phenone and *p*-chlorobenzophenone.

3. The Tischtschenko reaction with (+)2-methylbutanal leads to ester, the alcohol and acid portion of which have suffered the same extent of racemization.

EVANSTON, ILLINOIS RECEIVED OCTOBER 18, 1948

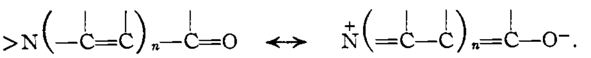
[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Resonance and Polarity in the Molecules of Three Colored Compounds[1]

BY LAWRENCE M. KUSHNER AND CHARLES P. SMYTH

Dipole moment measurements made in this Laboratory have been used[2,3,4,5] to throw light on the resonance conditions in the molecules of certain un-ionized dyes, the results being satisfactorily correlated with the light absorption of the compounds. Dr. L. G. S. Brooker of the Eastman Kodak Company recently suggested to us measurements on three further colored compounds and furnished samples.

The three compounds are 3-ethyl-5-[4-(1-ethyl-3,3-dimethyl-2(3)-indolylidene)-butenylidene]-rhodanine (I), 1,3-diethyl-5-[4-(1-ethyl-3,3-dimethyl-2(1)-indolylidene)-2-butenylidene]-2-thiobarbituric acid (II) and 1,3-diethyl-5-[(1,3-diethyl-2(3)-benzimidazolylidene)-butenylidene]-barbituric acid (III), all three belonging to a new group of un-ionized dyes known as the merocyanines.[5a] These dyes contain the amide system, the essential grouping of which is



$$>\mathrm{N}\left(-\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}\right)_n-\overset{|}{\mathrm{C}}=\mathrm{O} \longleftrightarrow \overset{+}{\mathrm{N}}\left(=\overset{|}{\mathrm{C}}-\overset{|}{\mathrm{C}}\right)_n=\overset{|}{\mathrm{C}}-\mathrm{O}^-.$$

In such dyes one of the two extreme resonance structures is uncharged while the other is a dipole. Some discussion of these dyes from the resonance standpoint has already appeared.[5b] Proof was advanced that in I the polar structure Ib (see Discussion of Results) must be of higher energy and contribute less than the non-polar structure Ia, since replacement of the indolenine ring by one that was more basic (in the restricted sense used by Brooker) reduced the deviation in $\lambda_{\max.}$, whereas replacement by a less basic nucleus increased the deviation. Nevertheless the dipole moment of the compound was expected to be considerable.

Experimental Method

The dipole moments were measured in solution in benzene or dioxane. The benzene used as solvent for the more soluble compounds, I and II, was a thiophene-free product from the Barrett Company, which was purified by drying with sodium wire followed by distillation from the wire (boiling point, 80.55–80.90° at 772.8 mm.; dielectric constant at 30°, 2.2672). The dioxane used as solvent for the almost insoluble compound III was "practical" 1,4-dioxane from the Carbide and Carbon Chemicals Corporation, which was distilled from 101.1 to 101.5° at 762.9 mm., dried over sodium wire and redistilled from the sodium wire, the fraction used boiling at 101.0° at 757.7 mm. Its dielectric constant, measured directly at 30°, was 2.1984 ± 0.0002.

Because of the virtual insolubility in benzene and very low solubility in dioxane of compound III, the preparation of the solutions presented a problem. It was overcome by weighing out the compound in a small glass cup on a high sensitivity analytical balance and transferring both cup and compound to a 100-cc. weighing bottle, to which the dioxane was then added. In the case of the most concentrated solution, it was necessary to warm the mixture to achieve true solution. As there was obviously a risk of evaporating some dioxane, the final weighing to determine the weight of dioxane in the solution was not made until all the solid had been dissolved and the solution had cooled.

The dielectric constants of the dilute solutions were measured with a heterodyne beat apparatus developed from one which has been previously described.[6] The precision of the apparatus was increased by replacing the precision measuring condenser formerly used by a General Radio Company 722–D instrument, on which an 1100 micromicrofarad scale was employed. The dielectric cell was similar to that previously described.[7] The densities of the benzene solutions were measured at 30° with an Ostwald–Sprengel pycnometer, the technique employed being similar to that previously described.[8] The dipole moments were calculated from the experimental data by the method of Halverstadt and Kumler.[9] The dielectric constants, ϵ_{12}, and specific volumes, v_{12}, of the solutions were found to be linear functions of the mole fractions, c_2, of the solutes according to the equations

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[1] This research was carried out with the support of the Office of Naval Research.

