

THEORETICAL DESCRIPTION OF CONFORMATIONAL ISOMERS IN THE AZASTILBENES: A STUDY USING MODIFIED NEGLECT OF DIFFERENTIAL OVERLAP (MNDO) AND INTERMEDIATE NEGLECT OF DIFFERENTIAL OVERLAP/SPECTROSCOPIC (INDO/S)

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(Received January 18, 1982)

Summary

The energies of the ground state S_0 and the first excited state S_1 of the planar rotational *ortho* and *meta* isomers of *trans*-styrylpyridine and symmetric dipyridylethylene were computed by means of modified neglect of differential overlap (MNDO) and intermediate neglect of differential overlap/spectroscopic (INDO/S) calculations. The study was aimed at interpreting the photophysical properties of these substances which indicate the presence of quasi-isoenergetic yet distinguishable species in solutions containing such isomers. The differences between the ground state energies and the excitation energies of various isomers were corrected in an approximate fashion to account for solvent effects. The results obtained are in overall satisfactory agreement with experimental observations.

1. Introduction

Trans-disubstituted ethylenes of the general formula $\text{Ar}-\text{CH}=\text{CH}-\text{Ar}'$ can exist in a variety of isomers whenever Ar or Ar' or both do not have C_{2v} symmetry with respect to the bond axis. For the cases considered here (Ar \equiv phenyl, Ar' \equiv 2,3-pyridyl; Ar \equiv Ar' \equiv 2,3-pyridyl) there are two and three planar isomers respectively as shown in Fig. 1 for the two-pyridyl case, and more isomers are possible if the requirement of planarity is relaxed. In general, the tendency to planarity of the extended system and the extent of the non-bonded interactions are the relevant factors that determine the relative energies of the different rotational isomers and of the barriers separating them from each other [1].

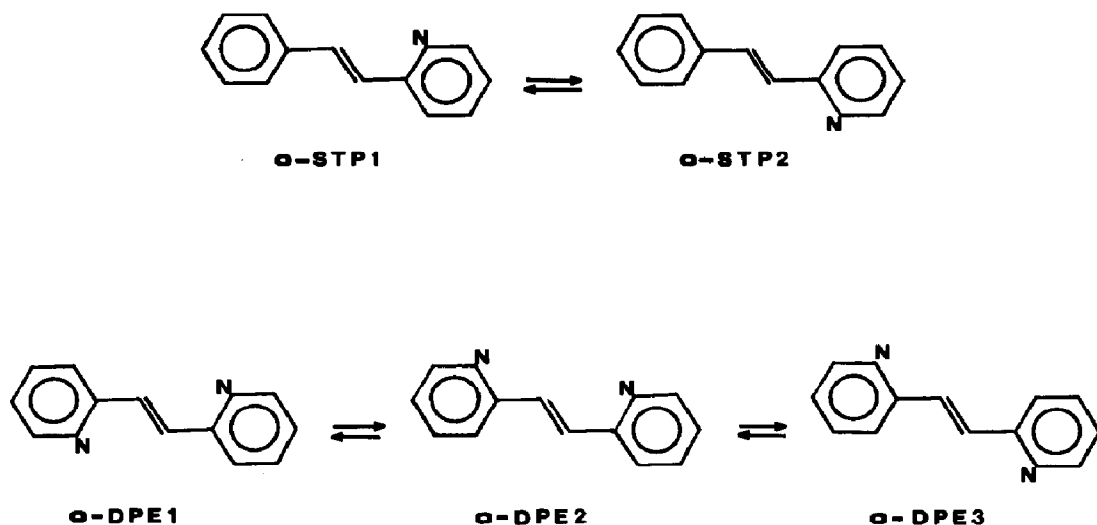


Fig. 1.

