Triplet energy accepting properties of styrenes: examination of the relationship between the degree of "non-vertical" behaviour and the magnitude of a specific single-bond torsional angle

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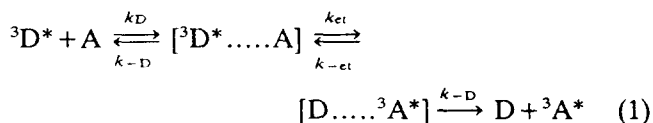*Department of Chemistry, University of Manchester, Manchester, M13 9PL, UK*

Abstract

The triplet energy accepting properties of phenylethene (styrene), 2-methyl-1-phenylpropene and phenyladamantylidene have been examined. It is shown that the degree of "non-vertical" behaviour, i.e. the donor triplet energy range over which non-classical behaviour is observed, increases with the degree of torsion about the formal single bond between two adjacent components of a conjugated π system. The result strongly supports the contention that the key to "non-vertical" behaviour, as it applies to conjugated π systems, is torsion about formal single bonds on the ground state surface.

Keywords: Non-vertical transfer; Triplet state; Styrenes; Triplet energy transfer; Sandroz plots

1. Introduction

In the early 1960s, it was discovered that triplet energy transfer (see Eq. (1))

$$^3D^* + A \underset{k_{-D}}{\overset{k_D}{\rightleftharpoons}} [^3D^* \ldots A] \underset{k_{-et}}{\overset{k_{et}}{\rightleftharpoons}}$$

$$[D \ldots {}^3A^*] \xrightarrow{k_{-D}} D + {}^3A^* \quad (1)$$

to certain flexible π systems, typified by *cis*-stilbene, exhibited unusual properties [1–4]. The behaviour of these acceptor π systems was characterized [5] by non-adherence to the Sandros equation (Eq. (2)) [6].

$$k_{obs} = k_D \, e^{-\Delta E_T/RT}(1 + e^{-\Delta E_T/RT})^{-1} \quad (2)$$

This equation, which is based on the assumption that k_{et} and k_{-et} are fast relative to other processes, has been used routinely as a guide to classical behaviour. As the donor triplet energy is decreased, a point is reached where energy transfer becomes less than the optimum exothermic value. For classical acceptors, a further reduction in the donor triplet energy causes the rate constants to decrease rapidly as a consequence of their exponential dependence on ΔE_T, the difference between the acceptor and donor triplet energies. In the case of *cis*-stilbene and its relatives, the rate constants decrease much less dramatically as the apparent "en-

dothermicity" increases as the donor triplet energy decreases by several kilocalories. This behaviour led to the term "non-vertical" triplet energy transfer, a phenomenon which has been the subject of much discussion over more than two decades [7–14]. Once produced, the triplet states of flexible π systems relax by torsion about their formal double bonds and, until recently, it has generally been accepted that the "non-vertical" transfer of triplet energy to such systems involves entry of the molecule into the triplet surface at some lower energy point along the coordinate corresponding to the aforementioned double-bond torsion [9,12,14]. The details of how this occurs have been controversial [12–14].

In contrast with the above, we have recently presented evidence [15–19] indicating that the "non-vertical" behaviour is in fact a consequence of low-energy single-bond torsional modes available at room temperature, and that this behaviour is restricted to significantly non-planar π systems whose S_0 and T_1 equilibrium geometries will be appreciably different with respect to such single-bond torsion. In Fig. 1, we show schematically the changes in the relationship of the S_0 and T_1 surfaces as torsion about a formal single bond is enforced by steric interactions. The following factors are taken into consideration. (a) The equilibrium energies of both surfaces will increase with single-bond torsion. (b) Because the π bond order across the formal single bond
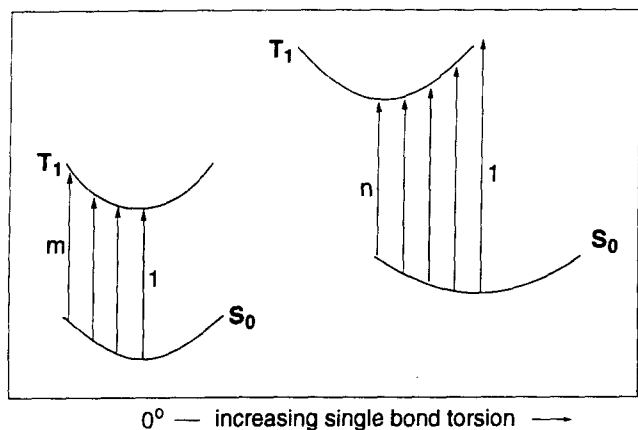
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Fig. 1. Schematic representation of the relationship between the S_0 and T_1 surfaces as a planar conjugated π system is forced into non-planarity by steric interactions.

