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The stable and photochemical isomers of some merocyanines: a ^{1}H NMR and theoretical CS INDO study of the structures and electronic spectra

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Abstract

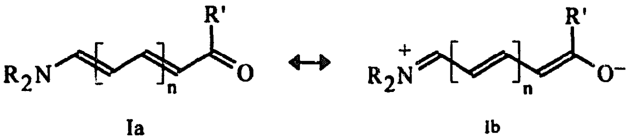
The conformations and electron distributions of four merocyanines were investigated by ^{1}H NMR spectroscopy in low-polarity solvents and CS INDO calculations on the isolated molecules. The two approaches gave consistent results. Some information about the torsional dynamics of these dyes in the ground state was obtained from a rough ^{1}H NMR line shape analysis, and ^{1}H NMR experiments performed on photolysed samples made it possible to identify the conformations of the longest-lived photoisomers of three compounds and to provide an estimate of their lifetimes.

The effects of an increase in the solvent polarity on the structures and absorption spectra of the four dyes were investigated by, respectively, measuring their ^{1}H NMR spectra in three more solvents with increasing dielectric constants, and CS INDO CI calculations of the electronic spectra, including solvent shift effects, evaluated within the classical solvaton model. All the results related to the medium polarity effects could be interpreted according to the generally accepted description of the merocyanine chromophore as the resonance hybrid of a neutral and a charge-separated form. © 1997 Elsevier Science S.A.

Keywords: Stable isomers of merocyanines; Photochemical isomers of merocyanines; ^{1}H NMR spectroscopy; CS INDO Calculations

1. Introduction

The chromophore of merocyanine dyes consists of a polymethine chain terminated by a carbonyl and a dialkylamino group. An example of open chain merocyanines is shown below.



The large difference between the electronegativities of the nitrogen and oxygen terminal atoms confers a strong asymmetry to the electronic structure of these dyes, which can be described in terms of resonance between forms Ia and Ib, the degree of charge separation being influenced by the polarity of the molecular environment [1]. This, together with other remarkable properties of these compounds, such as the often strong solvatochromism in the visible spectral region [2], the high second order polarizability [3,4], and the ability to photosensitize the formation of singlet oxygen [5], are exploited for a number of applications of these dyes. The dyes are, in fact, employed in medicine as diagnostic and therapeutic agents [6], as probes in studies of biological membranes [7] and as indicators in biochemical analysis [8], as silver halide sensitizers in photography [9] and as electrophotographic receptors [10], in non-linear optical materials for second harmonic generation [3,4], and as partners of spiropyrans in the coloured–colourless pair of photochromic materials [11].

The experimental observations most largely employed to probe the response of the electronic structure of merocyanines to a change in polarity of the medium have been the UV–visible [2,12], ^{1}H NMR [12] and ^{13}C NMR [13] spectra. Radeglia and Dähne showed that, although the dependence of the maximum absorption wavelength of the simple merocyanines I (R is CH_3, R' is H, $n = 1, 2, 3$) on the number of double bonds was less than linear in low-polarity solvents, i.e., similar to the behaviour of polyenes, it became linear, as

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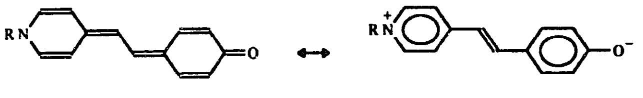
observed with symmetrical polymethine cyanines, in polar solvents [12]. The reference to the two model chromophores—polyenes, characterized by alternation of the π bond orders and uniformity of the π electron densities at carbon atoms, and polymethine cyanines, having uniform π bond orders and alternate π electron densities at the carbon atoms of the chain—provided a sounder basis to the early explanation of Brooker and coworkers for the observed solvatochromism of merocyanines [1]: the neutral form Ia prevails over the zwitterionic form Ib in low-polarity solvents, giving non-uniform π bond order distribution and polyene-like spectroscopic behaviour. On the other hand, as a result of the increase of the relative weight of structure Ib, a more uniform distribution of π bond orders and polymethine-like spectroscopic behaviour, with a bathochromic shift of the lowest energy band, are obtained in polar solvents, so that positive solvatochromism is observed. However, negative solvatochromism can arise when the terminal nitrogen and oxygen atoms form parts of larger groups or heterocycles having stronger electron donating and/or electron accepting abilities [1,14]. As a result, the contribution of the zwitterionic structure is already comparable with that of the neutral form in low-polarity solvents and becomes overwhelming upon increasing the solvent polarity, so that a blue shift of the lowest-energy absorption band results. Indeed, for merocyanines having strong, but not too strong, electron donating and accepting terminal groups, an inversion of solvatochromism could be observed [14], the inversion point being interpreted as the solvent polarity at which the electronic structure of the dye was closest to the polymethine cyanine model.

