THEORETICAL STUDY OF THE EXCITED STATE PROPERTIES OF 4-ACETYLDIPHENYLSULFIDE

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abstract: The experimental data on 4-acetyldiphenylsulfide (I) were previously explained by considering the possibility of twisted intramolecular charge transfer (TICT) excited state formation. In the present paper solvent dependent semiempirical calculations were performed in solvents of different polarities. The ground and excited states potential energy surfaces were built in terms of the torsion angle about the single bond joining the two aromatic fragments of the molecule, acting as D and A. The ground state has quasiplanar geometry, but in the excited states also the orthogonal conformation corresponds to a minimum, stabilised in methanol due to the large charge separation between the D and A fragments. The possibility of forming TICT excited states for I and the solvent polarity effect on the relative stability of the TICT state is discussed.

Introduction

The TICT concept was firstly used by Grabowski et al. [1] to explain dual fluorescence of aromatic compounds with single bonded donor (D) and acceptor (A) moieties. Subsequent to absorption of light, the molecule can reach two different excited states from which it can then emit, the Franck-Condon or locally excited (LE) state, planar or quasi-planar, and the TICT state, in which the two fragments of the molecule have an orthogonal relative position. In the emission spectra, one will observe the band corresponding to the LE state, at shorter wavelengths, named band B, and another one at longer wavelengths, corresponding to the TICT state, namely band A [2÷6]. As the TICT state has a large dipole moment, the equilibrium LE→TICT will be shifted to the right in polar solvents, due to solvation interaction, so the B/A intensity ratio will decrease with increasing solvent polarity. Theoretical studies on potentially TICT forming compounds were conducted most frequently by single point calculations [7÷11]. They indicate a minimum on the excited state PES for the orthogonal geometry, which is stabilised in polar solvents, and a large D→A charge transfer. Recently, the presence of the TICT excited states was assumed for compounds in which a sulphur containing moiety acts as donor [12÷14], such as 4-acetyldiphenylsulfide (Fig.1).

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Fig.1: *Structural formulae of the title compound.*

In our previous paper on **I** [14], we have shown that although no two distinct fluorescence bands could be evidenced, the large broadening of the emission band in going from a nonpolar to a polar solvent is consistent with the presence of two overlapped bands. The deconvolution of the experimental spectra pointed out that the ratio of the areas of the two bands was solvent dependent, the band at longer wavelength being enhanced in polar solvents. The emission at about 350 nm was assigned to the normal fluorescence and that at 400 nm to a TICT band. The experimental data were modelled by *in vacuo* calculation of the potential energy surface (PES) in respect with the torsions about the two single bonds joining the sulphur atom to the two aromatic moieties. The calculations showed that only the rotation of the C_6H_5S fragment is significant for the formation of a twisted configuration in which there is a charge transfer from the donor to the acceptor fragment. Adding at the heat of formation the solvation free energy estimated in terms of the Onsager model using the calculated value of the excited dipole moment, we have obtained that in polar solvents the twisted conformation is strongly stabilised and becomes comparable in energy to the Frank-Condon excited state.

The aim of this paper is to give further theoretical support to the experimental data. The possibility of performing solvent dependent optimisations in the frame of the AMSOL program was used to evidence the role of the solvent in the TICT states stabilisation.

Computational Details

The calculations were performed using the AM1 hamiltonian and the charge model SM5.4A of the AMSOL [15÷18] program. The optimisations were carried out using either the EFOLLOW or the TRUSTE procedures. The key words for the excited states were OPEN(2,2), SINGLET or TRIPLET, C.I.=2 and MECI. The potential energy surfaces for the ground and excited states were built considering fixed values for the torsion (τ=5432 in Fig. 1) about the single D-A bond in the range -20^0 to 200^0 and allowing the relaxation of all other internal coordinates. The optimisation of the excited states was difficult to perform. The minima are rather flat and the heats of formation plus the solvation energies ($\Delta H + \Delta G_{sol}$) do not change to a great extent for the gradient norm lower than 4. Therefore the condition GCOMP=2 was used for the cases in which either changes in the geometry or in the heat of formation were no more significant. For the critical points on the potential energy surfaces the total charges on the D and A fragments were calculated by summing up the charge densities on all the atoms including the hydrogens. Both the charges obtained by the Mulliken population analysis (M) and the CM1 (charge model 1) ones were considered for comparing reasons, although the SM5.4A model only uses the CM1 charges. The

