Photophysics of stilbenoid dye systems: A comparison of experiment and theory

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Abstract Stilbenes undergo multidimensional adiabatic photochemistry in
the excited state involving the twist of the central double and of the
adjacent single bonds. By bridging the single bonds chemically, dimen-
sionality is reduced, and only one product state, the "phantom singlet
state" P^*, remains. From the solvent polarity dependence of fluorescence
quantum yields and lifetimes, the solvatokinetic response of the photo-
reaction towards P^* can be extracted. It is shown that P^* is highly polar
in the case of unsubstituted stilbene but weakly polar for
dimethylamino-cyano-stilbenes, consistent with a change of the electro-
nic nature of P^* in agreement with recent theoretical models describing
double-bond twisting. Quantum chemical calculations within the CNDO/S
framework support these results.

INTRODUCTION

Recent theoretical models including both Twisted Intramolecular Charge
Transfer "TICT" states and "sudden polarization" /1-3/ allow to predict
the nature of the excited states of compounds with flexible single
and/or double bonds. Application to donor-acceptor-substituted stilbene
dye systems leads to the expectation, that the so-called "phantom-sing-
let" state P^* (twisted double bond) changes its dipolar nature from
highly polar to weakly polar along the substituent polarity scale.

These predictions are confirmed by stationary and time-resolved fluores-
cence measurements, as well as by semiempirical SCF-CI calculations,
within the following series of flexible and single-bond bridged stilbene
systems.
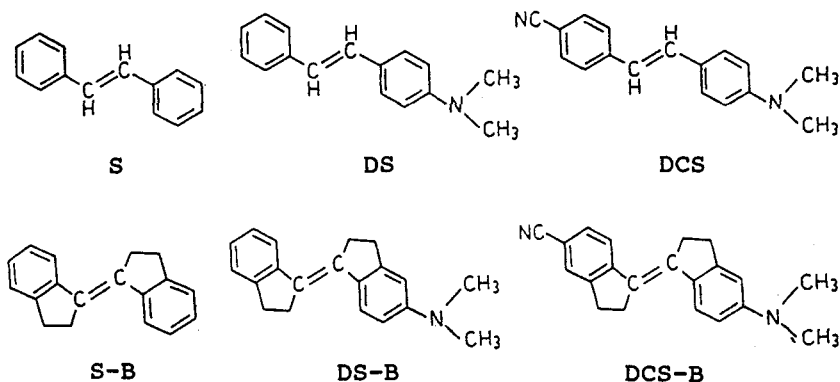
The comparison between the rigidized and the flexible stilbenes allows to pinpoint the intramolecular rotation around the single bond connecting the phenyl rings /4,5/ as a further important photochemical/photophysical relaxation channel in addition to the formation of P^*.

EXPERIMENTAL

The compounds were synthesized as described in /5,6/ and purified by recrystallization. Solvents were of spectroscopic quality (Merck Uvasol). Care was taken to subtract the solvent background fluorescence for the very weakly emitting bridged compounds. Fluorescence quantum yields were measured for optically thin solutions with respect to quinine bisulfate (ϕ_f = 0.55), and decay times were determined using a time-correlated single photon counting equipment described in /7/ with the excitation wavelength from BESSY synchrotron radiation tuned close to the maximum of the longest wavelength absorption band. Time resolution was ca 0.1 ns.

The quantum chemical calculations for double-bond twisted stilbenes were performed using the CNDO/S formalism /8,9/ with standard geometries and a weak symmetry breaking procedure for unsubstituted stilbene /10/ which consisted in mimicking the breathing vibration of the benzene rings. This resulted in localization of the frontier orbitals on the separated molecular moieties (see below) and avoided complications in the determination of S_0-S_1 energy gaps /10/.