Explicit consideration of the different forms possible has been allowed for in theoretical investigations dealing with these systems [2 - 7], but no explicit conclusion on energetic preference has been drawn, although Perkampus *et al.* [3] have considered the structure DPE1 for dipyrindylethylene (DPE) to be more probable than the alternatives and the results of Favini *et al.* [2] have been taken to imply, by comparison with experimental values of the dipole moment [8], that the most stable form of *o*-styrylpyridine (*o*-STP) is *o*-STP1. The main aim of these theoretical investigations was the interpretation of the spectroscopic behaviour of these molecules. In particular, a study using intermediate neglect of differential overlap/spectroscopic (INDO/S) [7] showed that the first excited state in *o*- and *m*-STP1 and in symmetric *o*- and *m*-DPE1 is of $\pi\pi^*$ character and is essentially of ethylenic nature.

In view of the quasi-single character of the bond coinciding with the rotation axis and of the size of the anticipated differences in non-bonded interactions, both energy barriers and energy differences are expected to be low. Therefore the various rotational isomers are likely to coexist, to be almost degenerate and to interconvert at high rates which means that high resolution is required to detect them separately.

Recent investigations of the photophysical properties of STPs [9] and DPEs [10] have succeeded in separating the emission spectra of these molecules by exploiting the technique of selective excitation. The spectra of each of two species, the coexistence of which is considered to be responsible for the λ_{ex} dependence of the emission spectra and the λ_{em} dependence of excitation spectra, were separated from the complex experimental spectrum. The attribution of these effects to different excitation energies of corresponding states of similar chemical species, rather than to close non-communicating states of the same molecule, was supported by the

observed effects of temperature changes and solvent changes on these phenomena which are easily rationalized in terms of two equilibrating chemical systems. The reconstructed single-species spectra were termed A (red shifted) and B (blue shifted).

The problem we are faced with is the assignment of A and B to specified members of the set of structures shown in Fig. 1 and to explain why a third species C does not occur in DPE. In order to do this two theoretical quantities were considered, *i.e.* the ground state energy and the energy of the first excited state. A molecular orbital description based on the modified neglect of differential overlap (MNDO) hamiltonian was chosen for the ground state energy from the current semiempirical methods because it is known to reproduce conformations of a wide variety of molecules correctly [11]. The program was also used to give an approximate description of the excited state S_1 in terms of a single open-shell configuration with a relaxed geometry in the central butadiene skeleton. A program based on the INDO/S hamiltonian of Ridley and Zerner [12] was utilized for a more accurate description of the excited state. In this method a self-consistent field closed shell was determined from the ground state geometry followed by a singly excited configuration interaction (SECI) calculation in a space of 49 excited configurations.

2. Results and discussion

Table 1 contains the ground state energies and dipole moments of the 10 species examined. The first fact emerging from these data is the more pronounced energy difference in the *ortho* species compared with the *meta* species. This can easily be explained in terms of the non-bonded interactions between *o*-hydrogen and ethylenic hydrogen being different in the *o*-STP1 and *o*-STP2 species for example, while no such difference is present in the *m*-STP1 and *m*-STP2 species where the corresponding non-bonded interactions are almost zero.

These results, however, are only applicable to isolated molecules. The situation in solution is changed because the rotational isomers not only have different energies but also have different dipole moments and experience a differentiated energy reduction in the solvent. The relevant correction has been calculated from the approximate formula [13]

$$E_{\text{solv}} = - \frac{M^2}{a^3} \frac{n^2 - 1}{2n^2 + 1}$$

where M is the molecular dipole moment, a is the molecular radius and n is the refractive index of the solvent. In the present calculation the n value of ether-isopentane-ethanol, a solvent for which experimental data [9, 10] are available, was chosen and the value of a was set to 5 Å. When this correction is introduced the picture is significantly altered, as shown in the last

TABLE 1

Ground state energies E_0 , dipole moments μ and ground state energy differences ΔE_0 between the rotamers (uncorrected and corrected for solvent effects) for STP and DPE species^a

