Some Studies of Benzenoid-Quinonoid Resonance

Part 2.—The Effect of Solvent Polarity on the Structure and Properties of Merocyanine Dyes

By H. G. Benson and J. N. Murrell

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

The SCF π-electron theory with bond length optimization, described in part 1, has been used to calculate the effects of solvent polarity on the structure and spectroscopic properties of a simple merocyanine dye. The calculations predict a minimum in energy and oscillator strength of the first absorption band over the range of solvent parameters used, but these extrema should not occur at the same solvent compositions. The measured u.-v. spectra can be interpreted from these results, and the n.m.r. chemical shifts, which change with solvent, can be correlated with calculated net atom charges.

1. INTRODUCTION

Many papers have been written on the effects of solvents on the electronic spectra of merocyanine dyes. These molecules can show very large shifts in the absorption bands on increasing the polarity of the solvent, and these shifts can be to higher or lower frequencies. The most widely accepted theory is based on the assumption that the ground and excited state can be represented as a mixture of benzenoid and quinonoid valence structures whose balance changes with the nature of the solvent. There are many studies of this theory; Platt[1] gives complete references up to 1956, Investigations in this paper refer to a molecule for which the two structures are as follows:
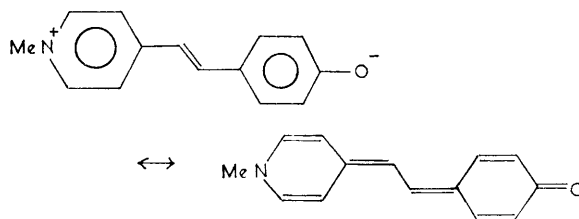
We use the π-electron theory with bond length optimization which was described in part 1 to study the geometry of the molecule and to explain the effect of solvent on its electronic and n.m.r. spectra.

In acid media the molecule is protonated on the oxygen and in protonic polar solvents there is presumably specific solvent nteraction with both the oxygen and nitrogen atoms. The work of Bayliss and McRae[2] has established that the solvent shifts of the merocyanine dyes is only substantial when such solvation can occur; in other words the bulk dielectric effect of the solvent has a small effect on the spectrum.

In part 1 of this series we have listed π-electron parameters for the groups, O, OH, N and NH. We shall assume that the N—Me group has the same parameters as NH. The effect of solvent will be simulated by choosing parameters for solvated

oxygen which lie between those for O and OH, and for solvated NMe by choosing parameters between those for NH and N. In other words we assume that a dipolar solvent will attach with its positive end to the oxygen and its negative end to the nitrogen, making the oxygen more and the nitrogen less electron attracting.

We assume that the one-centre core integrals and one-centre electron repulsion integrals are all linearly related to a solvation parameter k by expressions of the type

$$U(O\text{---}S) = (1-k)U(O)+kU(OH)$$

$$\gamma_{11}(N\text{---}S) = (1-k)\gamma_{11}(NH)+k\gamma_{11}(N) \qquad \text{etc.}$$