[2] Brooker, Sprague, Smyth and Lewis, THIS JOURNAL, **62**, 1116 (1940).

[3] Brooker, White, Keyes, Smyth and Oesper, *ibid.*, **63**, 3192 (1941).

[4] Brooker and Sprague, *ibid.*, **63**, 3203 (1941).

[5] Brooker and Sprague, *ibid.*, **63**, 3214 (1941).

[5a] Papers dealing with these dyes are in course of preparation in Dr. Brooker's Laboratory.

[5b] Brooker, "Frontiers in Chemistry," Vol. III, Interscience Publishers Inc., New York, N. Y., 1945, p. 129.

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

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

[8] Lewis and Smyth, *ibid.*, **61**, 3063 (1939).

[9] Halverstadt and Kumler, *ibid.*, **64**, 2988 (1942).

$$\epsilon_{12} = \epsilon_1 + \alpha' c_2$$
$$v_{12} = v_1 + \beta' c_2$$

The dielectric constants, ϵ_1, and specific volumes, v_1, for the pure solvents given by these equations when applied to the plots of the experimental data against c_2 agreed well with the directly measured values. The calculated values along with the values of α' and β', the slopes of the lines, were used to calculate the polarization of the solute at infinite dilution

$$P_\infty = 3\alpha' v_1 M_1/(\epsilon_1 + 2)^2 + (M_2 v_1 + M_1\beta')(\epsilon_1 - 1)/(\epsilon_1 + 2)$$

in which M_1 is the molecular weight of the solvent and M_2 is that of the solute. The dipole moment was then obtained from the usual equation

$$\mu = 0.01281 \times 10^{-18} [(P_\infty - R_D)T]^{1/2}$$

The molar refractions for the D sodium line, R_D, which could not be measured directly because of the color of the compounds, were calculated from values of bond refractions in the literature.[10] A small correction of 2 cc. was added to the values as a rough estimate of the exaltation arising from the conjugated systems in the molecules. The effects of errors in the calculation of R_D and of the approximation made in using R_D instead of the true sum of the electronic and atomic polarizations are negligible in comparison with the experimental errors in the determination of P_∞.

The low solubilities of these large and highly polar molecules in non-polar solvents cause the errors in the dipole moment values to be larger than is usual in solution measurements, particularly, in the case of compound III, which was too insoluble for measurement in benzene and soluble in dioxane only to the extent of mole fraction 3×10^{-6} at 30°. Since it was unprofitable to attempt to measure the densities of the extremely dilute solutions of III, the value of v_1 was calculated in this case from the density of pure dioxane[11] and its temperature coefficient.[12] The value of β' was roughly estimated by assuming that the volume of the most concentrated solution was that of the dioxane alone, dividing this volume by its weight, and using the value of v_{12} thus obtained along with that for v_1 to calculate β'. Although this rough value of β' is, presumably, too large, the effect of its error upon the moment value is small in comparison with that of the errors in the dielectric constant values, which vary over a range of only 0.001 from the value for the solvent, but show, nevertheless, a satisfactory linear dependence upon c_2.

Experimental Results

The values of ϵ_{12} and v_{12} for the solutions are given in Table I and the values of the constants calculated from them in Table II.

TABLE I

DIELECTRIC CONSTANTS AND SPECIFIC VOLUMES AT 30°

Solvent	$c_2 (\times 10^4)$	ϵ_{12}	v_{12}
I 3-Ethyl-5-[4-(1-ethyl-3,3-dimethyl-2(3)-indolylidene)-butenylidene]-rhodanine			
Benzene	2.79	2.2866	1.15215
	4.04	2.2953	1.15194
	9.55	2.3301	1.15101
	18.88	2.3920	1.14957
	26.51	2.4439	1.14816
II 1.3-Diethyl-5-[4-(1-ethyl-3,3-dimethyl-2(1)-indolylidene)-2-butenylidene]-2-thiobarbituric acid			
Benzene	1.643	2.2904	1.15229
	3.108	2.3103	1.15199
	4.456	2.3265	1.15173
	5.891	2.3448	1.15134
	5.998	2.3481	1.15134
III 1.3-Diethyl-5-[(1.3-diethyl-2(3)-benzimidazolylidene)-butenylidene]-barbituric acid			
Dioxane	0.00634	2.1984	
	.00985	2.1986	
	.02462	2.1993	
	.03075	2.1994	