^{1}H and ^{13}C NMR spectroscopy were also employed to reveal solvent polarity-induced changes in the electronic structure and geometry of merocyanines. Radeglia and Dähne found that the ^{1}H and ^{13}C chemical shifts of the polymethine chain atoms of two merocyanines of type I and the corresponding vicinal H–H scalar spin coupling constants changed regularly, almost linearly, with the solvent polarity measured by the ET empirical parameter [12]. Such changes were observed closely to parallel (respectively) the changes in π electron densities and in π bond orders obtained from two approximate quantum chemical calculations, and were interpreted in terms of the neutral zwitterionic structure description, the weight of the latter increasing with solvent polarity. Similar observations were made and similar explanations were given for two merocyanines containing a benzene ring in the polymethine chain and also showing positive solvatochromism [15].

Numerous theoretical studies, attempting to describe the solvent effects on the electronic structure and spectra of merocyanines, have been reported during recent decades [16–21]. A common aspect of almost all these papers [16–18,20,21] was the study of the same prototypical merocyanine M (R is H, CH$_3$), regarded as a resonance hybrid of a neutral (quinonoid) form Ma and a charge-separated (benzenoid) form Mb, representative of the molecule in the extreme cases of apolar and strongly polar media.



Ma Mb

The cited papers, however, differed from one another in the model employed to incorporate the solvent effects into the SCF calculations. Such models, generally implemented at a semiempirical π electron [16] or all valence electron [17–21] level, were based either on a continuum [17,19,21] or on a discrete [18] picture of the solvent, but even more elementary simulations of the solvent were attempted [17,20]. Leaving aside any detailed analysis of theoretical work on merocyanines, here we note that no homogeneous picture has been provided until now for the changes in structure and spectra accompanying a change in solvent polarity. As an example, for the merocyanine M, the virtual charge model, as applied by Botrel et al. [17] within the CNDO/S method, predicted that, with increasing solvent polarity, the colour band would initially shift to the red (positive solvatochromism) and then to the blue (negative solvatochromism), whereas, according to the reaction field model recently applied by Albert et al. at the INDO level [21], the solvatochromism of M should be positive in the whole range of solvent polarity. On the other hand, experiments performed in pyridine–water [1](b) and chloroform–methanol [16] mixtures revealed a negative solvatochromism throughout the solvent binary composition range. The behaviour in less polar solvents, however, remained unexplored because of solubility limitations. Thus, although the interpretation of the observed properties of merocyanines in terms of the resonance of a neutral and a zwitterionic structure, the relative weights of which change with the polarity of the solvent, is qualitatively acceptable, the application of this scheme requires caution considering that the corresponding theoretical framework is still fragmentary, and that each compound can reveal its specificity by showing deviations from the predictions of the model.

With this paper, we undertake a combined, experimental and theoretical, study of the photochemical behaviour and the excited-state properties of the four merocyanines in Fig. 1. Of these, N1 and N2 are prototype compounds representative of the tri- and pentamethine chromophores, and N3 and N4 are new merocyanines, each featuring a specific modification of the original pentamethine chromophore: N3 incorporates a fused benzene ring, and N4 features a double, locally symmetric carbonyl termination. Our purpose is, similarly to our previous work on three asymmetric cationic polymethine cyanines [22], to investigate the consequences of the large difference in the electronic properties of the end groups of merocyanines for their excited-state properties, thus showing their similarities with the two reference models, the polyene and the polymethine cyanine, and their specificities. The present paper is introductory to the photochemical study and has a twofold purpose: we first establish, through ^{1}H NMR spectroscopy, the conformations of the most stable ground-state

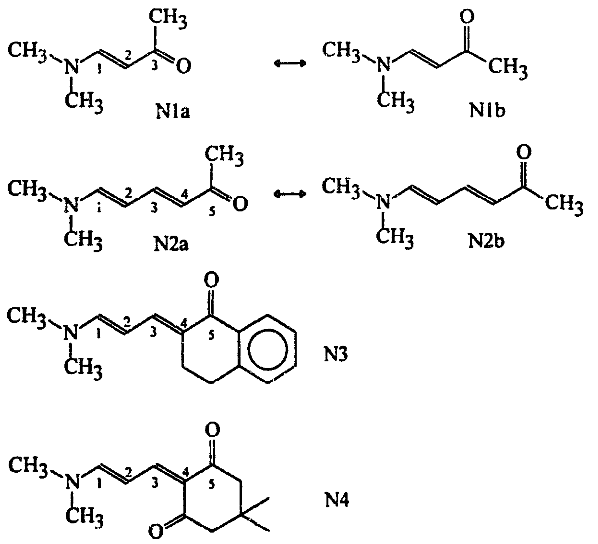


Fig. 1. The merocyanines investigated.

isomers and of the longest-lived photoisomers of merocyanines N1–N4, also obtaining information about their electronic structures and how these depend on the solvent polarity; the interpretation of these observations is supported by the results of CS INDO calculations of the structures and electron density distributions of these compounds. We shall then discuss their solvatochromism on the basis of selected experimental data and a simple theoretical approach using the solvaton model [23] as an introduction to a forthcoming study of this problem based on a more comprehensive theoretical treatment.