is enhanced in T_1 relative to S_0, the T_1 surface will rise more steeply from the equilibrium position than will that of S_0. (c) Because of the difference in these π bond orders, a system with a planar equilibrium geometry on S_0 must have a planar equilibrium geometry on T_1 with respect to single-bond torsion. (d) Where non-planarity is enforced by steric interactions, the π bond order across the single bond is reduced and the S_0 surface should be significantly flatter. (e) Because of the difference in the π bond order, where non-planarity is sterically enforced, the excited state equilibrium geometry will be closer to planarity than that of S_0. The well-known case of biphenyl exemplifies this point. We have proposed [19] that the observed "non-vertical" behaviour for significantly non-planar systems results from the occupancy of a series of single-bond torsional levels on S_0. Because of the torsional displacement of the equilibrium geometries, a series of vertical transitions (1–n; see Fig. 1) will have significantly different triplet excitation energy requirements. For high donor triplet energies, all transitions will be exothermic and an optimum rate constant will be observed. As the donor triplet energy is systematically lowered, a point will be reached where transition 1 will become endothermic. The "non-vertical" or torsional progression [19] region then follows, where transitions 1 to n become sequentially endothermic. When all transitions are endothermic, standard activated behaviour is observed as the donor triplet energy is lowered further.

If this explanation based on the scenario of Fig. 1 is correct, one would anticipate that the greater the single-bond torsional angle (i.e. the greater the sterically induced ground state distortion from planarity), the lower the π bond order, the greater the angular amplitude of the available single-bond torsional modes and the more pronounced the "non-vertical" behaviour. In other words, we would anticipate that the donor triplet energy range covering the transitions 1 to n in

Fig. 1 would increase with the single-bond torsional angle. To date, a direct comparison of the triplet energy accepting properties of a unique chromophore subjected to different degrees of single-bond torsion has been unavailable. The aim of this work is to provide such a comparison. In choosing the particular π system, the following considerations were addressed.

(1) To avoid ambiguities of the type associated with the cis-stilbenes, which have two different single-bond torsional angles [16], the π system chosen needed to possess a unique single bond whose torsional angle could be manipulated.

(2) The chromophore needed to be such that reasonably comprehensive Sandros plots could be constructed over a donor triplet range specified by available sensitizers.

(3) The acceptor triplets, once formed, needed to be able to undergo rapid decay as a consequence of efficient relaxation to a perpendicular state formed by twisting about a formal and unique double bond, i.e. not constrained within a ring. In other words, there would be no artificial restriction on double-bond torsion which could be construed as influencing the results.

A chromophore which appears to accommodate the above criteria is that of styrene, and we report here the triplet energy accepting properties of the styrenes 1–3 which, according to a combination of molecular mechanics calculations and X-ray structure determinations, have equilibrium phenyl–vinyl torsional angles of approximately 0°, 34° and 45° respectively.

1   2   3
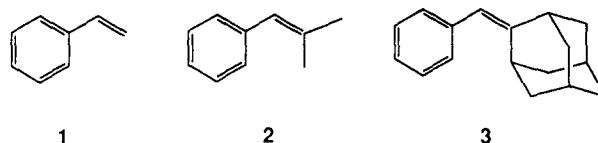
2. Experimental section

2.1. Time-resolved techniques

Pulse radiolysis and laser flash photolysis experiments were performed as described earlier [15,20].