TABLE II

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

ϵ_1	v_1	α'	β'	P_∞	R_D (calcd.)	$\mu (\times 10^{18})$
Compound I						
2.268	1.1526	66.4	−1.675	1077	114.8	6.91 ± 0.10
Compound II						
2.269	1.1527	130.0	−2.233	2020	124.7	9.70 ± 0.15
Compound III						
2.1982	0.9782	435	(−4.5)	6383	116.8	17.7 ± 1.3

Discussion of Results

The dipole moment found for the molecule of compound III is the largest yet observed for a molecule other than that of a salt or a zwitterion. The reason for the large moments of these compounds becomes apparent when one considers the polar structures, b, shown below, which can be readily formed by shift of an electron pair from a nitrogen in the non-polar structure, a, through the conjugated system to a carbonyl oxygen. The term "non-polar" is used to distinguish the structures of relatively low polarity from those in which an electron pair has shifted from one side of the molecule to the other.

If the polar structures, b, are not very different in energy from the non-polar, a, resonance between the a and b structures will give rise to dipole moments whose size depends largely on the amounts of the contributions of the polar structures. The moments of the non-polar structures should differ somewhat from one another and cannot be calculated with exactness. None of them should exceed 2.5×10^{-18} and little error will arise in our considerations from the assignment of a rough value $m_a = 2.0 \times 10^{-18}$ to the non-polar structure

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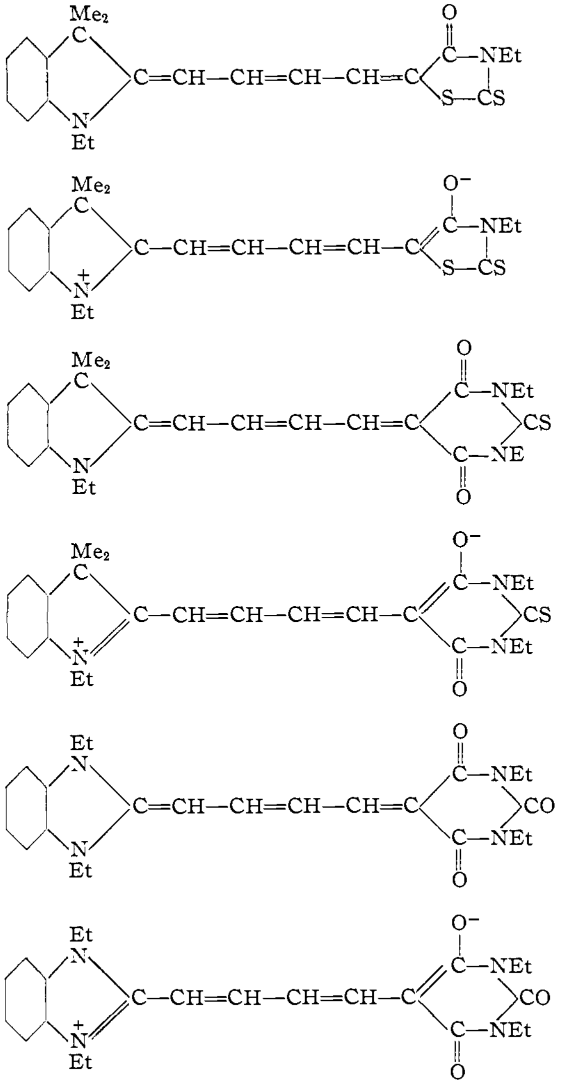
[10] Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., Reinhold Publishing Corp., New York, N. Y., 1931, Chap. VIII.

[11] Kumler, THIS JOURNAL, **62**, 3292 (1940).

[12] Smyth and Walls, *ibid.*, **54**, 2261 (1932).



I (1 structure)

II (2 structures)

III (4 structures)

of each of the three compounds. Compound I can have only one contributing polar structure, b, compound II has two identical polar structures, while compound III has four polar structures indistinguishable from one another. The conceivable doubly charged structure for compound III cannot arise for, as soon as one nitrogen and one oxygen are charged, the other oxygen and nitrogen are no longer connected by a conjugated chain. The polar structures should have approximately equal energies and approximately equal dipole moments, m_b. The large values found for the dipole moments in Table II as compared to the relatively small values calculated for the non-polar structures, a, show the considerable stability of the polar structures, b. The increase in moment from compound I to II to III corresponds qualitatively to the increase in the number of contributing polar structures from 1 to 2 to 4. In most molecules, the possible polar structures are so much less stable than the non-polar that their contributions are relatively small and their amounts, as indicated by the dipole moment, are a fair measure of the amount of resonance. This is not far from being the case in compound I, but in compound III, the four polar structures make so large a contribution that, as shown by the absorption measurements of Dr. L. G. S. Brooker and his colleagues, increased stabilization of the polar structures by the use of a polar solvent decreases the amount of resonance.

