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CONFORMATIONAL STUDIES ON SOME *p*-DIMETHYLAMINOSTYRYL DYES

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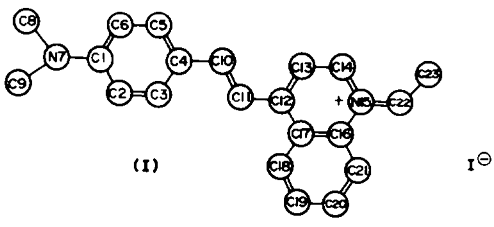
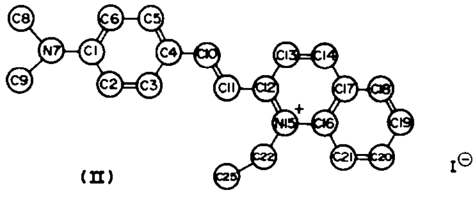
Abstract—PCILO computations have been carried out on the conformations of five *p*-dimethylaminostyryl dyes derived from quinoline-4 (I), quinoline-2 (II), pyridine-4 (III), pyridine-2 (IV) and benzothiazole (V). The stable conformations of I–IV are found to be nonplanar, while V is almost planar. The results have been explained in terms of various possible steric interactions.

In view of the importance of the molecular structure with respect to the spectra and many other useful properties (photosensitization, fluorescence, laser efficiency, thermochromic and photochromic behaviour) of dye stuffs, we have undertaken theoretical studies on the conformation of the cations of some styryl dyes derived from the condensation of *p*-dimethylamino benzaldehyde with five different heterocyclic bases, quinoline-4 (I), quinoline-2 (II), pyridine-4 (III), pyridine-2 (IV), and benzothiazole (V). Some of the dyes of this series (e.g. II, IV and V) are reported to be quite powerful sensitizers, while some others (e.g. I) do not possess any sensitizing property at all, although, apparently all of them bear quite close structural resemblance to each other. This, in itself, is an interesting theoretical problem, whose solution, we think, may lie in the difference in their conformations. Besides, a vast amount of experimental and theoretical work[1,2] on the stilbenes, azobenzenes and the closely related benzylideneanilines, indicate a nonplanar structure for some of these compounds. Since the compounds under report are quite similar to stilbenes (the phenyl ring in stilbene is substituted by a heterocyclic ring), we intend to find out whether similar interactions also operate in case of styryl dyes in deciding their most stable conformations.



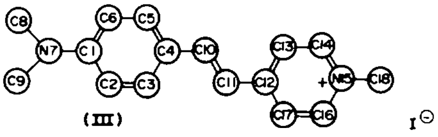
(I)

p-Dimethylaminostyryl dye from N-ethylquinoline-4



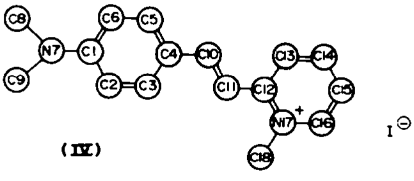
(II)

p-Dimethylaminostyryl dye from N-ethylquinoline-2



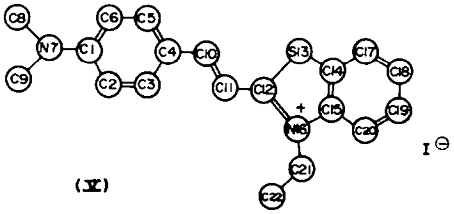
(III)

p-Dimethylaminostyryl dye from N-methylpyridine-4



(IV)

p-Dimethylaminostyryl dye from N-methylpyridine-2



(V)

p-Dimethylaminostyryl dye from N-ethylbenzothiazole-2

METHOD

Among the more recently developed theoretical methods with all valence electrons, the PCILO (Perturbative Configuration Interaction using Localized Orbitals) method[3,4] is extensively used for conformational studies. This method is based on the expansion of the molecular orbitals in terms of localized bond orbitals constructed from pairs of hybrid orbitals. The excited state is built from a set of antibonding orbitals which are used to obtain a configuration interaction matrix. The lower eigenvalues of the CI matrix are calculated by a Rayleigh–Schrodinger perturbation expansion. The superiority of PCILO method over other quantum chemical methods in dealing with conformational problems has been proved[5–8] for different types of molecules. We have, therefore, chosen the PCILO method for the present work.