2. Computational details

In the theoretical part of the work, we calculated structures and electronic spectra of the stable isomers of N2, N3 and N4 (Fig. 1) using the CS INDO CI method, which has proved reliable in predicting conformational and spectroscopic properties of large conjugated molecules ([24] and references cited therein). The general description of the CS INDO method can be found in ref. [24]. Here we give only a few details concerning parametrization, geometries and configuration interaction (CI). Briefly:

1. The CS INDO screening constants $k_{\alpha\beta}$, defined on a hybrid AO basis set (α, $\beta=\sigma$, π, n) [25], were given the following values: $k_{\sigma\sigma}=1$, $k_{\pi\pi}=0.55$, $k_{\sigma\pi}=0.68$, $k_{n\pi}=0.64$, $k_{n\sigma}=0.74$, $k_{nn}=0.71$.
2. The two-centre repulsion integrals were calculated according to Ohno and to Klopman [26].
3. For the calculations of the core repulsion energy E^{CR}_{AB} [24a], the atomic pair parameter α_{CO} was taken equal to 1.25 (a.u.)$^{-1}$ on the basis of C–O bond length optimization in some test molecules. All other α_{AB} parameters were kept equal to 1, as in the previous CS INDO applications.
4. The bond lengths of the chromophoric chains were optimized at the CS INDO SCF level, and fixed standard values were assigned to all other geometrical parameters.
5. Transition energies, oscillator strengths (f) and electronic distributions of the ground and excited states were derived from CI calculations, both limited to single excitations (S-CI) and including single plus double excitations (S+D-CI). For the single excitations the MO active space included all the MOs of π (π^*) and n types, whereas for the double excitations a MO active space of smaller dimensions was used.

The solvent shift effects on the electronic spectra were calculated within the simple solvaton model, in the improved version proposed by Heidrich et al. [23], already adopted by us to evaluate the electrostatic solvation energy at equilibrium [24b,27,28]. In practice, according to this model the equilibrium solute–solvent interaction energy in an electronic state, say the ground state S_0, is expressed by

$$E^{\Sigma S} = -\frac{1}{2}\left(1-\frac{1}{\varepsilon}\right)\sum_{A}\sum_{B}\frac{Q_A Q_B}{R_{AB}+R_{eff}}$$

where ε is the static dielectric constant of the solvent, Q_A and Q_B are the net charges on atoms A and B in the vacuum, R_{AB} is the interatomic distance, and R_{eff} is an average effective atomic radius (taken equal to 4 a.u.).

Following the Franck–Condon transition to the excited electronic state, the net atomic charges instantaneously change ($\approx 10^{-15}$ s) from Q_A to Q_A^*, but the solvaton charges, representing the local reaction fields generated by the oriented solvent dipole distribution, retain the values acquired in the starting equilibrium state. Thus, the difference between the solute–solvent interaction energy in the excited state $E^{\Sigma S*}$ and that in the ground state $E^{\Sigma S}$ is given by

$$\Delta E^{\Sigma S} = E^{\Sigma S*} - E^{\Sigma S} = -\frac{1}{2}\left(1-\frac{1}{\varepsilon}\right)\sum_{A}\sum_{B}\frac{\Delta Q_A Q_B}{R_{AB}+R_{eff}}$$

where $Q_A = Q_A^* - Q_A$. The transition energies in a solvent with a given dielectric constant ε (ΔE_S) were obtained by adding $\Delta E^{\Sigma S}$ to the transition energy calculated for the isolated molecule (ΔE_v).

3. Experimental section

Compounds N1–N4 were synthesized and purified as described previously [29–31]. Highly deuterated benzene, toluene, acetone and methanol (Aldrich) were employed for the NMR measurements. Carbon tetrachloride, cyclohexane and dimethyl sulphoxide (Merck) were of either analytical or spectrophotometric grade.

All NMR spectra were measured on a Bruker AMX 400 WB spectrometer operating at 9.395 T, equipped with a 5 mm X/H inverse probe-head. Proton and carbon-13 spectra were acquired by standard pulse sequence. In the case of carbon-13, a WALTZ-16 sequence (proton soft pulse length

100 μs) was employed for proton broad band decoupling. Proton–proton nuclear Overhauser effects (NOEs) were measured as steady-state NOEs, obtained as the difference between the on-resonance selective saturated spectra and the corresponding off-resonance irradiated spectra. Saturation of irradiated multiplets was obtained by a saturation pulse train of 3.2 s total length composed of 100 ms pulses whose frequencies were swept cyclically over all the peaks constituting the irradiated multiplets.

Solutions of N1, N2 and N3 in benzene-d_6 and methanol-d_4 were photolysed at room temperature with a glass-filtered medium-pressure mercury lamp. Because of the shorter lifetime of the N4 photoisomer, toluene-d_8 and methanol-d_4 solutions of this merocyanine were photolysed with the same apparatus at about 215 K. The ^{1}H NMR spectra were recorded at different irradiation times and at different delay times after irradiation. UV–vis absorption spectra were measured on a Perkin-Elmer λ15 spectrophotometer.