One can write[13] three equations for the moments, μ, of the molecules

$$\mu_{\text{I}} = (1 - x_{\text{I}})m_a + x_{\text{I}}m_b$$
$$\mu_{\text{II}} = (1 - x_{\text{II}})m_a + x_{\text{II}}m_b$$
$$\mu_{\text{III}} = (1 - x_{\text{III}})m_a + x_{\text{III}}m_b$$

where x is the fractional contribution of all the polar structures for each molecule, m_a is the moment of the so-called non-polar structure, which, because of its relatively small size, can, without serious error, be taken as the same for all three molecules, and m_b is the moment which should be virtually the same for all the polar structures. If m_a is taken as 2.0×10^{-18}, the observed values can be put in for μ_{I}, μ_{II} and μ_{III} and the equations solved simultaneously for the ratios of the fractional contributions of the polar structures, m_b being eliminated by substitution. The ratios thus obtained are

$$x_{\text{II}}/x_{\text{I}} = 1.57 \text{ and } x_{\text{III}}/x_{\text{I}} = 3.21$$

The absorption measurements indicate that the amount of resonance in compound II is not greatly affected by increase in the polarity of the solvent. This suggests that, in the non-polar solvent, the contribution of the polar forms may be somewhat less than half, an amount which may be increased to somewhat more than half by a polar solvent without greatly altering the amount of resonance. If, in line with this suggestion, x_{II} is set equal to 0.4, x_{I} is given by the calculated ratios as 0.25 and x_{III} as 0.81, values which are consistent with the fact that the absorption measurements show that a polar solvent increases the amount of resonance in compound I and decreases it in compound III. It might be argued qualitatively that since, in

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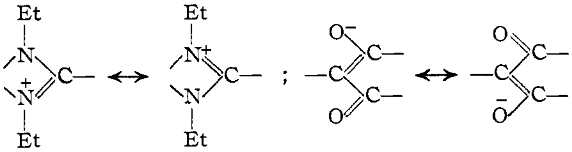
[13] Smyth, THIS JOURNAL, **63**, 57 (1941).

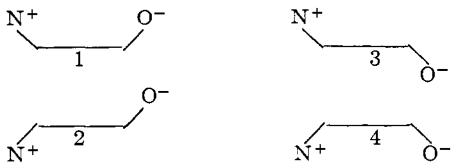
compound II, the amount of resonance is not far from a maximum, the contributions of the non-polar structure and of each of the two polar structures should be nearly equal, that of the non-polar structure being slightly greater in a non-polar solvent than that of each of the two polar structures. In this case, $(1 - x_{\mathrm{II}})$ would be about 0.4 and $x_{\mathrm{II}}/2$ about 0.3. This would make $x_{\mathrm{I}} = 0.38$ and $x_{\mathrm{III}} = 1.22$, an impossibly large answer. It is evident that, since x_{III} must be less than 1, x_{I} must be less than 0.31, x_{II} must be less than 0.49, and m_{b} must be greater than 18×10^{-18}.

Substitution of the value $x_{\mathrm{II}} = 0.4$ in the equation for μ_{II} or of the corresponding values of x_{I} and x_{III} in the other equations gives $m_{\mathrm{b}} = 21.4 \times 10^{-18}$ for the moment of the polar structures. The maximum value which the polar structure could have is the moment of the structure with an extended, planar, zig-zag chain, in which the charges are separated by a maximum distance. The value calculated approximately for this structure from the bond lengths and angles is 42×10^{-18}, while the value calculated from the mean square moment for all the possible orientations around the bonds of the chain is 30×10^{-18}. Even the lower of these two values is much higher than the value 21.4, estimated on the basis of reasonable values for the amounts of the contributions of the polar structures. Conversely, the use of the moments calculated for the ionic structures without allowance for decrease of moment by an empirically introduced inductive distortion[14] would give lower values than those assumed for the amounts of the contributions from the polar structures, as previously observed.[13]

Consideration of the four polar structures, IIIb, for compound III shows that they can change from one to another by shifts of electrons at the ends of the butenylidene chain.