RESULTS AND DISCUSSION

Table 1 contains the room temperature quantum yields for the 6 compounds investigated. Generally, the bridged compounds possess reduced quantum yields with respect to the flexible ones, but this trend is strongly amplified for the donor-acceptor compound DCS. For the latter, the

Table 1: Room temperature fluorescence quantum yields, 77 K-lifetimes and derived nonradiative decay rate constants for various D-A-stilbenes in nonpolar and polar solvent.

compound	solvent	ϕ_f	τ_{77}[a] (ns)	k_{nr}[b] $(10^9 s^{-1})$
S	MCH/IH	0.05[c]	1.3	14.6
	CH_3CN	0.04[d]		18.5
DS	n-hexane	0.03	1.7	19
	EOE	0.03[f]		19
	CH_3CN	0.04[f]		14
DCS	n-hexane	0.02	1.7[e]	29
	EOE	0.03[g]		19
	CH_3CN	0.11[g]		4.8
S-B	MCH	0.002[c]	1.6	312
	CH_3CN	0.0007[d]		890
DS-B	n-hexane	0.0055	1.7	106
	ethanol	0.0016		370
	CH_3CN	0.0028		210
DCS-B	n-hexane	0.002	1.7	294
	EOE	0.002[g]		294
	CH_3CN	0.006[g]		97

a) from measurements in ethanol, ether, n-butyl chloride and/or n-butyronitrile; b) $k_{nr} = k_f(\phi_f^{-1}-1)$ assuming $k_f=1/\tau_{77}$; c) J. Saltiel and J.T. D'Agostino, J. Am. Chem. Soc. 94 (1972) 6445; d) value relative to alkane solvent; e) lifetime maximum observed at T>77K /4,5/. Using this value instead of τ_{77} reduces k_{nr} to ca 75% of the values given; f) /14/; g) /5/

yields clearly increase with increasing solvent polarity, and the reverse is true for unsubstituted stilbene S. These effects are more pronounced in the bridged compounds. As intersystem crossing is of minor importance in these compounds /11,12/, the 77K lifetimes also contained in the table yield an estimate of the radiative rate and allow to calculate the nonradiative rate constant k_{nr} at room temperature. Smaller quantum yields translate into larger nonradiative rates, hence k_{nr} increases in the same direction as solvent polarity for S and more pronouncedly for S-B, while a decrease of k_{nr} is observed for DCS and DCS-B for increasing solvent polarity (Table 1).

Table 2: Comparison of fluorescence lifetimes and derived nonradiative rate constants for D-A-stilbenes at various temperatures in nonpolar and polar solvents.

temperature	compound	solvent[a]	τ (ns)	k_{nr} $(10^7 s^{-1})$
163 K (-110 °C)	S-B	et$_2$O +ethanol	< 0.1	>900
	DS-B	et$_2$O	0.34	235
		ethanol	0.12	770
	DCS-B	et$_2$O	0.2	440
		ethanol	0.6	108
	DS	et$_2$O	1.71	b)
		ethanol	1.91	b)
	DCS	et$_2$O	2.1	b)
		ethanol	2.2	b)

a) at 163 K, ethanol is more viscous than diethyl ether by a factor > 27, see CRC Handbook of Chemistry and Physics, CRC Press, Inc, Ed. R.C. Weast; b) k_{nr} ~0, with complication due to population of A* state (lifetime maximum, compare τ_{77} in table 1)

This opposite solvent polarity dependence is supported by direct kinetic measurements at low temperature (Table 2). DS-B behaves similarly to S-B (Table 1) in that it shows an increase of k_{nr} with increasing solvent polarity (despite a considerably larger viscosity of the polar solvent), and the reverse is true for DCS and DCS-B. The comparison of the different compounds in the same solvent and at the same temperature (decreasing k_{nr} for increasing rotor volume S-B < DS-B < DCS-B) allows to conclude that the nonradiative process is a large-amplitude motion consistent with twisting of the double bond. For the unbridged compounds measured, k_{nr} is significantly reduced, and the behaviour of these compounds is complicated by an initial lifetime lengthening for temperatures larger than 77 K indicative that more than one state emit as discussed in detail in /4,5,13,14/. This further state (A* in Fig. 1),
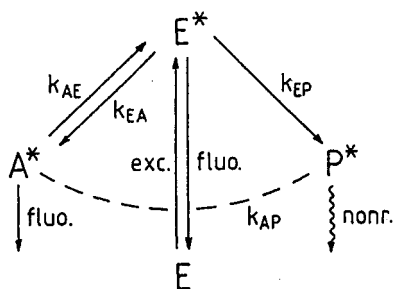