4. Results

4.1. ^{1}H NMR spectral data

The ^{1}H chemical shifts δ and H–H scalar spin coupling constants J of the merocyanines N1–N4 in four different solvents are reported in Table 1. The reported assignment of the signals and the identification of the most stable isomers as the ones depicted in Fig. 1 resulted unambiguously from NOE spectra in carbon tetrachloride (N1) and in benzene (N2–N4). In fact, a NOE was observed in all cases between H_1 and H_2 on one side and the $N(CH_3)_2$ protons on the other. A NOE was also observed, with comparable intensities, between the CH_3CO protons and both H_1 and H_2 of N1 and H_3 and H_4 of N2, indicating that, at room temperature, the two conformations in Fig. 1 are present in comparable amounts in solutions of these two compounds. As the same, narrow singlet is observed for the CH_3CO protons in all solvents, we conclude that twisting about the C_2–C_3 bond of N1 and the C_4–C_5 bond of N2, leading to the interchange of the two sketched conformers, always occurs rapidly compared with the NMR time-scale: assuming a frequency difference $\Delta\nu$ between the CH_3CO signals of the two conformers of the order of 50–100 Hz, deduced from the separation between the N-methyl signals of N1 in methanol (104 Hz) and of N4 in all solvents (from 40 to 120 Hz, see Table 1), we may estimate the room temperature rate constants for the N1a↔N1b and N2a↔N2b interchanges to be much larger than their coalescence values [32], $2\pi p\Delta\nu = 150$–$300\ s^{-1}$, p being the mole fraction of the starting conformer and taken equal to 0.5. This, in turn, combined with the assumption of a typical range of values for a monomolecular pre-exponential factor, 10^{11}–$10^{14}\ s^{-1}$, sets an upper limit to the activation energy for the twisting about the C_2–C_3 bond in N1 and about the C_4–C_5 bond in N2 of 60 ± 10 kJ mol^{-1}. On the other hand, the appearance of the $N(CH_3)_2$ proton signals is more variable and suggests significant differences in the dynamics of twisting about the N–C_1 bond in different merocyanines and solvents. In fact, whereas for N2 and N3 only one signal is observed in all solvents, suggesting an extension of the previous kinetic estimates to the torsion about the N–C_1 bonds of these compounds, two well separated, narrow signals are observed for N4 in all solvents, with some broadening only in carbon tetrachloride. Therefore, the previously estimated 60 ± 10 kJ mol^{-1} activation energy is a lower limit in this case. For N1, a singlet with a halfwidth of ≈ 5 Hz is found in benzene; it broadens to ≈ 15 Hz in carbon tetrachloride, to ≈ 30 Hz in acetone and finally splits into two rather broad signals with halfwidths of about 20 Hz in methanol. Therefore, the temperature of the samples in these

Table 1

^{1}H NMR spectral data for merocyanines N1–N4. δ values are in ppm, J values in Hz. Solvents: C = carbon tetrachloride, B = benzene, A = acetone, M = methanol

Compound	Solvent	δ_1	δ_2	δ_3	δ_4	$\delta_{N\text{-Met}}$	$\delta_{\text{Met-CO}}$	J_{12}	J_{23}	J_{34}
N1	C	6.61	4.22			2.28	1.29	12.8		
	B	7.57	5.18			2.20	2.35	12.8		
	A	7.56	5.12			2.98	2.10	12.9		
	M	7.83	5.30			3.32, 3.06	2.27	12.7		
N2	C	5.89	4.34	6.32	5.03	2.22	1.38	12.8	11.3	14.9
	B	6.15	5.15	7.59	6.35	2.22	2.39	12.8	11.4	14.8
	A	7.05	5.29	7.38	5.84	3.06	2.18	12.7	11.6	14.6
	M	7.22	5.47	7.63	5.94	3.15	2.34	12.5	11.6	14.6
N3	C	6.07	4.43	6.67		2.27		12.65	12.2	
	B	6.36	5.29	8.32		2.28		12.5	11.9	
	A	7.18	5.43	7.66		3.14		12.5	12.2	
	M	7.35	5.60	7.88		3.21		12.24	12.28	
N4	C	6.49	6.43	6.92		2.45, 2.55		12.5	12.1	
	B	6.37	7.78	8.51		1.9, 2.1		12.2	12.9	
	A	7.80	7.37	7.89		3.27, 3.5		12.1	13.3	
	M	8.02	7.52	8.08		3.39, 3.55		11.7	13.8	

Table 2
Polymethine-proton NMR data of the photoisomers of compounds N2–N4. Solvents: B = benzene, T = toluene, M = methanol. N4p data were measured at 210 K, N2p and N3p data at 300 K. τ_{25} is the estimated photoisomer lifetime at 25°C

Compound	Solvent	δ_1	δ_2	δ_3	δ_4	J_{12}	J_{23}	J_{34}	τ_{25}
N2p	B	6.30	7.52	6.59	5.88	12.9	≈ 12	10.6	days
N3p	B	6.39	7.74	6.64		13.5	11.2		25 min
N4p	T	10.55	5.0	8.71			≈ 11	≈ 11	seconds or shorter
	M	10.16	5.92	7.99			11.5	12	

experiments, 300 K, roughly coincides with the coalescence temperature for the interchange of the *N*-methyls, and 60 ± 10 kJ mol^{-1} is now, subject to the validity of the mentioned assumptions, an estimate of the activation energy for twisting about the N–C_1 bond of N1 in the more polar solvents.