calculations were performed in cyclohexane (CHX) and methanol, as nonpolar and polar protic solvents.

Results and Discussion

The calculated geometrical parameters indicate that only the simple bonds of the S atom change upon excitation. Their values decrease from 1.69-1.70 Å to 1.63-1.65 Å. The frontier orbitals are differently localised for the planar and orthogonal conformations, as it can be seen in Fig. 2. From the pattern of linear combination of atomic orbitals in the frontier orbitals it could be seen that subsequent to twisting the degree of localisation of HOMO and LUMO on the phenyl-sulf (D) and acetylphenyl (A) fragments, respectively, and lack of conjugation between the two aromatic moieties increases. In the case of the planar conformer, HOMO is mainly localised on the sulfur atom, but also the atoms in the phenyl and acetyl-phenyl fragments have non-zero coefficients, while LUMO is delocalised on the entire molecule, with larger coefficients on the acetyl-phenyl moiety. For the twisted state, HOMO is entirely localised on the D fragment, whereas LUMO is localised on A. The conjugation between the two rings is interrupted.

Supposing that the first transition, S_0-S_1, is the HOMO-LUMO transition, an intramolecular charge transfer from phenyl-sulf to acetylphenyl is expected in the first excited singlet state. For the orthogonal conformation the charge transfer will presumably be larger, as it is the transition of one electron between two orbitals localised on the D and A fragments, respectively.

The PES for the ground state presents two minima (see Table 1), corresponding to 12.6^0 and 164.6^0 in CHX and 8.6^0 and 172.8^0 in methanol, while the orthogonal conformation corresponds to a maximum in both polar and non-polar solvents. The rotational barrier has a value of about 1.8-1.9 kcal/mol, not depending to a great extent on the polarity of the solvent. As the molecule is symmetrical to the rotation about the D-A bond, only one quasi-planar conformer was considered in the tables below. The PES for the excited state of **I** calculated in CHX and methanol are presented in Fig. 3. In the excited state, *in vacuo* calculation, the stable conformers are the planar ones [14]. However, a minimum for $\tau=90^0$ can be evidenced, attesting the possibility that a twisted state can be reached, although a rotational barrier of 4.23 kcal/mol is predicted. The behaviour of **I** in CHX is similar, the planar conformers being the most stable ones, but the rotational barrier decreases to 2.00 kcal/mol. Increasing the polarity of the solvent from CHX to methanol, an inversion of the minimum energy conformers is predicted, the twisted conformer being more stable than the planar one. That means that in the emission spectrum, although it is possible that both bands be present even in non-polar solvents, the B/A bands intensity ratio decreases as the solvent polarity increases. This result correlates well with the results obtained by deconvolution of the emission spectrum reported in our previous paper [14], which indicate a B/A intensity ratio of 3.40 in CHX and a value of 1.40 in methanol.
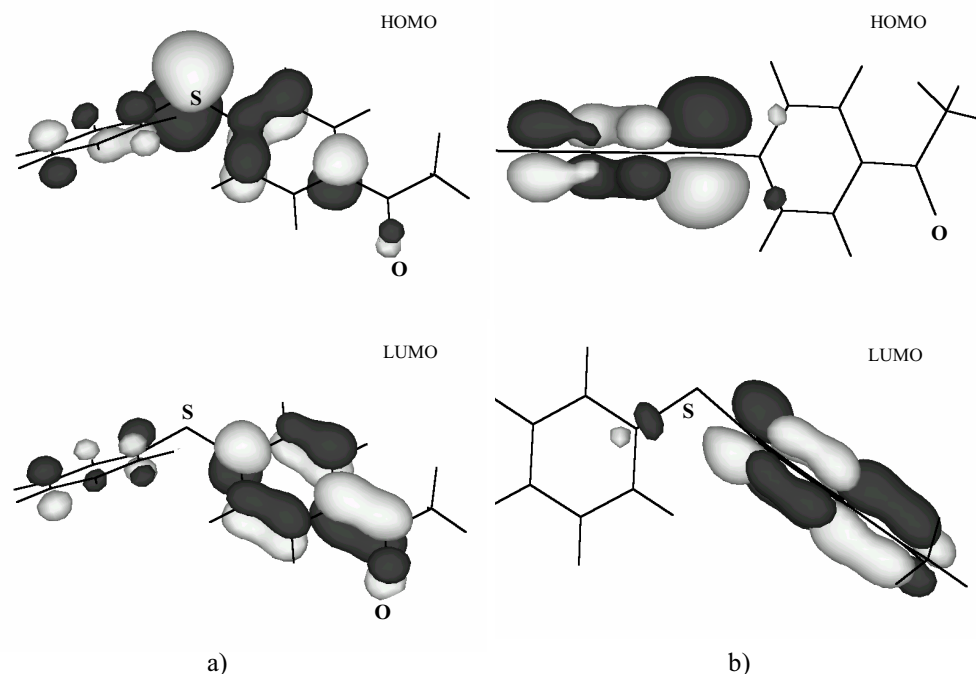
Fig. 2: *Frontier molecular orbitals in methanol, a) planar, b) orthogonal conformers.*