The four polar structures, represented schematically below, are hereafter referred to as 1, 2, 3 and 4.



The total wave function, ψ_{III}, for the system can be expressed as

$$\psi_{\mathrm{III}} = a\phi + b(\chi_1 + \chi_2 + \chi_3 + \chi_4)$$

where ϕ is the wave function of the non-polar structure, χ_{i} is the wave function of the i^{th} polar structure, and a and b are constants representing the contribution of each structure to that of the molecule as a whole. The total energy, W_{III}, of the system is given by the expression

$$W_{\mathrm{III}} = \int \psi^*_{\mathrm{III}}\, H\psi_{\mathrm{III}}\, \mathrm{d}\tau / \int \psi^*_{\mathrm{III}}\, \psi_{\mathrm{III}}\, \mathrm{d}\tau$$

Substitution for ψ_{III} in the above equation with the assumptions that ϕ and χ_{i} are normalized and orthogonal functions and that the integrals representing the resonance between structures 1 and 4, and 2 and 3 are small compared with the other exchange integrals, leads to the expression

$$W_{\mathrm{III}} \cong [a^2C + 8abE_{\mathrm{CP}} + 4b^2\,(P + E_{\mathrm{N}} + E_{\mathrm{O}})]/(a^2 + 4b^2)$$

where

$C = \int \phi^* H\phi \mathrm{d}\tau$ = energy of non-polar structure

$P = \int \chi_{\mathrm{i}}^* H\chi_{\mathrm{i}} \mathrm{d}\tau$ = energy of the i^{th} polar structure (all polar forms are assumed to have the same energy)

$E_{\mathrm{CP}} = \int \phi^* H\chi_{\mathrm{i}} \mathrm{d}\tau$ = exchange energy between the non-polar and any polar structure

$E_{\mathrm{N}} = \int \chi_1^* H\chi_2 \mathrm{d}\tau = \int \chi_3^* H\chi_4 \mathrm{d}\tau$ = exchange energy between structures 1 and 2. 3 and 4

and $E_{\mathrm{O}} = \int \chi_1^* H\chi_3 \mathrm{d}\tau = \int \chi_2^* H\chi_4 \mathrm{d}\tau$ = exchange energy between structures 1 and 3. and 2 and 4.

Minimizing the energy with respect to the quantities a and b, gives the ratio

$$a/b = 4E_{\mathrm{CP}}/(W_{\mathrm{III}} - C)$$

and the expression

$$W_{\mathrm{III}} = [(P + C + E_{\mathrm{N}} + E_{\mathrm{O}}) \pm ((P - C + E_{\mathrm{N}} + E_{\mathrm{O}})^2 + 16E^2_{\mathrm{CP}})^{1/2}]/2$$

Since the minimum energy is desired, it is obvious that the negative sign must be used. Substitution for W_{III} in the expression for a/b, yields the equation

$$a/b = 2K/[1 - (1 + K^2)^{1/2}]$$

where

$$K = 4E_{\mathrm{CP}}/(P - C + E_{\mathrm{N}} + E_{\mathrm{O}})$$

Substitution for ψ_{III} in the equation

$$\mu_{\mathrm{III}} = \int \psi^*_{\mathrm{III}}\, \mu\psi_{\mathrm{III}}\, \mathrm{d}\tau / \int \psi^*_{\mathrm{III}}\, \psi_{\mathrm{III}}\, \mathrm{d}\tau$$

with the assumption that integrals of the type $\int \phi^* \mu\chi_{\mathrm{i}} \mathrm{d}\tau$, $\int \chi^*_{\mathrm{i}} \mu\chi_{\mathrm{j}} \mathrm{d}\tau$ are negligible in comparison with those of the type $\int \phi^* \mu\phi \mathrm{d}\tau$ and $\int \chi_{\mathrm{i}}^* \mu\chi_{\mathrm{i}} \mathrm{d}\tau$, gives

$$\mu_{\mathrm{III}} \cong (a^2\mu_{\mathrm{c}} + 4b^2\mu_{\mathrm{i}})/(a^2 + 4b^2)$$

where $\mu_{\mathrm{c}} = \int \phi^* \mu\phi \mathrm{d}\tau$ = dipole moment of the non-polar form, and $\mu_{\mathrm{i}} = \int \chi_{\mathrm{i}}^* \mu\chi_{\mathrm{i}} \mathrm{d}\tau$ = dipole moment of the i^{th} polar form (it is assumed that all the polar forms have the same moment).