By looking at the data in Table 1, we note that the chemical shifts of the polymethine protons of N1, N2 and N3 show a uniform oscillatory behaviour: in all solvents, H_1 is deshielded relative to H_2, which is shielded relative to H_3, which is deshielded relative to H_4. For N4, the chemical shifts of H_1, H_2 and H_3 still show oscillatory behaviour, but strongly reduced relative to the other compounds and with an exception in benzene. On increasing the solvent polarity, we observe a general and regular deshielding of the polymethine protons: the chemical shifts increase by about 1 and 0.2 ppm on moving from carbon tetrachloride to acetone to methanol. Benzene provides a well known exception in this trend [33], as it causes a general deshielding of the polymethine protons relative to carbon tetrachloride, a solvent with a similarly low polarity. The H_1–H_2 scalar spin coupling constants J_{12} are independent of solvent polarity for N1, and show a tendency to decrease with increasing solvent polarity for the other compounds, particularly for N4. J_{23} also shows a particularly pronounced increase for this compound, being lower than J_{12} in carbon tetrachloride and becoming much higher in methanol. Although it is essentially independent of the solvent for N3, J_{23} increases slightly for N2 on increasing the polarity of the medium; as J_{34} slightly decreases, the oscillatory behaviour of the three J values of this compound is slightly damped on going from carbon tetrachloride to methanol.

The room temperature ^{1}H NMR spectra of compound N2 in all solvents employed show, in addition to the signals due to isomers N2a and N2b (Fig. 1), another series of signals attributable to a secondary species which is already present at its equilibrium abundance of ≈ 6% as soon as its ^{1}H NMR spectrum could be measured, i.e., a few minutes after sample preparation. In benzene, these signals fall at 6.28 ppm (d, $J = 12.8$ Hz), 5.37 ppm (t, $J \approx 12$ Hz), 8.18 ppm (dd, $J = 11.5$, 14.5 Hz) and 6.76 ppm (d, $J = 14.6$ Hz). A NOE was observed between the first two signals and the $N(CH_3)_2$ signal at 2.26 ppm, between the first and third and between the second and fourth signals, leading to their assignment to protons H_1 to H_4, respectively. Apparently, the geometry of this species is the same as that of the main isomers N2a and N2b as far as the $(CH_3)_2N(CH)_4$ moiety is concerned, a conclusion also supported by the generally small deshielding of the four signals relative to the corresponding ones of the main species (slightly more pronounced for H_3) and by the similarity of the J values. Very similar behaviours were observed in the other three solvents. In no case could we observe a CH_3CO signal or any NOE between the H_3 or H_4 bands and any other signal in the high-field region of the spectrum. We cannot, therefore, identify this secondary species.

A secondary isomer was also observed in solutions of N3, its amount changing from sample to sample but generally increasing with time. It turned out to coincide with the photoisomer of this dye, as its signals increased upon irradiation of its solutions in benzene with a mercury lamp and slowly decreased, in the dark, to an equilibrium abundance of 5–6% of the stable isomer population at 296 K. Its main ^{1}H NMR data are reported in Table 2 and its configuration, obtained by twisting of the starting species about the C_3–C_4 bond, is shown in Fig. 2. This assignment results from the observation of a NOE between the singlet of $N(CH_3)_2$ at 2.38 ppm and the H_1 and H_2 signals, between H_1 and H_3, and between H_3 and the CH_2 signal at 2.92 ppm. The changes in the chemical shifts of the polymethine protons relative to those of the starting isomer, strong deshielding and shielding for H_2 and H_3, respectively, and a negligible shift of the H_1 signal are

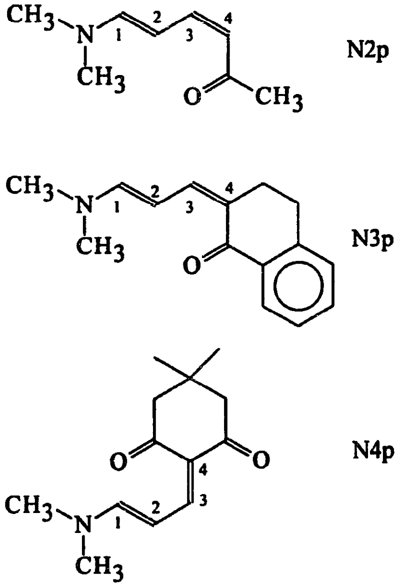


Fig. 2. The longest-lived photoisomers of compounds N2–N4.

also consistent with the change in the C=O group position obtained by photoisomerization to N3p. The back-isomerization of N3p to N3 was monitored in benzene by measuring and analysing the ^{1}H NMR spectra at different times after irradiation: a lifetime estimate of ≈ 25 min at 296 K was obtained, suggesting, in the assumption of a 10^{13} s^{-1} pre-exponential factor, a barrier of the order of 92 kJ mol^{-1} for the twisting about the C_3–C_4 bond.

