dipole moment is complicated by the possibility of seven different stereoisomeric configurations of the cationic portion of the molecule.



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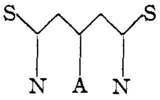

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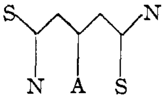

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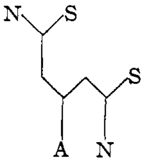

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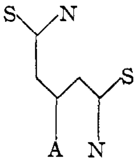

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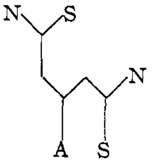

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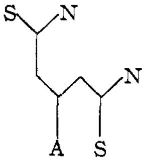
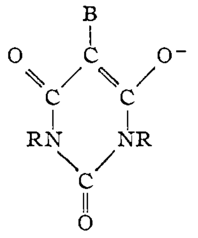


7

The moments due to the full charge separation may be calculated for all seven cases (identical for I and II) from known bond angles and distances.[12] The average position of the positive charge is midway between the two nitrogens in the cationic portion B of the molecule, and that of the negative charge is located midway between the two carbonyl oxygens taking part in the resonance in the anionic portion A. The resultant moments are listed in Table II under μ_C. In addition to the full charge separation, the contributions of the benzothiazole nuclei must be considered. Taking 1.45 as the moment value in the direction of the carbon bond from the heterocyclic ring,[13] the resultant moment is calculated for each configuration and the results are listed in Table II under μ_B. The contribution of the acidic nucleus A is difficult to calculate because of the following possible extreme resonance structures arising from the pair of electrons on each nitrogen.



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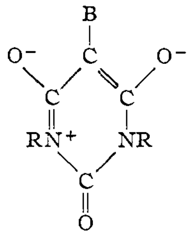

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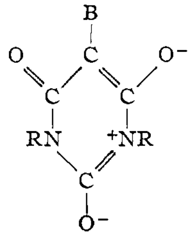

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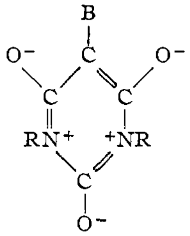

11

It is impossible to determine the relative importance of each structure but as a good approximation the small contributions from (9), (10) and (11) can be considered to cancel out and only (8) need be taken into account. The resultant moments are calculated from known bond moments[14] for both I and II and the results are listed in Table II under μ_{RI} and μ_{II}. Finally, for compound I, the total moment for each of the seven structures is calculated by means of the equation for the resultant moment of movable dipoles[14,15] and the results are listed in Table II under μ_I.

TABLE II

CALCULATED MOMENT VALUES (× 10^{18})

Configuration	μ_c	μ_B	μ_{RI}	μ	μ_{II}
1	11.0	9.5	9.1	9.4	9.4
2	1.1	0.4	0.8	2.0	0.5
3	6.5	5.3	4.9	5.3	5.2
4	10.9	11.7	11.3	11.4	11.6
5	12.3	13.5	13.1	13.2	13.4
6	16.2	17.2	16.8	16.9	17.1
7	17.7	19.0	18.7	18.8	19.0

To calculate the average moment it is assumed that all seven forms are in equilibrium in equal concentrations, and from the equation

$$\overline{\mu^2} = \frac{1}{n}\,\Sigma\mu^2$$

the values, $\overline{\mu_I} = 12.3 \times 10^{-18}$ and $\overline{\mu_{II}} = 12.4 \times 10^{-18}$, are obtained. However, examination of scale drawings of the seven configurations using van der Waals radii of the groups[11] indicates that (2) is highly improbable because of excessive crowding of the N-ethyl groups and the acidic nucleus. Omitting (2) from consideration and recalculating the moments for the remaining six configurations yields the values $\overline{\mu_I} = 13.3 \times 10^{-18}$ and $\overline{\mu_{II}} = 13.4 \times 10^{-18}$, the latter value being in close agreement with the observed. Finally, the probability of occurrence of structures (3), (4), (5) and (7) can be considered small for the same steric reasons as above, and omitting them entirely from the calculations yields the values $\overline{\mu_I} = 13.7 \times 10^{-18}$ and

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[12] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, pp. 79, 167, 172, 203.

[13] P. F. Oesper, G. L. Lewis and C. P. Smyth, THIS JOURNAL, **64** 1130 (1942).

[14] C. P. Smyth, ref. 4, pp. 234, 244–245.

[15] H. Eyring, *Phys. Rev.*, **39**, 746 (1942).