2. CALCULATIONS

Our calculations show that the dye in a non polar solvent ($k = 0$) should have the quinonoid structure. The resulting bond lengths and net charges are shown in fig. 1. The bond lengths in both rings are close to those found in part 1 for γ-pyridone, in which the NH and O are attached to the same ring. The results for the limiting form in highly polar solvents ($k = 1$), also shown in fig. 1, indicate that the molecule has a benzenoid structure with this set of parameters.
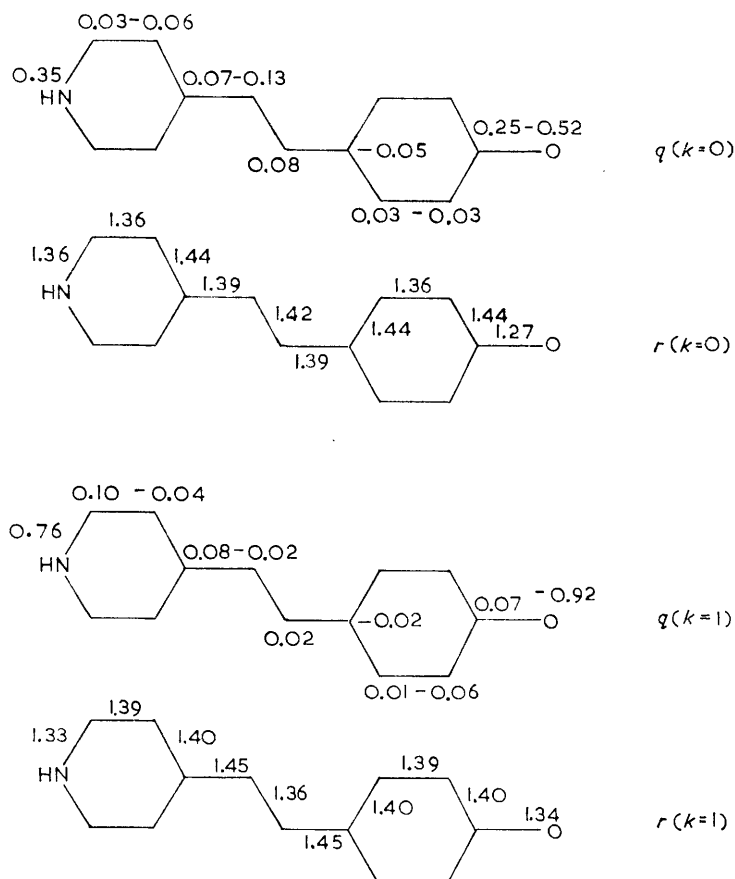

FIG. 1.—Bond lengths and net charges for the limits of non polar ($k = 0$) and polar ($k = 1$) solvents. To the limits of the accuracy specified there is 2-fold symmetry in each ring.

Fig. 2 shows the excitation energy to the first singlet excited state calculated on the assumption that the excited state can be represented by the electron configuration obtained by promoting an electron from the highest occupied to the lowest vacant molecular orbital. With increasing solvent polarity the absorption band shifts first to low energies and then to high, with the minimum being at $k = 0.2$. We also show in the figure the calculated oscillator strength (f). This shows a rapid decrease from $k = 0$ to $k = +0.4$ followed by a slow variation with a minimum at $k = 0.7$.
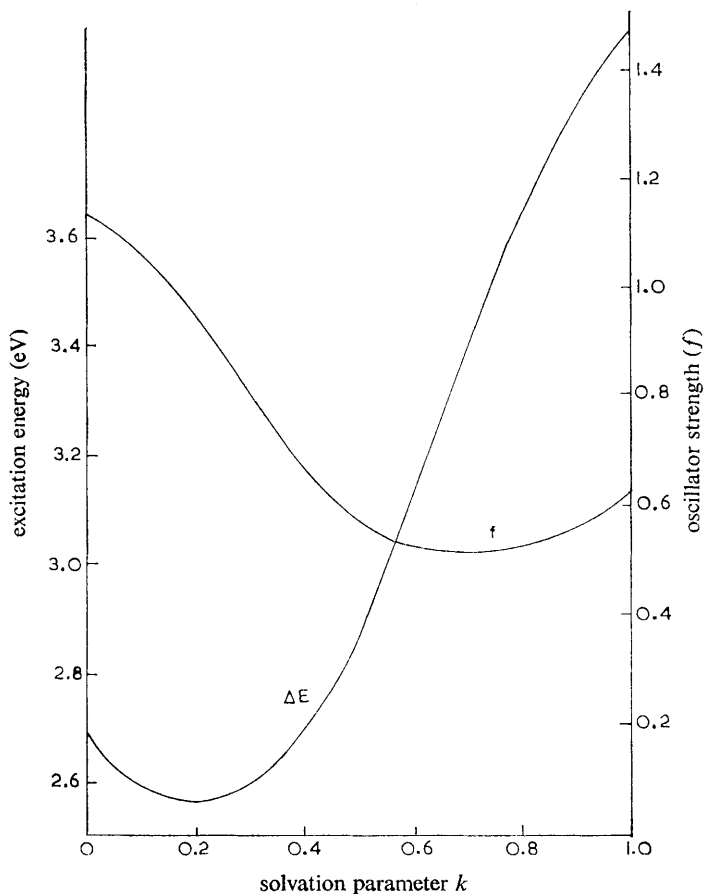

FIG. 2.—Calculated excitation energy and oscillator strength as a function of k.