Although no long-lived photoisomer was observed for N1, a very long-lived species was obtained upon irradiation of N2 in benzene. Its main ^{1}H NMR spectral features comprise, similarly to N3p, a strong deshielding of H_2 and a shielding of H_3 relative to N2. These, together with the low J_{34} value, clearly lead, by analogy with the case of N3, to the assignment of the photoisomer configuration as N2p in Fig. 2, obtained from the starting species by twisting about the C_3–C_4 bond. The evolution of this species after irradiation is very slow: its NMR signals are still readily measurable several days after irradiation. If we assume a lifetime of the order of one day for this photoisomer, we get a lower-limit estimate for the ground-state C_3–C_4 torsional barrier of about 100 kJ mol^{-1}.

Finally, the photoisomer of N4 in toluene and methanol was too short-lived to be observable at room temperature. It could be frozen in and investigated by irradiating these samples and measuring their ^{1}H NMR spectra at temperatures of about 215 K (Table 2). The spectral signal pattern is the same in the two solvents, suggesting that the same photoisomer is obtained. A strongly deshielded doublet is observed at values of δ higher than 10 ppm, whereas the triplet is distorted and shielded by more than 1.5 ppm relative to the starting spectrum. This suggests a configuration of the type N4p in Fig. 2 for the photoisomer, obtained by twisting about the C_2–C_3 bond. It is obviously a crowded structure, with the H_1 and O atoms very close to each other and significant torsions about the polymethine C–C bonds, as confirmed by the decrease of both J_{12} and J_{23} and the very low room temperature lifetime, probably associated with a C_2–C_3 pre-twisted configuration.

4.2. *Calculated ground-state structures and absorption spectra*

The CS INDO ground-state bond lengths and charge distributions of the chromophores of compounds N2–N4 are reported in Fig. 3. Quite expectedly, the merocyanine N3 and its simpler homologue N2 exhibit a very similar pattern of bond lengths and charge distribution. They have the same negative charge on the N atoms and the same N–C_1 bond length. Proceeding along the polymethine chain, from C_1 to C_5, we find a similarly alternating behaviour of the C–C bond lengths, which are only slightly longer in N3 than in N2. The net charges on the C atoms are alternatively positive and negative and have similar values in the two compounds, with the aromatic substituent simply draining some negative charge from C_1, C_3 and O to C_2 and C_5. A good qualitative correlation is found for these two compounds between the calculated net charges at the polymethine C atoms and the chemical shifts of the H atoms bonded to them, and between the calculated polymethine C–C bond lengths and the corresponding vicinal H–H scalar spin coupling constants measured in carbon tetrachloride (compare Fig. 3 and Table 1). On the other hand, merocyanine N4 features, relative to the former two compounds, a more pronounced net charge alternation and more equalized C_1–C_2, C_2–C_3 and C_3–C_4 bond lengths. Whereas the latter feature is consistent with the closer values of J_{12} and J_{23} found in carbon tetrachloride with respect to the corresponding values for N2 and N3, the former is at variance with the very similar chemical shifts of the three polymethine protons measured in the same solvent. In particular, H_2 is strongly deshielded with respect to the corresponding protons of merocyanines N2 and N3. This is probably due to the anisotropic shielding effects caused by the neighbouring carbonyl group, here particularly pronounced as a result of the short distance between H_2 and the C=O group and of their favourable relative positions [34].

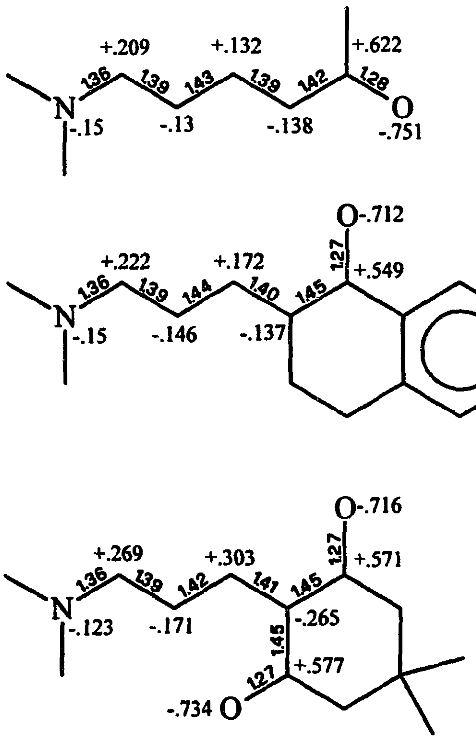


Fig. 3. Calculated ground-state bond lengths and corresponding charge distributions for the chromophores of merocyanines N2–N4.