A comparison of the solvation energies in methanol calculated by the Onsager model [14] and the SM5.4A solvation model indicates a serious underestimation of ΔG_{sol} in the first case. The calculations made in the frame of the Onsager model result in a value of about 2-4 kcal/mol, depending on the solvation radius considered. The SM5.4A model predicts 23.13 kcal/mol for ΔG_{sol}, such as the TICT state is largely stabilised and becomes the first excited state.

**Table 1 Heat of formation and energy of solvation in CHX and methanol
for different stable conformers in the ground and excited states**

State	*In vacuo*[a]		CHX		CH_3OH	
	τ (deg)	ΔH (kcal/mol)	τ (deg)	$\Delta H + \Delta G_{sol}$ (kcal/mol)	τ (deg)	$\Delta H + \Delta G_{sol}$ (kcal/mol)
S_0	8.1	16.28	12.6	3.69	8.6	1.57
S_1	0.1	70.85	0.0	58.12	1.0	55.87
	88.6	75.08	90.0	60.12	92.3	51.95

[a] reference [14]
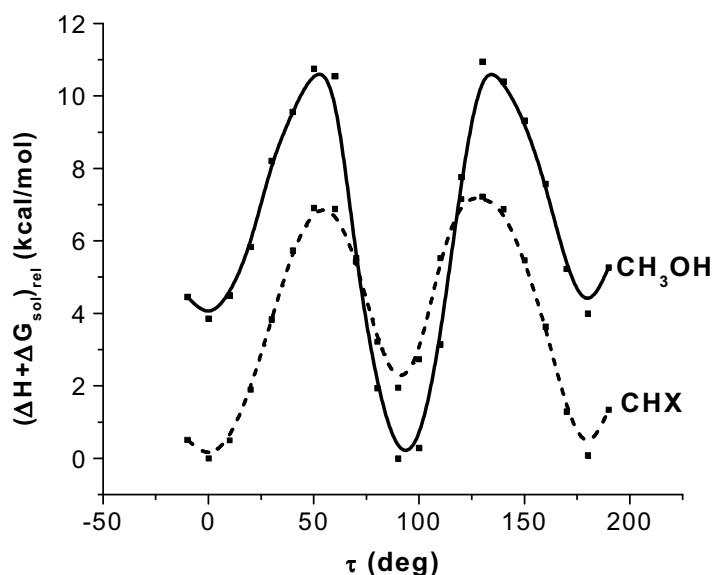
Fig. 3: *Calculated PES in the excited state in cyclohexane and methanol.*

The Mulliken and CM1 electronic charge transferred from the donor to the acceptor in the ground and the excited state are listed in Table 2.