Substitution for a/b gives the final equation

$$\mu_{\mathrm{III}} = [K^2\mu_{\mathrm{c}} + \mu_{\mathrm{i}}(2 - 2(1 + K^2)^{1/2} + K^2)]/2(1 - (1 + K^2)^{1/2} + K^2),$$

where μ_{c} is the moment of the non-polar structure. Substitution of the values $\mu_{\mathrm{III}} = 17.7 \times 10^{-18}$, $\mu_{\mathrm{c}} = 2.0 \times 10^{-18}$ and $\mu_{\mathrm{i}} = 40.0 \times 10^{-18}$, an approximation slightly lower that the maximum possible value, gives $E_{\mathrm{CP}}/(P - C + E_{\mathrm{N}} + E_{\mathrm{O}}) = -1.41$, and 0.766 and 0.321 for a and b, respectively.

The similarities of the structures of compounds I, II and III are such that it is reasonable to as-

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[14] Hugill, Coop and Sutton, *Trans. Faraday Soc.*, **34**, 1518 (1938).

sume that the non-polar and polar wave functions do not change significantly from one compound to another. Therefore, the wave functions for compounds I and II are obviously

$$\psi_{\mathrm{I}} = a\phi + b\chi$$

and

$$\psi_{\mathrm{II}} = a\phi + b(\chi_1 + \chi_3)$$

By procedures similar to these previously described, the following relations are obtained for compound I.

$$W_{\mathrm{I}} = (a^2C + 2abE_{\mathrm{CP}} + b^2P)/(a^2 + b^2)$$

where $a = 0.940$ and $b = 0.359$, and

$$E_{\mathrm{CP}}/[P - C] = -0.455$$

For compound II

$$W_{\mathrm{II}} = [a^2C + 4abE_{\mathrm{CP}} + 2b^2(P + E_{\mathrm{O}})]/[a^2 + 2b^2]$$

where $a = 0.891$ and $b = 0.319$ and

$$E_{\mathrm{CP}}/[(P - C) + E_{\mathrm{O}}] = -0.478$$

From these equations, it is possible to arrive at the following energy relationships

$$W_{\mathrm{III}} = 1.97E_{\mathrm{CP}} + 0.41E_{\mathrm{N}} + 0.41E_{\mathrm{O}} + (0.59C + 0.41P)$$

$$W_{\mathrm{I}} = 0.67E_{\mathrm{CP}} + (0.87C + 0.13P)$$

$$W_{\mathrm{II}} = 1.10E_{\mathrm{CP}} + 0.20E_{\mathrm{O}} + (0.80C + 0.20P)$$

where

$$(P - C) = -2.20E_{\mathrm{CP}},\ E_{\mathrm{O}} = 0.10E_{\mathrm{CP}},\ E_{\mathrm{N}} = 1.39\ E_{\mathrm{CP}}$$

In the case of compound I, there is resonance between the non-polar and polar structures which gives rise to a resonance energy term $0.67E_{\mathrm{CP}}$, and a dipole moment of 6.9×10^{-18}. Compound II, in addition to having a somewhat larger contribution to the total energy of the system, $1.10E_{\mathrm{CP}}$, arising from the existence of two polar structures, has an energy term $0.20E_{\mathrm{O}}$ which is due to resonance between the two polar structures. The calculations show that this energy term is rather small, since $E_{\mathrm{O}} = 0.10\ E_{\mathrm{CP}}$, and, therefore, the polar structures are stabilized only to the extent of raising the dipole moment from 6.9×10^{-18} to 9.7×10^{-18}. In compound III, the polar form is stabilized to a much greater extent by resonance between structures 1 and 2, and 3 and 4, the resonance energy here being $0.41E_{\mathrm{N}}$, plus $0.41E_{\mathrm{O}}$, arising from resonance between the polar structures as mentioned for compound II. Since here there are four polar structures, the energy term corresponding to resonance between the non-polar and polar structures is larger than that for compounds I or II. It is seen then that the dipole moment of compound III, 17.7×10^{-18}, is very large, not only because there are four possible polar structures, but because there is resonance between the polar structures which gives them added stability. Similarly, even though there are two polar structures for compound II, there is not much resonance between them, and the dipole moment is lower than would be expected.