Species	E_0^b (eV)	μ (debye)	ΔE_0 (cm^{-1})	$(\Delta E_0)_{\text{corr}}$ (cm^{-1})
<i>o</i> -STP1	-2022.9293 (-2000.3879)	1.3837	902	698
<i>o</i> -STP2	-2022.8176 (-2000.2690)	1.7732 ^c		
<i>m</i> -STP1	-2022.8454 (-2000.0570)	2.0462	-35	-99
<i>m</i> -STP2	-2022.8498 (-2000.0577)	2.1387		
<i>o</i> -DPE1	-2088.0777	0	1095	\approx 1095
<i>o</i> -DPE2	-2087.9413	3.0524	691	\approx 691
<i>o</i> -DPE3	-2087.8556	0		
<i>m</i> -DPE1	-2087.9063	0	-14	\approx -14
<i>m</i> -DPE2	-2087.9080	3.4593	-57	\approx -57
<i>m</i> -DPE3	-2087.9151	0		

^aGeometry: central C=C bond length, 1.355 Å; carbon-phenyl and carbon-pyridyl bond lengths, 1.465 Å; carbon-phenyl and carbon-pyridyl bond angles, 130°; C=C bond angle, 117°.

^bThe values in parentheses are from MINDO/3 calculations.

^cExperimental value, 1.85 debye [8].

column of Table 1 where the corrected energy differences between the rotamers are reported. In the case of *o*-STP the dominating factor is the isolated molecule energy difference and this is partly counteracted by the solvent effect, whereas in *m*-STP the solvent effect is more important and reinforces the isolated molecule energy difference. The corresponding equilibrium constants are 33.0 for *o*-STP, with *o*-STP1 being more stable, and 1.6 for *m*-STP, with *m*-STP2 being more stable.

The correction for solvent effects is less straightforward for the DPEs. Indeed, if we were to consider only the net dipole moment, the *o*-DPE2 and *m*-DPE2 species would be the only ones stabilized by the solvent and we would expect only *m*-DPE2 to be present in solution, in contrast with the experimental data. However, owing to the polarity of each pyridine moiety, it is expected that the energies of the *o*-DPE1, *m*-DPE1, *o*-DPE3 and *m*-DPE3 species would also be affected by the solvent. A physically reasonable method of estimating the relative stabilization is to assign a dipole moment to each ring and to consider the stabilization of the molecule as the sum of the stabilization of each ring. If the dipole moment assigned to each ring is the same, the stabilization obtained for every conformer is the same.

The properties of the excited states are illustrated in Tables 2 and 3. In this case, as in the case of the ground states, the *ortho* isomers appear to

TABLE 2

MNDO calculations of excited configuration energies E_1 , dipole moments μ and excitation energy differences ΔE_1 between the rotamers (uncorrected and corrected for solvent effects) for STP and DPE species

Species	E_1 (eV)	μ (debye)	ΔE_1 (cm^{-1})	$(\Delta E_1)_{\text{corr}}$ (cm^{-1})
<i>o</i> -STP1	-2018.7643	1.4239	108	144
<i>o</i> -STP2	-2018.6660	1.7441		
<i>m</i> -STP1	-2018.7558	2.3700	-74	-133
<i>m</i> -STP2	-2018.7520	2.5221		
<i>o</i> -DPE1	-2083.8149	0	-331	\approx -331
<i>o</i> -DPE2	-2083.7202	3.2313	139	\approx 139
<i>o</i> -DPE3	-2083.6517	0		
<i>m</i> -DPE1	-2083.8295	0	79	\approx 79
<i>m</i> -DPE2	-2083.8213	3.2926	89	\approx 89
<i>m</i> -DPE3	-2083.8172	0		

TABLE 3

INDO/S calculations of excitation energies E_{ex} , oscillator strengths f , and radiative and intersystem crossing rate constants k_r and k_{ISC} for STP and DPE species

Species	E_{ex} (eV)	f	$k_r \times 10^{-8}$ (s^{-1})	$k_{\text{ISC}} \times 10^{-8}$ (s^{-1})
<i>o</i> -STP1	4.0409	0.9472	2.96	15.5
<i>o</i> -STP2	4.0470	1.0400	3.26	18.3
<i>m</i> -STP1	4.1530	1.1632	3.84	1.98
<i>m</i> -STP2	4.1180	1.0026	3.26	1.36
<i>o</i> -DPE1	3.9778	0.9378	2.84	21.8
<i>o</i> -DPE2	3.9846	0.9759	2.97	39.0
<i>o</i> -DPE3	3.9725	1.0218	3.09	23.6
<i>m</i> -DPE1	4.1228	1.1604	3.77	1.20
<i>m</i> -DPE2	4.0937	1.0342	3.32	24.3
<i>m</i> -DPE3	4.0763	0.9809	3.12	1.6