Table 2 Mulliken and CM1 charge densities transferred from D→A
in the planar and twisted conformers in cyclohexane and methanol.

	Δq_{S0} (D→A)		Δq_{S1} (D→A)	
	CHX	CH$_3$OH	CHX	CH$_3$OH
M-0	0.215	0.220	0.301	0.324
M-90	0.234	0.244	0.825	1.044
CM1-0	0.049	0.013	0.175	0.188
CM1-90	0.070	0.079	0.557	0.736

The results point out that the transferred charge is dependent on both the polarity of the solvent and the adopted D-A conformation, the larger values being obtained for the twisted conformation in methanol. The use of the CM1 charge densities predicts a reduced polarity in comparison with that reflected by the Mulliken charges. The differences are mainly due to the charges of the sulphur atom and the carbons directly joined to him. The charge transfer increases in the excited state, as expected from the electronic structure of the frontier orbitals.

The dipole moment results presented in Table 3 indicate that the dipole moment enhances for the orthogonal conformation even for the ground state, but in the excited state there is a four-fold increase. In fact, the value of the dipole moment continuously increases with increasing value of the dihedral τ. The polarity of the solvent also influences the value of the dipole moment. The twisted state in methanol has a dipole moment of 16.741D calculated by the Mulliken population analysis and 17.638 D calculated by the CM1. This

explains the relative stabilisation in methanol of the twisted state comparing to the LE one, which has a value of no more than 4.9-5.9 D.

Table 3. Dipole moments (D) in the ground and excited states calculated in cyclohexane and methanol.

	μ_{S0}		μ_{S1}	
	CHX	CH$_3$OH	CHX	CH$_3$OH
M-0	2.864	3.569	3.641	4.861
M-90	2.901	3.722	11.593	16.741
CM1-0	2.951	3.884	4.316	5.913
CM1-90	3.168	4.351	11.449	17.638

We also calculated the absorption and emission features. Frank-Condon absorption wavelength, λ_a, was obtained considering the sequence of states calculated at the geometry of S$_0$, while the fluorescence emission maximum was estimated from the relative order of states calculated at the geometry of S$_1$, at the C.I.=2 level, involving the frontier molecular orbitals. The results indicate a value of 339 nm in both solvents for the absorption band at long wavelengths, larger, but in rather good agreement with the experimental values of 303-305 nm. The fluorescence maxima were found to have too low values, in the range of the IR light, and could not be correlated to the experimental data. On the other hand they illustrate the red shift in polar solvents.

Conclusions

The PES for **I** in the ground and the excited states were built along the dihedral about the single D-A bond in two solvents of different polarities, cyclohexane and methanol. The frontier orbitals are differently localised on the D and A fragments, depending on the twisting dihedral. For the orthogonal conformer, HOMO is localised on D, while LUMO is localised on A. The conjugation is interrupted. The results on building of the PES by the SM5.4A solvation model confirm the previous calculation made in the frame of the Onsager model, but the value of the solvation energy is larger. Thus, in methanol the twisted excited state is the most stable one. The present results qualitatively correlate with the previous experimental results, which yielded a decrease of the B/A intensity ratio on increasing solvent polarity. A large charge transfer upon twisting in the excited state was found and a four-fold increase of the value for the dipole moment.

These facts prompt us to conclude that TICT excited state formation is possible for single bonded D-A sulfur containing aromatic compounds such as 4-cetyldiphenylsulfide.

Acknowledgement

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