Difficulties that may arise in the use of PCILO method involving delocalized bonds have been discussed in some detail by Martin *et al.*[9] in connection with conformational studies on phenylethylamine. By employing three different criteria to perform computations on both Kekule structures, they found a satisfactory agreement between all the three results. Jacques and Faure[5] have reported the conformational study of benzylideneaniline by PCILO method. Although they have not explicitly mentioned, there is evidently no significant falsification of the results by an arbitrary choice of one of the localized bond structures. We had also found in connection with PCILO conformational studies on some *p,p'*-disubstituted benzylidene anilines that identical conformations are obtained for both the Kekule structures.[10]

The dihedral angles of the phenyl and the heterocyclic rings with respect to the central methine chain are measured in terms of torsion angles Φ and θ respectively, which are defined as:

$$\Phi = \text{C }3-\text{C }4-\text{C }10-\text{C }11$$

$$\theta = \text{C }10-\text{C }11-\text{C }12-\text{C }13,$$

the clockwise direction being positive. The *cis* and *trans* dihedral angles have been taken as 0° and 180° respectively. Since no crystallographic studies are reported for these compounds, the input geometries (bond lengths and angles) have been adopted from certain related molecules.

(i) The dimethylaminobenzene part from the crystallographic studies of Nakai *et al.* on *p*-dimethylamonobenzylidene-*p*-nitroaniline.[1]

(ii) Geometry of the quinoline-4, from the crystallographic studies of Yoshioka and Nakatsu on 1,1'-diethyl-4,4'-cyanine bromide.[11]

(iii) Quinoline-2 geometry from Nakatsu *et al.* on the structure of 1,1'-diethyl-2,2'-cyanine iodine.[12]

(iv) Pyridine-2 and pyridine-4 geometries from the crystallographic results of Rerat on pyridine hydrochloride.[13]

(v) Benzothiazole geometry from the crystallographic studies on 3,3'-diethylthiatricarbocyanine iodine by Potenza *et al.*[14]

In conformity with the reports of the above crystallographic studies, the phenyl and the heterocyclic rings (excluding the side chain Me or Et substituents) have been taken to be planar.

The PCILO energies have been computed as a function of Φ and θ at 30° intervals with preselected values of the other geometrical parameters.

RESULTS AND DISCUSSION

The global minima and other energy regions of interest along with the energies of the planar structures are described in Table 1.

Styryl dye from quinoline-4 (I). The most stable conformation for dye I is obtained with $\Phi = 30°$ and $\theta = 120°$ which is stabler than the planar structure ($\Phi = 0°, \theta = 0°$) by an amount of energy 1.13 kcal/mole. The two quinoline rings in 1,1'-diethyl-4,4'-cyanine bromide have been reported to be twisted out of plane due to steric interaction between the two *ortho* (with respect to —CH=) hydrogen atoms. In case of dye I the twisting of the quinoline ring is perhaps due to the steric interaction between H(C 10) and H(C 13) and possibly due also to some extent, the interaction between H(C 11) and H(C 18). This argument is borne out from the appropriate interatomic distances, which are 1.87 and 2.00 Å, respectively, for the planar structure and 4.13 and 3.38 Å for the non-planar structure. A weak interaction between H(C 3) and H(C 11) is indicated by the fact that the 0–120 conformation is only of 0.16 kcal/mole higher energy.

Styryl dye from quinoline-2 (II). The lowest energy conformation for the dye II is the one in which the *p*-dimethylaminobenzene and the quinoline rings are twisted by 30° each in opposite directions with respect to the plane containing the central atoms. The energy barrier for the planar structure ($\Phi = 0°, \theta = 0°$) is 3.39 kcal/mole. However that for the structure in which the phenyl ring is in the same plane with the central atoms and only the quinoline ring is twisted ($\Phi = 0°, \theta = 30°$) is only 0.11 kcal/mole, which can be overcome in solutions or crystal packing. A much higher rotational energy barrier (3.33 kcal/mole) is, however, involved for the quinoline ring to be in plane with the central atoms ($\Phi = -30°, \theta = 0°$). The twisting of the quinoline ring is quite close to the reported crystallographic value of 23.7° and 22.8° for 1,1'-diethyl-2,2'-cyanine iodide.[12] This twisting may be due to a steric interaction between

Table 1. Preferred conformations of *p*-dimethylaminostyryl dyes

Molecule	Energy of the planar ($\Phi = 0, \theta = 0$) confm. kcal/mole	Global minimum		Other energy regions		
		Φ(deg)	θ(deg)	Φ(deg)	θ(deg)	Energy kcal/mole
I	10.62	30	120	0	120	0.16
				120	0	2.38
II	3.39	−30	30	0	30	0.11
				−30	0	3.33
III	4.66	30	150	0	150	0.06
				30	0	4.61
				0	90	2.4
IV	4.73	30	−60	0	−60	0.04
				30	0	4.79
				−30	30	1.26
V	0.02	−30	30	0	30	0.07
				−30	0	0.01

H(C 10) and H(C 13) (the interatomic distances are 1.78 and 2.09 Å for the planar and the non-planar structures respectively). The low energy rotational barrier for the non-planarity of the phenyl ring is perhaps due to a weak interaction between H(C 3) and H(C 11).