have a wider spread of energies than the *meta* isomers. Comparison of Tables 1 and 2 shows that for STP the overall effect has the same sign for the ground states, the excited states and the energy differences. This means that the red-shifted species is the most stable rotamer, in agreement with the data reported in refs. 9 and 10. The theoretical values of 144 for *o*-STP and -133 for *m*-STP show that the shift is underestimated in comparison with the experimental values 688 and -455 obtained for the two isomers. MNDO calculations fail to predict the correct trend for the DPEs. However, since as discussed above the solvent correction is believed to be comparable for all rotamers, an alternative comparison can be made on the basis of the differences between the INDO/S excitation energies reported in Table 3.

Theoretical values of 55 and 140 are obtained for the differences between *o*-DPE2 and *o*-DPE1 and between *m*-DPE3 and *m*-DPE2 respectively compared with experimental values of 805 and 1070. Thus the calculation predicts the trend only, and a more sophisticated type of description, including geometry optimization and a quantitative assessment of differences in the solvent effects, appears to be required for quantitative agreement to be obtained.

Additional calculations were carried out on the *cis* isomers of the STP species where an increased effect of non-bonded interactions and hence larger differentiations between the rotamers would be expected. This inference is confirmed by the data shown in Table 4.

The radiative rate constants k_r , the intersystem crossing rate constants k_{ISC} and the total decay rate constants k_T for the *trans* species, where photo-physical parameters are available and indeed provided the initial motivation for the present investigation, were calculated as described in ref. 7 from the transition energies, the excited state wavefunctions and the oscillator strengths obtained from INDO/S calculations. k_r and k_{ISC} are also included in Table 3.

An examination of the results shows that the STP species with lower energies (and lower excitation energies) also have lower k_r values. If it is assumed that the values of ϕ_r at low temperatures, although similar, are proportional to the radiative rate constants (which is in agreement with the small variation observed in the calculated k_{ISC} s), then a lower value of ϕ_r is expected for the more stable rotamer, a conclusion which is confirmed by the data reported in ref. 10.

It is interesting to note that the asymmetric *m*-DPE rotamer is sharply distinguished from the others on the basis of the k_r/k_{ISC} ratio which has a value very similar to those obtained for the *o*-DPE rotamers. The fact that the observed photophysical properties of *m*-DPE are markedly different from those of *o*-DPE appears to eliminate the possibility that this rotamer is the dominant species and thus supports the conclusions reached above,

TABLE 4

MNDO calculations of the ground state energies E_0 and INDO/S calculations of the excitation energies E_{ex} , radiative rate constants k_r and energy differences ΔE_0 and ΔE_{ex} for *cis*-STP species^a

Species	E_0 (eV)	ΔE_0 (cm^{-1})	$(\Delta E_0)_{\text{corr}}$ (cm^{-1})	E_{ex} (eV)	ΔE_{ex} (cm^{-1})	$k_r \times 10^{-7}$ (s^{-1})
<i>o</i> -STP1	-2022.6405	-1221	-940	4.067	637	8.87
<i>o</i> -STP2	-2022.7920			3.988		12.5
<i>m</i> -STP1	-2022.6907	97	428	4.140	589	16.4
<i>m</i> -STP2	-2022.6787			4.067		7.33

^aThe out-of-plane angle was set to 35°.

indicating that the proposed explanation for solvent effects in disubstituted molecules is physically sound.

3. Conclusions

The study performed has allowed a plausible assignment to be made of the species responsible for the different emission spectra of *o*- and *m*-STP and of symmetric *o*- and *m*-DPE. Despite the limitations of the description adopted, the main spectral features have been rationalized and a first attempt to interpret the relevant photophysical data has been outlined.

Acknowledgment

This work was carried out under the auspices of the Project Piano Finalizzato per la Chimica Fine e Secondaria, Linea di Ricerca Ah1.

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