The behaviour shown in fig. 2 is typical of many merocyanine dyes. However, we shall show that the region in which the excitation energy reaches a minimum cannot be investigated for the compound we are studying because it is insoluble in non polar solvents.

Fig. 3 shows the variation in π-electron charge at the carbon atoms labelled as shown. We correlate these charges with the proton chemical shifts in the n.m.r. spectra. The dominant feature in the range of $0.2 > k > 1$ is that there is little change in the electron densities at a, b, e and f but a large change in the densities at c and d.
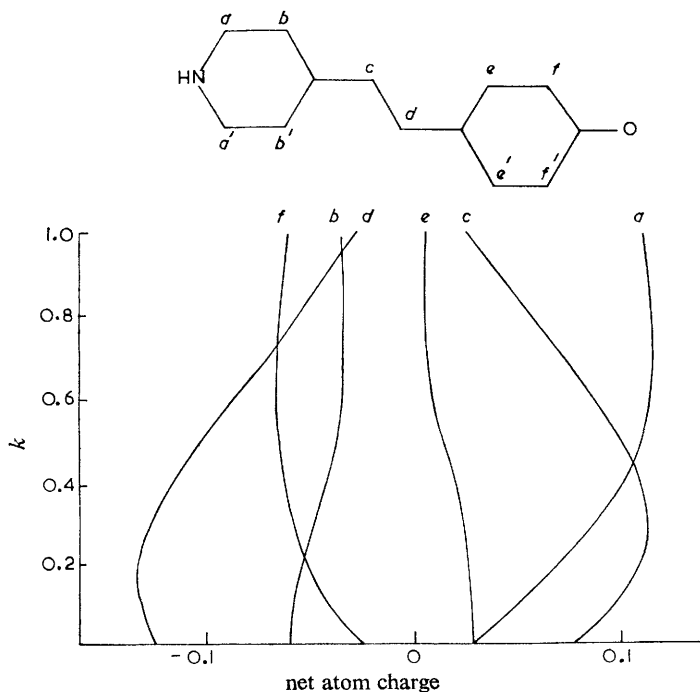
FIG. 3.—Calculated net atom charges as a function of k.   To the limits of ± 0.01 the charges at the primed and unprimed positions are equal.

3.   THE ELECTRONIC SPECTRUM

The compound under investigation is insoluble in hydrocarbon solvents and only sparingly soluble in chloroform.   It is readily soluble in methanol and other solvents
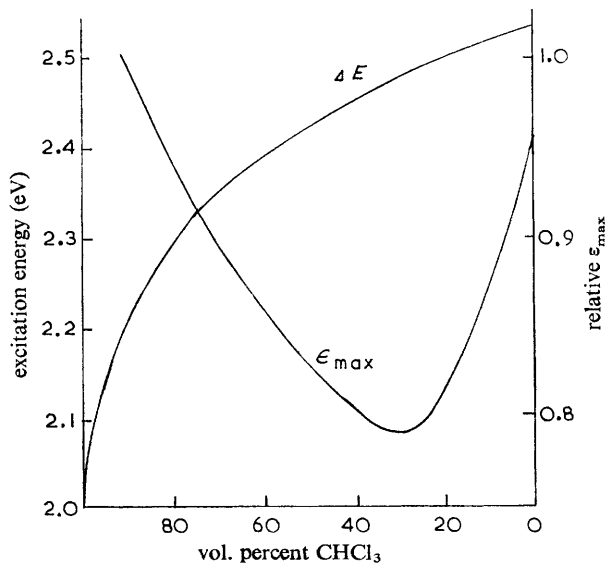

FIG. 4.—The variation of the excitation energy and ε_{max} (relative to 90 % CHCl$_3$ solutions) with solvent composition.

of comparable polarity, and acid-base equilibria are established. In order to concentrate our attention on the spectrum of the unprotonated dye, we have used solvents which contain a small amount of KOH.