Styryl dye from pyridine-4 (III). Dye III is expected to show conformational characteristics very close to those of dye I derived from quinoline-4. The heterocyclic pyridine ring in dye III is, however, twisted to a greater extent in its most stable conformation ($\theta = 150^\circ$), which has 4.66 kcal/mole less energy than the planar ($\Phi = 0^\circ, \theta = 0^\circ$) conformation. This again must be due to steric interaction between H(C 10) and H(C 13). The interatomic distance increases from 1.69 Å in the planar to 4.47 Å in the non-planar structure. The phenyl ring is twisted by an angle of 30° involving a small energy barrier with respect to this ring being in plane with the central atoms ($\Phi = 0^\circ$, $\theta = 150^\circ$), possibly due to a weak interaction between H(C 3) and H(C 11). The energy barrier for the pyridine ring to be coplanar with the central atoms ($\Phi = 30^\circ$, $\theta = 0^\circ$) is 4.61 kcal/mole. The energy for the conformation, which is identical to that of dye I ($\Phi = 30^\circ$, $\theta = 120^\circ$), is 2.4 kcal/mole higher. This could be due to the benzosubstitution in I and also because of the difference in N-substitution.

Styryl dye from pyridine-2 (IV). Dye IV bears the same resemblance with dye II as III bears with I. The global minimum occurs at $\Phi = 30^\circ$ and $\theta = -60^\circ$, which is stabler than the planar structure ($\Phi = 0^\circ$, $\theta = 0^\circ$) by 4.73 kcal/mole. Here again $0-(-60)$ conformation is only of 0.04 kcal/mole higher energy while the $30-0$ conformation has an energy barrier of 4.79 kcal/mole, thus indicating a strong steric interaction between H(C 10) and H(C 13), (the interatomic distance is increased from 1.83 Å in the planar conformation to 2.82 Å in the most stable conformation) and a weak interaction between H(C 3) and H(C 11). The conformation analogous to that of II ($\Phi = -30^\circ$, $\theta = 30^\circ$) has 1.26 kcal/mole higher energy.

Styryl dye from benzothiazole (V). Although, theoretically the most stable conformation for V is found to be the one in which the phenyl and the benzothiazole rings are twisted out of the central plane by 30° each in opposite directions the energy barriers for the planar structure ($\Phi = 0^\circ$, $\theta = 0^\circ$) or for the structures in which one of the rings is coplanar with the central atoms, are exceedingly low, as can be seen from Table 1. V can therefore be thought of as existing more or less in a planar structure. This is understandable because as in case of the other four dyes the interaction between H(C 3) and H(C 11) is weak, while, there is no *ortho*-hydrogen in benzothiazole ring (corresponding to H(C 13) to interact with H(C 10)). The planar conformation of dye V is in conformity with all the earlier crystallographic findings on benzothiazole cyanine iodides.[14,15]

The above conclusions may be summarized by stating that the heterocyclic rings in dyes I–IV are twisted with high rotational energy barriers. Although in the theoretically most stable structures for I, II, III and IV, the phenyl ring is twisted by 30°, the energy barriers for the coplanar conformation are very small, so that for all practical purposes the phenyl ring may be taken to be lying in the same plane as that bearing the central atoms. Again, from energy considerations, V may be considered to be planar. The twisting of the heterocyclic rings is possibly due to steric interaction between one of the chain hydrogens and the *ortho*-hydrogen of the heterocyclic ring, a phenomenon similar to stibenes and benzylideneanilines.[2,10]

Table 2. Molar extinction coefficients (ε) and sensitization properties of the styryl dyes

Dye	ε	Ref.	Sensitization property	Ref.
I			Not a sensitizer	16
II	56,000	17	Sensitizer	17, 18
III	41,690	19		
IV	37,150	19	Sensitizer	20
V	79,000	21	Sensitizer	21

Table 2 describes the molar extinction coefficients (ε) and photographic sensitization properties of the dyes. A connection between the extent of acoplanarity and decreased intensity of absorption is evident. The same is true in case of their sensitization properties, since it has been established that non-planar dyes are nonsensitizers.[15]

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