The values of x and a and b have been calculated for the other seemingly possible values of $m_{\mathrm{b}} = \mu_{\mathrm{i}}$, and all are summarized in Table III. Since x represents the total fractional contribution of polar structures for each compound, while, for compounds I, II and III, $a^2_{\mathrm{I}} + b^2_{\mathrm{I}} = 1$, $a^2_{\mathrm{II}} + 2b^2_{\mathrm{II}} = 1$, and $a^2_{\mathrm{III}} + 4b^2_{\mathrm{III}} = 1$, for comparison with x, the values of b are listed as $4b^2_{\mathrm{III}}$, $2b^2_{\mathrm{II}}$ and b^2_{I}.

TABLE III

CONTRIBUTIONS OF POLAR STRUCTURES CALCULATED FOR DIFFERENT MOMENT VALUES FOR THE POLAR STRUCTURES

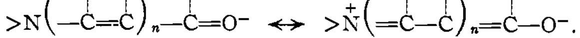
m_{b}	x_{I}	x_{II}	x_{III}	b^2_{I}	$2b^2_{\mathrm{II}}$	$4b^2_{\mathrm{III}}$
>18	<0.31	<0.49	<1.0	..	..	..
21.4	.25	.40	.81	..	..	..
30	.18	.28	.56	0.17	0.28	0.44
40				.13	.20	.41
42	.12	.19	.39			

$x_{\mathrm{III}} = 3.21\ x_{\mathrm{I}};\ x_{\mathrm{II}} = 1.57\ x_{\mathrm{I}}$

No solutions for a and b could be obtained for $\mu_{\mathrm{i}} = 21.4$ or lower, which shows that the seemingly reasonable assumption, $x_{\mathrm{II}} = 0.4$, based on the observed absorption is not justified. Since the dipole moment calculated for an undistorted polar structure has been found, in other cases, to indicate an unexpectedly small amount of resonance, it would seem that the fractional contributions based on the intermediate value 30 for the moment of the polar structures may be the most reasonable. Table III shows that, within the limits $m_{\mathrm{b}} = \mu_{\mathrm{i}} = 30 - 40$, the total contributions of the polar structures for each molecule do not change greatly. Therefore, although the exact contribution in the case of each molecule cannot be stated, their relative values are known, and suffice to explain the magnitudes of the measured moments.

Acknowledgment.—The writers wish to express their deep indebtedness to Dr. L. G. S. Brooker of the Kodak Research Laboratories for materials, information and advice and to Professor Walter Kauzmann for aid in the quantum mechanical calculations.

Summary

The dipole moments of three dyes of the merocyanine series have been measured in very dilute solutions. The merocyanines are un-ionized dyes characterized by the amidic resonating system  $>N\left(-\overset{|}{C}=\overset{|}{C}\right)_n-\overset{|}{C}=O^- \leftrightarrow >\overset{+}{N}\left(=\overset{|}{C}-\overset{|}{C}\right)_n=\overset{|}{C}-O^-$. One molecule receives a contribution from one polar structure, one from two polar structures and one from four polar structures. The large dipole moments increase as the number of contributing polar structures increases to such an extent that the moment of the molecule with four contributing polar structures is larger than that previously found for any molecule other than that of a salt or a zwitterion. The dipole moment values qualitatively confirm predictions of the relative polarities of the substances and make possible exact calculations of the relative contributions of the polar structures. The absolute amounts of these contributions are cal-

culated on the basis of reasonable values for the moments of the polar structures. A quantum mechanical calculation of the relative energies of the structures explains the quantitative deviations from the amounts of the contributions to be expected merely on the basis of the number of contributing polar structures.

PRINCETON, NEW JERSEY RECEIVED NOVEMBER 19, 1948

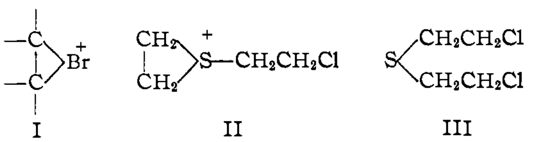
[CONTRIBUTION FROM THE WOLCOTT GIBBS LABORATORY OF HARVARD UNIVERSITY]

Kinetics of Hydrolysis and Displacement Reactions of β,β'-Dichlorodiethyl Sulfide (Mustard Gas) and of β-Chloro-β'-hydroxydiethyl Sulfide (Mustard Chlorohydrin)[1]