Some properties of the most relevant singlet and triplet states of merocyanines N2–N4, resulting from CS INDO CI calculations, are reported in Table 3. As shown, the colour band is essentially due to the transition to the π_H–π_L^* state. This is the second excited singlet state for the first two molecules, whereas it is the third one for compound N4, according to the calculations on the isolated molecule. However, the solvent shift effects evaluated according to the simple solvaton model (see Section 2, Computational details) indicate that it should become the S_1 state for N3 and N4 in a highly polar medium. This state interchange results from a strong stabilization of the ground and excited π–π^* states relative

Table 3

Some electronic properties of the lowest singlet and triplet states of merocyanines N2–N4. ΔE are the transition energies from the ground state calculated in vacuum (v) and in a medium with $\varepsilon=40$ (s), and measured in cyclohexane (c) and dimethyl sulphoxide (d). All values are in eV. f values are the oscillator strengths of the transitions and μ values are the electric dipole moments in Debye

Compound	State	ΔE_v	ΔE_s	ΔE_c^{exp}	ΔE_d^{exp}	f	μ
N2	S_0						9.17
	S_1 ($n-\pi^*$)	3.20	3.85			0.00	3.24
	S_2 ($\pi_H-\pi_L^*$)	4.19	4.12	3.70	3.37	0.71	14.72
	T_1 ($\pi_H-\pi_L^*$)	2.28					
	T_2 ($n-\pi^*$)	3.09					
N3	S_0						6.83
	S_1 ($n-\pi^*$)	3.65	4.54			0.00	3.32
	S_2 ($\pi_H-\pi_L^*$)	4.27	4.09	3.21	2.84	1.15	12.31
	T_1 ($\pi-\pi^*$)	2.51					
	T_2 ($n-\pi^*$)	3.47					
N4	S_0						3.46
	S_1 ($n-\pi^*$)	3.26	4.23			0.00	4.36
	S_2 ($n-\pi^*$)	3.53	4.75			0.00	1.54
	S_3 ($\pi_H-\pi_L^*$)	3.88	4.01	3.04	3.01	0.81	6.73
	T_1 ($\pi_H-\pi_L^*$)	2.23					
	T_2 ($n-\pi^*$)	3.14					

to the $n-\pi^*$ states due to solvation. On the other hand, only a small solvent shift is calculated for the $\pi_H-\pi_L^*$ transition, slightly positive for N2 and N3, slightly negative for N4. These solvation effects agree roughly with the simple expectations based on the dipole moments calculated for the various states of the first two molecules. Indeed, the $n-\pi^*$ and $\pi_H-\pi_L^*$ states have, respectively, the smallest and the largest dipole moments, and these retain nearly the same orientation as the S_0 dipole moment. For N4, instead, the dipole moment magnitudes are closer to each other and bear no direct relationship with the calculated solvation effects. In fact, the S_1 and S_2 state dipole moments have different orientations from S_0, so that solvation is expected to cause a destabilization of these states. On the other hand, the dipole moment of the S_3 ($\pi_H-\pi_L^*$) state is larger than that of S_0 and parallel to it; in spite of this, S_3 is also slightly destabilized relative to S_0 in a polar medium. Most likely, this indicates that local electrostatic solute–solvent interactions, which are accounted for in the solvaton model but are blurred out in a global dipole moment description, become important in this case. To check these results, the absorption spectra of the three compounds were measured in a low-polarity solvent (cyclohexane, $\varepsilon=2.02$) and in a highly polar one (dimethyl sulphoxide, $\varepsilon=46.7$). As seen in a detailed analysis to be published elsewhere, these solvents do not give any specific effect with the solutes. The measured transition energies (Table 3) indicate that N2 and N3 undergo a moderate positive solvatochromism, in qualitative agreement with the theoretical predictions, whereas the absorption spectrum of N4, for which a slightly negative solvatochromism is calculated, is almost insensitive to the solvent polarity.

5. Discussion

The picture of the electronic structures and spectra of merocyanines N1–N4, and of their sensitivities to changes in the solvent polarity, that results from the reported data is characterized by gradual changes along the series of compounds. However, although similarities prevail among N1, N2 and N3, the derivative carrying two carbonyl groups exhibits significant peculiarities.

A high room temperature torsional freedom was observed in all solvents for N1 and N2 about the C–COCH$_3$ bond and for N2 and N3 about the C–N(CH$_3$)$_2$ bond. For N1, the kinetics of the latter torsion matches the kinetics of coalescence of the *N*-methyl ^{1}H NMR signals in the polar solvents, so that an increase in the N–C$_1$ bond order, brought about by an increase in the solvent polarity, leads to consequences observable at room temperature. The much slower torsion of N4 about the C–N(CH$_3$)$_2$ bond indicates a much higher N–C$_1$ π bond order, a result not reproduced by the bond length calculation. These pieces of information can be combined with other results, such as the scalar spin coupling constants and the back-isomerization kinetics, which reflect the polymethine chain C–C bond orders and lengths, and with the theoretical results to analyse the electronic structures of the four merocyanines in terms of relative weights of the resonance structures Ia and Ib and their relationship with the polyene and the polymethine cyanine models. Thus, the alternancy in the J values observed for N2, which is only slightly reduced in the polar solvents, together with the calculated alternancy in the C–C bond distances and the relatively high C$_3$–C$_4$ back-isomerization activation energy (≥ 100 kJ mol^{-1} in benzene), indicates a prevailing weight of the neutral form Ia and a polyene-like structure for this molecule, with only a small shift towards a more bond order equalized structure in the polar solvents. More equalized bond length and bond order distributions seem to characterize compounds N1 and N3. Although fewer data were collected for the former, and the conclusion as to its more polymethine cyanine-like structure relative to N2 rests only on the observed slower