2.2. Purification of materials

Benzene (AnalaR BDH) and sensitizers were purified as described previously [15,21]. Styrene (Aldrich) was purified by washing with 5% aqueous sodium hydroxide followed by water, drying over anhydrous magnesium sulphate and distillation at 25 °C under reduced pressure. It was shown to be better than 99.8% by gas–liquid chromatography (GLC) (10% OV351 on Chrom-W-

AW 80–100 mesh; 1.7 m×4.0 mm; 1.4 kg cm^{-2}; 200 °C injection; 60 to 200 °C at 4 °C min^{-1}).

2.3. Preparation of 2-methyl-1-phenylpropene (2)

(a) To magnesium (10 g) and mercuric chloride (5 mg) in ether (175 ml) was added 2-bromopropane (42 g) in aliquots. After initiation with a crystal of iodine and stirring at room temperature for 1 h, benzaldehyde (33 g) was added in aliquots to the stirred mixture. After a further hour, quenching with 10% aqueous ammonium chloride (200 ml) followed by standard aqueous/ether work-up gave 2-methyl-1-phenylpropan-1-ol (38 g) as a yellow oil.

(b) The latter was refluxed for 45 min in benzene (300 ml) containing p-toluenesulphonic acid (10 g) in a Dean and Stark apparatus. Cooling, repeated washing with 10% aqueous sodium bicarbonate, drying (MgSO₄) and removal of the benzene under vacuum gave a pale orange oil. Chromatography on Merck 60 silica gel (230–400 mesh) with hexane as eluent, followed by distillation (40 °C, 2.0 Torr) gave the required compound as a colourless oil (7.5 g), exhibiting the expected mass (MS), UV, IR and nuclear magnetic resonance (NMR) spectra. Purity by GLC (0.25 μm film of OV1; 8.0 m×0.22 mm (inside diameter (i.d.)); 0.15 kg cm^{-2}; 200 °C injection; 50 to 300 °C at 3 °C min^{-1}) was better than 99.5%.

## 2.4. Preparation of phenyladamantylidene (3)

In a protocol essentially identical to that given under (a) above, but using magnesium (2.42 g), ether (75 ml), benzyl bromide (13.7 g) and adamantanone (10.0 g in ether (50 ml)), 2-benzyl-2-adamantanol (38 g) was obtained as a yellow oily solid. With the identical procedure and purification described in (b) above, phenyladamantylidene (10 g) was obtained as a low melting white solid after distillation (100 °C, 2.0 Torr). ^{1}H NMR (300 MHz): δ 1.94 (broad S, 7H), 2.00 (broad S, 3H), 2.08 (broad S, 2H), 2.55 (broad S, 1H), 3.23 (broad S, 1H), 6.25 (broad S, 1H), 7.25 (M, 3H), 7.35 (M, 2H). MS (Cl with NH₃): 225 (100%, M$^+$ +1), 224 (63%, M$^+$), 242 (39%, M$^+$ +18). UV (ethanol): λ_{max} = 247 nm (ε = 13 100 l mol^{-1} cm^{-1}). The structure was confirmed by X-ray diffraction [22].

3. Results

3.1. Triplet lifetimes

It is well documented [23,24] that the triplet lifetime of styrene (1) is short (approximately 23 ns) as a consequence of rapid relaxation to the perpendicular triplet followed by cross-over to S₀. We have produced

the triplet states of 1, 2 and 3 by pulse radiolysis of benzene solutions (0.1 mol l^{-1}) both with and without the presence of β-carotene (10^{-3} mol l^{-1}) as a triplet monitor [25,26]. Given our current time resolution, these experiments only allow us to put an upper limit of about 30 ns on all three triplet lifetimes. Nevertheless, this clearly confirms that, as anticipated on the basis of literature data [23,24], all three triplets formed in the energy transfer experiments to be described can relax rapidly to the perpendicular state. For 2 and 3 this should be even more favourable than in the case of 1 due to steric effects. Twisting to perpendicularity about the formal double bond will be concomitant with twisting to planarity about the formal single bond to give a benzyl/alkyl biradical species (4) as the relaxed state. One can therefore be confident that any differences in triplet energy accepting properties are not associated with sterically imposed constraints on a decrease in the S₀–T₁ gap as the molecule progresses along the double-bond torsional coordinate.