$\overline{\mu_{II}} = 13.8 \times 10^{-18}$. It appears that the most probable values lie between the last two pairs of values. Calculations similar to those outlined above, when carried out on the non-polar forms, yielded the values 2.4×10^{-18} and 1.5×10^{-18} for compounds I and II, respectively. From these results it is evident that a full charge separation must exist in the molecule of II and a nearly full separation in that of I.

The reason why compound II should have an experimental moment 3.5 higher than that of I is not evident. The extinction coefficients of solutions of the two compounds were found to be identical within our experimental error with no indication of a second absorption peak corresponding to a non-polar form. Of course, unequal contributions from the various possible configurations can account for the observed difference but quantitative treatment is impossible.

Although the moments of these two compounds are high, they are not as high as the value 17.7×10^{-18} found previously for a very polar merocyanine[3] and the smaller of the two is of the same magnitude as the moments of three other dye molecules[4] previously investigated. The striking aspect of these values is that the moment of compound II is indistinguishable from the value calculated on the basis of a completely heteropolar structure and that for compound I is only 26% lower, while contributions from resonating non-polar structures normally lower the resultant moment[4] much more than 26%. In coördinate bonds, the moment is only 0.36 to 0.65 of the calculated value[16] and, for the almost pure ionic structures of salt molecules, the moments are reduced from 20 to 50% by mutual induction between the ions.[16] The good agreement between the moment value observed for compound II and that calculated for an undistorted heteropolar structure is like that obtained in the case of dipolar ions,[17] such as those of amino acids.

Acknowledgments.—The authors are indebted to Dr. R. C. Miller of the Frick Laboratory for assistance and advice during the course of this work.

[16] C. P. Smyth, ref. 4, pp. 248–250.

[17] C. P. Smyth, ref. 4, p. 394.

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Relative Electron Densities in Substituted Benzenes[1]

BY P. L. CORIO AND B. P. DAILEY

RECEIVED NOVEMBER 25, 1955

The proton magnetic resonance spectra of a number of monosubstituted benzenes have been studied in an attempt to derive values of the relative electron density from observations of the chemical shifts of the ring protons, and to study the effect of various functional groups on these shifts. Shifts are assigned to the protons at different ring positions, and these indicate differences in the electron distribution at the *ortho*, *meta* and *para* positions. The observed shifts are compared with data from other experimental sources, with theoretical calculations of electron densities in substituted benzenes and with the electronic theory of orientation effects in benzene substitutions. In particular, the importance of polarization effects in aromatic substitution reactions is emphasized.

Introduction

The position taken by an entering group in a substituted benzene appears to be intimately connected with the value of the electron density at the *ortho*, *meta* and *para* positions. Both problems have been the subject of numerous theoretical and experimental investigations.[2–5] A number of effects have been postulated (such as the ± I-effect, the ± E-effect, etc.), and these form the basis of the so-called "electronic theory of aromatic substitution." The success of this theory lends importance to any experimental method which will help to evaluate relative electron densities in these molecules.

It is now a well established fact that the chemical shifts observed in proton resonances reflect differences in the electron distribution about chemically non-equivalent protons.[6,7] These shifts arise from the small magnetic fields set up by the electrons which oppose the applied field and are directly proportional to it. This is commonly called a diamagnetic shielding of the protons by the electrons. The result of these shielding effects on the proton resonance is a set of absorption lines which correspond to the number of non-equivalent protons contained in the molecule. Ethanol for example, shows three principal groups of absorption lines which correspond to the non-equivalent CH_3, CH_2 and OH protons.

The conclusion that the chemical shifts can be taken as an approximate measure of electron density is subject to the restriction that no important changes in bond hybridization occur. Studies[8] of the proton shifts in aliphatic molecules containing single, double and triple bonds, show that the proton shift for an acetylenic proton has a value which is intermediate between the observed values for protons attached to carbon atoms using single and double bonds; thus chemical shifts are not simply related to changes in bond hybridization. Careful structural studies have shown no appreciable changes in C–H bond distances or

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[1] This research was supported by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command.

[2] (a) C. K. Ingold, *Chem. Revs.*, **15**, 225 (1934); (b) C. C. Price, *ibid.*, **29**, 3 (1941).

[3] L. N. Ferguson, *ibid.*, **50**, 47 (1952).

[4] G. W. Wheland and L. Pauling, THIS JOURNAL, **57**, 2806 (1935).

[5] H. H. Jaffe, *J. Chem. Phys.*, **20**, 279, 778 (1952).

[6] H. S. Gutowsky and C. J. Hoffman, *ibid.*, **19**, 1259 (1951).

[7] N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950); **76**, 243 (1952).

[8] L. H. Meyer, A. Saika and H. S. Gutowsky, THIS JOURNAL, **75**, 4567 (1953).