N–C_1 torsion, the same conclusion about N3 is supported by the closer values of J_{12} and J_{23}, which become equal in methanol, and by the lower activation energy for the C_3–C_4 back-isomerization (≈ 92 kJ mol^{-1} in benzene), although it is not confirmed by the bond length calculations, which give very similar results for N2 and N3. For merocyanine N4, instead, two equivalent zwitterionic structures of type Ib can be written and probably prevail in the description of the electronic structure in polar solvents. This is concluded from the very slow twisting about the N–C_1 bond, suggesting a high bond order, and the rapidly increasing difference between J_{12} and J_{23} with increasing solvent polarity. On the other hand, the J values in the low-polarity solvents indicate an equalized distribution of bond orders, i.e., a polymethine cyanine-like structure, in keeping with the smoother bond length distribution and the more pronounced net charge alternation calculated for the isolated N4 molecule relative to N2 and N3. The photoisomer back-isomerization kinetics cannot give useful information for N4 because, as already mentioned, it is probably strongly accelerated as a result of a pre-twisted configuration of the sterically hindered C_2–C_3 *cis*-like photoisomer.

The different weights of the resonance structures Ia and Ib in different merocyanines and, for the same compound, in different solvents are reflected by the theoretical and experimental absorption spectra. The moderate positive solvatochromism calculated and observed with N2 and N3 is consistent with the structural conclusion previously given, i.e., that both molecules have essentially a polyene-like Ia structure in low-polarity media and increasing polymethine cyanine character with increasing solvent polarity, the phenomenon being slightly more pronounced for N3. On the other hand, N4 exhibits almost no solvatochromism and the calculated $\pi_H \rightarrow \pi_L^*$ transition energy is even higher in the polar solvent than in vacuum. These results are consistent with the already high polymethine cyanine character suggested by the structural calculations and the observations in weakly polar solvents. The increase in the bond length alternancy associated with the increased weight of the zwitterionic form Ib in polar solvents is confirmed by a corresponding alternancy in the J values, but results in a negligible solvatochromism, rather than in a blue shift of the absorption maximum. A more detailed analysis of the solvent effects on the structure and spectra of merocyanines, based on a more comprehensive theoretical description of solute–solvent interactions in the ground and the excited state, is the subject of a paper in preparation.

Let us finally spare a few comments about the photophysics and photochemistry of merocyanines N2–N4. According to the theoretical spectra in Table 3, all isolated molecules have S_1 states of n–π^* nature and T_1 states of π–π^* nature. This suggests low fluorescence and good intersystem crossing yields to be expected in low-polarity media, even though the quite high S_1–T_1 energy gap could result in a reduction of the rate of the latter decay process. As a result of the general strong stabilization of the π_H–π_L^* states due to solvation, an increase in the radiative decay rate should occur in highly polar solvents for all molecules, and particularly for N3 and N4, for which S_1 becomes π_H–π_L^*. As to the rate of photoisomerization, which is probably the main S_1 deactivation path, the observation that the photoisomers of N3 and N4 are the same in all solvents suggests that no drastic changes in the S_1 torsional barriers are caused by a large change in the polarity of the medium. Work on the excited-state behaviour of these compounds is in progress.

6. Conclusions

Merocyanines N1–N4 exhibit structural and solvatochromic properties that can be qualitatively interpreted within the classical valence bond scheme based on the resonance structures Ia and Ib. A change in their relative weights corresponds to passage from the purely polyene-like form Ia to the pure charge-separated form Ib, with the polymethine cyanine-like structure, characterized by equalized C–C bond orders and a net charge alternation along the polymethine chain and the most red-shifted colour band, intermediate between the two. In principle, shifting from a Ia-like structure to a Ib-like structure is obtained on moving from an apolar to a strongly polar solvent. In reality, each merocyanine covers only a region in this range, depending on its intrinsic electronic nature determined by the chromophore length and geometry and by the nature and position of the substituents. Of the four investigated compounds, N2 is closest to the polyene-like structure Ia and shows a slight shift towards the polymethine cyanine behaviour in polar solvents, as indicated by the smoothed J alternancy and the moderate positive solvatochromism. A similar solvatochromism is exhibited by the aromatically substituted compound N3, but its J values are closer to each other, indicating a higher polymethine-like character. Finally, N4, which carries a double carbonyl termination, shows peculiar J distributions and a negligible solvatochromism, which indicate, in keeping with the calculated bond lengths, a polymethine cyanine-like electronic structure for the molecule in vacuum or in weakly polar solvents and a strong shift towards the zwitterionic form in polar media.

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