Fig. 1: Three-State Kinetic Scheme: E* corresponds to the near-planar Franck-Condon geometry, P* is the double-bond and A* the single-bond twisted species. The "Phantom Singlet" state P* is considered to be a nonradiative funnel. The TICT state A* can either depopulate radiatively or nonradiatively via the indirect route $k_{AE}+k_{EP}$ or via a possible direct route k_{AP}.

which is not accessible in the bridged compounds, is thus connected with a single-bond twisted geometry and is the reason for the reduction of k_{nr} for the compounds without bridge. Therefore, as can be seen in Fig.1, a three-state kinetic scheme has been proposed /4,5,13,14/.

In DCS, A^* is expected to be a higly polar Twisted Intramolecular Charge Transfer (TICT) state /4,5,13/ which is unavailable in the bridged compounds and energetically disfavoured in stilbene. Its formation competes with that of P^* and hence reduces the effective k_{nr} which occurs via this state. Here, however, we want to focus on the nature of P^* and E^*, and therefore the bridged model compounds without complication by the third state A^* yield a clearer picture. The opposite solvent polarity dependence of k_{nr} for S-B and DS-B with respect to DCS-B (Tables 1,2) can be understood by considering the polarity influence on E^*, P^* and the transition state (Fig.2). An increase of k_{nr} with solvent polarity (positive solvatokinetic behaviour) is indicative that the quenching state P^* is preferentially stabilized in the polar solvent, hence more polar than E^*, explainable on the basis of the Bell-Evans-Polanyi principle /15/ (Fig. 2). For DCS-B, on the other hand, the negative solvatokinetic dependence (slowing of nonradiative rates with increasing solvent polarity) signifies that P^* is less polar than E^*. These experiments thus indicate that the electronic nature of the P^* state changes as one goes from S-B to DCS-B: Higly polar for S-B, weakly polar for DCS-B. The same reasoning holds for the flexible stilbenes S, DS and DCS, with the additional complication of the intervening highly polar A^* state.
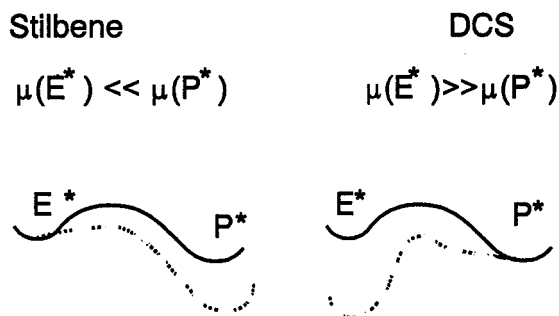
Stilbene   DCS

$\mu(E^*) \ll \mu(P^*)$ $\mu(E^*) \gg \mu(P^*)$

Fig. 2: Influence of a polar solvent (.. .. ..) on the relative energies of E^* and P^* in stilbene and donor-acceptor-stilbenes.