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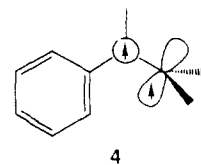
3.2. Triplet energy transfer experiments

A combination of pulse radiolysis and laser flash photolysis [15] has been used to determine the rate constants of triplet energy transfer in benzene from a series of donors to the styrenes 1–3. The donor ground state concentrations employed and the very short styrene triplet lifetimes ensured the absence of back transfer. A typical set of data is shown in Fig. 2 and rate constants are summarized in Table 1. In Fig. 3, Sandros plots of the data are shown for each styrene. Points to be emphasized are as follows.

(1) As anticipated on the basis of the single-bond torsional mechanism, the rate constants for energy transfer from a particular donor are always lower for the less planar π system (see below).

(2) The full line in Fig. 3 is that based on Eq. (2) for a molecule with a vertical triplet energy of 60.5 kcal mol^{-1}. Since recent work quotes a value of 60.8 kcal mol^{-1} for styrene [24], the data for 1 are in reasonable agreement with the theoretical line for classical transfer. However, it is quite clear that in the isoenergetic region the data points are somewhat lower than the theoretical expectation (see below).

(3) The significantly non-planar 2 and 3 exhibit gross "non-vertical" behaviour. Although the range of available donors has prevented us from clearly
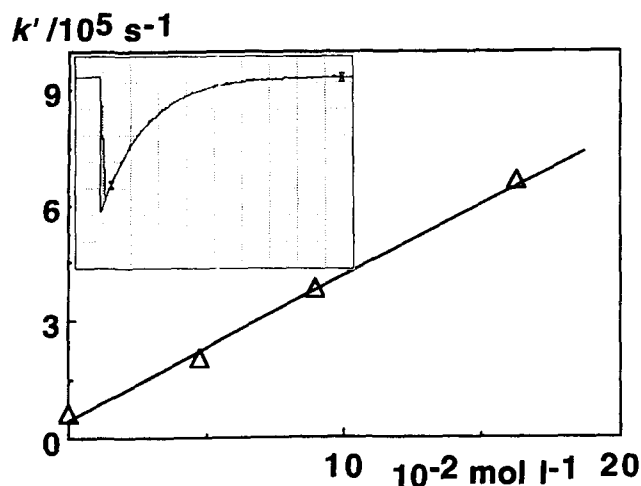
Fig. 2. Plot of pseudo-first-order rate constant (k') for decay of 2-acetonaphthone triplet in deaerated benzene as a function of the concentration of phenyladamantylidene (3). Inset: time dependence with first-order fit of the transient absorption monitored at 430 nm after absorption of a 4 mJ laser pulse (355 nm) by a deaerated benzene solution of 2-acetonaphthone (2×10^{-3} mol l^{-1}; $OD_{355} = 0.34$) containing phenyladamantylidene 3 (1.6×10^{-1} mol l^{-1}); $k' = 6.6 \times 10^5$ s^{-1}; 4.0% absorption per division; 1 μs per division.

Table 1
Rate constants (k_{obs}, l mol^{-1} s^{-1}) of triplet energy transfer in benzene to styrenes 1, 2 and 3 as a function of the donor triplet energy ($E_T(D)$, kcal mol^{-1})

Donor	$E_T(D)$ [a]	k_{obs} (1)	k_{obs} (2)	k_{obs} (3)
Acetophenone	73.6	7.2×10^9	5.2×10^9	3.7×10^9
4'-Methoxyacetophenone	71.8	6.8×10^9	4.4×10^9	2.6×10^9
Benzophenone	68.6	5.3×10^9	2.3×10^9	1.1×10^9
Biphenyl	65.7	4.0×10^9	1.4×10^9	3.2×10^8
Phenanthrene	61.9	2.0×10^9		
Naphthalene	60.9	8.5×10^8	1.9×10^8	2.9×10^7
2-Acetonaphthone	59.0	3.9×10^8	3.2×10^7	6.0×10^6
Chrysene	56.6	9.5×10^6	6.2×10^6	9.8×10^5
Fluoranthene	54.2	1.5×10^5	1.2×10^5	1.0×10^5

[a] Ref. [27].

defining the fully exothermic region for 2 and 3, it is apparent that the data for 3 become less than the optimum at higher $E_T(D)$ than for 2, and the region of the plot which exhibits non-classical behaviour is significantly greater (approximately 21 kcal mol^{-1}), as predicted.