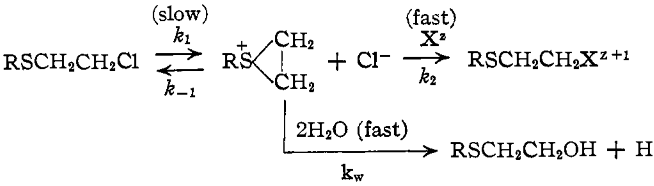
BY PAUL D. BARTLETT AND C. GARDNER SWAIN

Introduction

The existence of the ethylenebromonium ion (I) and its participation in bromination reactions were first postulated in 1937 by Roberts and Kimball.[2] An elegant demonstration of the participation of such ions in displacement reactions of β-bromoalkyl compounds was provided by Winstein and Lucas[3] in 1939. During World War II it was recognized by American workers that the closely analogous ethylenesulfonium ion (II) offered an attractive explanation of the *first-order* displacement reactions[4] of β,β'-dichlorodiethyl sulfide (mustard gas, III) a type of displacement kinetics not shown by any primary alkyl chloride.[5] Ogston, whose extensive studies of this reaction were the basis of most of the ideas used in the mustard program, observed certain facts which at the time appeared incompatible with the simple view of the mechanism expressed in eqn. 1 and indeed with any mechanism involving only this number of steps. The facts which presented the difficulty were: (1) that the "competition factor," defined as the ratio k_2/k_w for any molecule or ion X capable of reacting with the ethylenesulfonium ion, varied widely with the concentration of X in the case of chloride ion, whereas it was expected to be constant; and (2) that although, to a first approximation, the rates of reaction of mustard with all substances depended only upon the concentrations of mustard and of chloride ion, which are concerned in the first step of the mechanism, yet the initial measured first-order rate constant for the reaction of mustard with certain strong competitors such as sodium monothiophosphate was 10% greater than with water or weaker competitors.

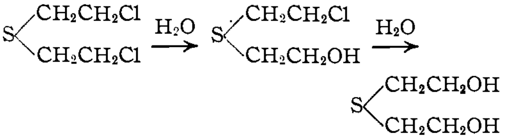


I II III



(1)

It was important to our work to obtain definite proof of the adequacy or inadequacy of Equation (1) to describe the displacement reactions of mustard gas. We therefore undertook some careful kinetic studies of the system and as a result were able to explain the above apparent anomalies satisfactorily within the scheme of Equation (1). The experimental approach had the following features. "Mustard chlorohydrin," β-chloro-β'-hydroxydiethyl sulfide, was prepared in a state of purity which permitted the two stages of mustard hydrolysis indicated in eqn. 2 to be studied separately. The progress of reaction was followed both by the convenient and accurate intermittent alkali titration of Peters and Walker[4] and by polarographic determination of the rate of liberation of chloride ion. The first of these methods was already adapted to following the kinetics of rapid reactions with half-periods of only a few minutes; we have adapted the polarographic method to the same purpose, thus permitting a comparison between the rates of liberation of chloride and hydrogen ions, which affords a test of the occurrence of appreciable concentrations of sulfonium ions during the reaction.



$$S\begin{array}{l}\diagup CH_2CH_2Cl\\ \diagdown CH_2CH_2Cl\end{array} \xrightarrow{H_2O} S\begin{array}{l}\diagup CH_2CH_2Cl\\ \diagdown CH_2CH_2OH\end{array} \xrightarrow{H_2O} S\begin{array}{l}\diagup CH_2CH_2OH\\ \diagdown CH_2CH_2OH\end{array} \qquad (2)$$

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[1] This work was performed during 1943-1944 under Contract NDCrc 136 between Harvard University and the National Defense Research Committee of the Office of Scientific Research and Development.

[2] I. Roberts and G. E. Kimball, THIS JOURNAL, 59, 947 (1937).

[3] S. Winstein and H. J. Lucas, *ibid.*, 61, 1576, 1581, 2845 (1939).

[4] R. A. Peters and E. Walker, *Biochem. J.*, 17, 260 (1923). A. G. Ogston, Peters Reports #34 (1941), #66 (1943), available through the British Ministry of Supply; *Trans. Faraday Soc.*, 44, 45 (1948).

[5] R. C. Fuson, C. C. Price and D. M. Burness, *J. Org. Chem.*, 11, 477 (1946). The hypothesis of the ethylenesulfonium ion was conceived independently by different workers. It was in use by the present authors late in 1941.