The visible absorption band in $CHCl_3/CH_3OH$ mixtures has a maximum which varies in the range of 618 nm ($CHCl_3$) to 490 nm (CH_3OH). In pure $CHCl_3$ the band has a shoulder at 589 nm but this disappears with the addition of less than 5 % CH_3OH, leaving a single peak of half-width approximately 2500 cm^{-1}. Fig. 4 shows the change in the excitation energy and relative max ε with solvent composition. There is no significant change in band width over the concentration range 10-100 % MeOH and hence ε_{max} is an adequate measure of the oscillator strength.

The calculated value of the excitation energy is in reasonable agreement with that observed. From the fact that no minimum is seen in the excitation energy with changing solvent polarity, as it is with many merocyanine dyes, we deduce that $CHCl_3/CH_3OH$ mixtures cover the range $k = 0.2 - 1.0$. However, our calculations do predict a minimum in the oscillator strength in this range, which is found experimentally.

4. NUCLEAR MAGNETIC RESONANCE

Nuclear magnetic resonance studies were initiated in the hope that the change from quinonoid to benzenoid structures could be followed from a change in coupling constants. However, in the range of $CHCl_3/CH_3OH$ solutions that could be studied, 10-100 %, there were no detectable changes in any coupling constant. On the other hand, the chemical shifts of all protons showed significant changes with solvent composition.

The n.m.r. spectrum of the dye can be analyzed as two AA′BB′ systems and one AB, and to facilitate the analysis deuterated species were prepared. The spectra of the compounds with deuterium at a, $a′$ and $c′$, and at f and $f′$ allowed a complete assignment apart from an ambiguity in the AA′BB′ cross ring coupling constants. The results of an analysis using the LAOCOON program are given in table 1.[3]

TABLE 1.—ANALYSIS OF THE N.M.R. SPECTRUM IN CH_3OD. CHEMICAL SHIFTS WERE MEASURED WITH RESPECT TO A FREQUENCY LOCK ON THE CH_3 RESONANCE OF THE SOLVENT.

chemical shift [τ]		coupling constants [Hz]	
$a,a′$	1.96	J_{ab}	6.4
$b,b′$	2.53	J_{cd}	15.5
c	3.45	J_{ef}	8.5
d	2.56	$J_{ab′}$	0.4
$e,e′$	2.80	$J_{ef′}$	0.1
$f,f′$	3.56		
		$\left| J_{aa′}+J_{bb′} \right|$	4.0
		$\left| J_{aa′}-J_{bb′} \right|$	2.0
		$\left| J_{ee′}+J_{ff′} \right|$	4.6
		$\left| J_{ee′}-J_{ff′} \right|$	1.0

Although one can expect no simple relationship between chemical shift and π-electron densities in this type of molecule, for, amongst other things, there is an appreciable contribution from the ring currents, it can be seen that the orders $\tau_b > \tau_a$ and $\tau_f > \tau_e$ are consistent with the results of fig. 3 which shows that for each pair there is a greater negative charge on the carbon atom with the more shielded proton. For the pair of protons c and d, however, the correlation is inverted. In styrene

itself the α proton has a τ value approximtely 1.0 less than the β protons, and this is attributed to the benzene ring current. The difference we observe could therefore be attributed to a greater ring current in the nitrogen ring than in the oxygen ring.