The different polarity and hence electronic nature found for the P^* state in stilbene and donor-acceptor-stilbenes can be correlated with the predictions from recent theoretical developments regarding biradicaloid states /1-3/. These theories predict that the double-bond twisted excited state P^* of ethylene or stilbene should be of higly polar or "hole pair" nature, see Fig. 3, and the ground state nonpolar, while a state-reversal between S_0 and S_1 should take place for sufficiently strong donor-acceptor substituents, and thus P^* should become of "dot-dot" nature with weakly polar properties. The theoretical expectation and the experiments described above mutually support each other. Explicit quantum chemical calculations (Table 3) also yield the same answer of a reversal of the nature of S_0 and S_1 upon donor-acceptor substitution. Interestingly, these results also predict, that DS-B should behave similarly to S-B, i.e. with a highly polar P^* state and therefore positive solvatokinetic dependence, and this is in fact what the experiments tell us (Tables 1 and 2).
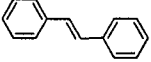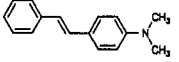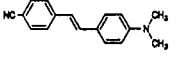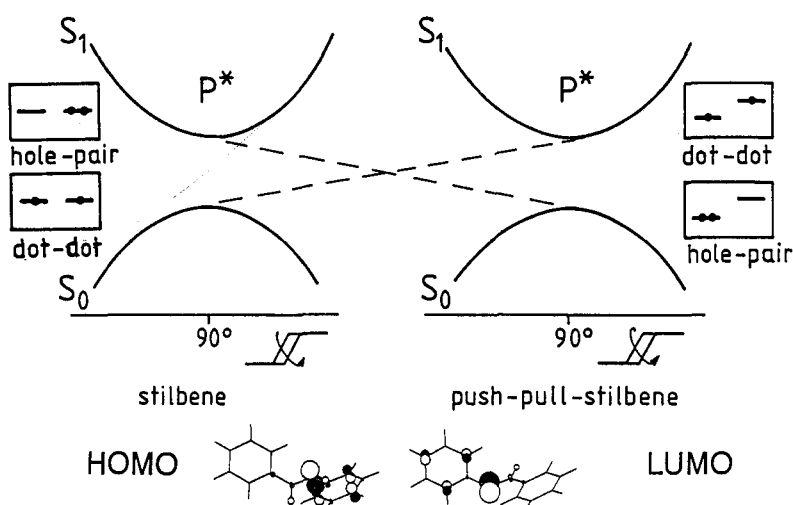
Fig. 3: The Biradicaloid Model predicts a state inversion for the double bond twisted species as one goes from symmetric stilbene to donor-acceptor-stilbenes. In stilbene, the usual closed-shell ground state configuration ("hole-pair" with doubly occupied HOMO) represents S_1. Due to the localization of HOMO and LUMO on the molecular subunits, for a slight geometric disturbance, this hole-pair configuration corresponds to a highly polar structure. The "dot-dot" configuration (HOMO-LUMO singly occupied) possesses nonpolar or weakly polar character and is S_0 in stilbene, but S_1 in DCS.

Table 3: Results of CNDO/S calculations on stilbenes in the planar (E, $\phi=0$) and the double-bond twisted conformation (P, $\phi=90°$). For P, the state reversal between (S, DS) and DCS can be seen from the dipole moments for ground (P_0) and excited state (P^*) and is indicated by the labels "hp" and "dd" for hole-pair and dot-dot type electronic structures. For the planar conformation (E^*), the dipole moment strongly increases with donor-acceptor substitution.

state	S	DS	DCS
E^* ($\varphi=0$, S_1)	$\pi\pi^*/$ 0 D	$\pi\pi^*/$ 7 D	$\pi\pi^*/$ 19 D
P^* ($\varphi=90$, S_1)	hp / 8 D	hp / 10 D	dd / 3 D
P_0 ($\varphi=90$, S_0)	dd / 0 D	dd / 1.5 D	hp / 15 D

To summarize, we have shown that solvatokinetic experiments and qualitative as well as quantitative theoretical models yield a satisfactory description to explain the photophysical behaviour of a whole range of bridged stilbenes restricted to the photochemical transition towards the phantom singlet state P^*. The electronic nature of P^* changes as the donor-acceptor strength of the substituents increases.

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