Fig. 5 shows how the difference in chemical shifts for the three proton pairs in the spectrum change with solvent composition. All resonances move down-field relative to internal CH_3 (in CH_3OD) as the amount of CH_3OD is increased. The largest changes occur with high $CHCl_3$ concentrations, but for reasons of solubility no spectrum could by obtained in 100 % $CHCl_3$. We attach no significance to the overall movement because the CH_3 resonance is sensitive to the composition of the solvent. The spectral region covered by protons d, b and e becomes quite confused in the region of 50 % (by volume) CH_3OH, and no detailed spectral analysis was attempted. Fig. 5 therefore shows only the dominant features of the chemical shift differences.
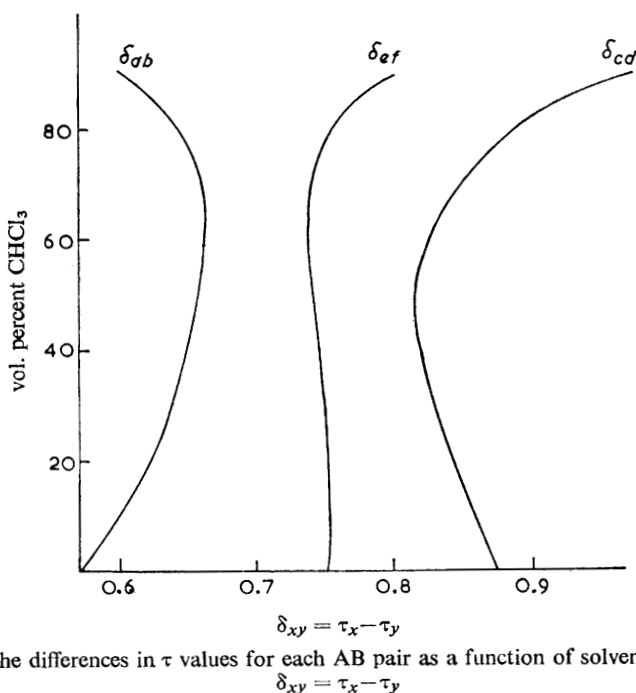

FIG. 5.—The differences in τ values for each AB pair as a function of solvent composition.
$$\delta_{xy} = \tau_x - \tau_y$$

We note that δ_{cd} shows the greatest change with solvent composition. From fig. 3 we see that the largest difference between the electron densities in atoms c and d occurs in the region $k = 0.2\text{-}0.3$ and this should bring the τ values closer together (in opposition to the ring currents). The differences in the charges for the pairs a—b and e—f show small changes in the region $k = 0.2\text{-}1.0$; likewise the chemical shift differences are smaller. Thus although the n.m.r. chemical shifts cannot be simply related to π-electron densities, the results of fig. 3 explain some of the features that we have observed.

5. CONCLUSIONS

The results in this and the previous paper show that a π-electron SCF theory with bond-length optimization accounts satisfactorily for the properties of molecules

whose structures and stabilities are traditionally described in terms of benzenoid-quinonoid resonance. It was shown in the previous paper, by the example of some Wheland intermediates, that those molecules for which resonance can be invoked have additional stability in molecular orbital theory. However, this is only developed to its full extent when optimum bond lengths are used. Although the valence-bond-resonance theory in many cases explains qualitatively orders of stability and charge distributions it is difficult to put the theory into quantitative form. Molecular orbital theory does not have this limitation.

EXPERIMENTAL

The merocyanine was obtained by condensing parahydroxybenzaldehyde with γ picoline-methiodide in methanol. After refluxing for 20 min and cooling, red crystals of the mero-cyanine acid salt precipitated. These were dissolved in water and filtered into concentrated ammonia to give the neutral dye. This was recrystallized from methanol and dried over P_2O_5 to give blue hygroscopic crystals. The deuterated species required for the n.m.r. analysis were prepared in a similar way using deuterated benzaldehyde or deuterated γ-picolinemethiodide. Deuteration was achieved by refluxing the parent compound with D_2O for several days until an n.m.r. analysis showed greater than 97 % deuteration. For benzaldehyde deuteration was assisted by a trace of triethylamine.

N.m.r. spectra were measured on a Varian HA100 instrument and U Vspectra were obtained with a Cary 14 spectrophotometer.

[1] J. R. Platt, *J. Chem. Phys.*, 1956, **25**, 80.
[2] N. G. Bayliss and E. G. McRae, *J. Amer. Chem. Soc.*, 1952, **74**, 5803.
[3] A. A. Bothner-By and S. Castellano, Carnegie-Mellon University, Pittsburgh, Pa.