(4) We have pointed out the deviation from anticipated classical behaviour in the isoenergetic region for the planar 1. As far as we are aware, this is normally the case for flexible planar π systems. This is exemplified in Fig. 4, which shows Sandros plots for 1 and the essentially planar trans-stilbene [5] and (E,E)-2,4-hexadiene [28]. The data for the latter pair have been displaced along the abscissa (see caption to Fig. 4) to aid comparison, and it is clear that all three structurally distinct but es-
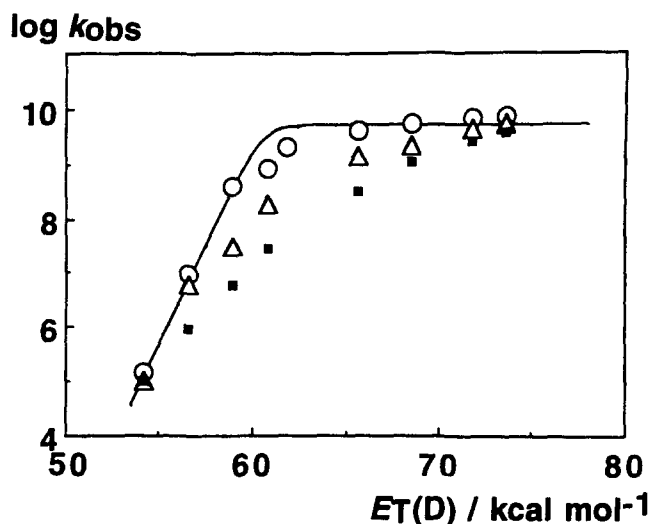

Fig. 3. Plot of logk_{obs} vs. $E_T(D)$ for triplet energy transfer from donors to styrenes 1 (circles), 2 (triangles) and 3 (squares) (see Table 1). The full line is that expected for a vertical acceptor with a triplet excitation energy requirement of 60.5 kcal mol^{-1} and an optimum rate constant for exothermic transfer of 7.0×10^9 l mol^{-1} s^{-1}.
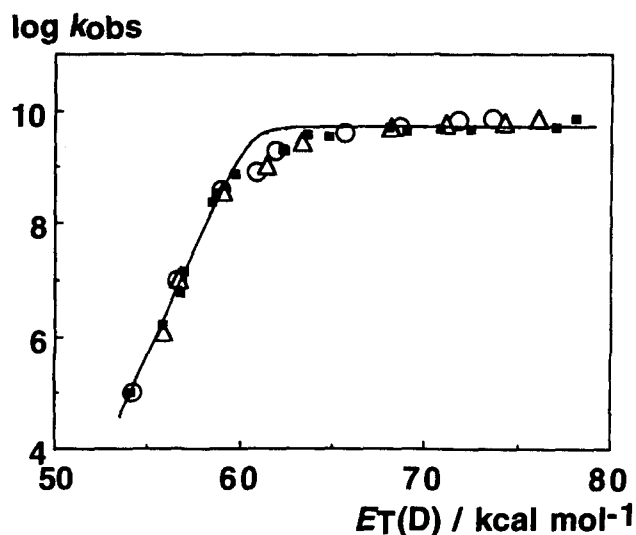

Fig. 4. Plot of logk_{obs} vs. $E_T(D)$ for triplet energy transfer from donors to the essentially planar molecules styrene 1 (circles), trans-stilbene [5] (squares) and all-trans-hexa-2,4-diene [28] (triangles). For the latter two acceptors, the data points have been displaced to higher donor triplet energies, 11 kcal mol^{-1} and 2.5 kcal mol^{-1} respectively, to facilitate comparison. The full line is as defined in Fig. 3.

sentially planar molecules show identical sensitivity to donor triplet energies, including the isoenergetic region. There is a simple, albeit unproven, explanation for the small deviation from truly classical behaviour in this region. The equilibrium geometries of S_0 and T_1 are both planar for these molecules (see Fig. 1) and this has important consequences. Firstly, the optimum π bond order on S_0 means that the amplitude of single-bond torsions possible

at room temperature will be less. Secondly, the relationship between the two surfaces minimizes the difference in the triplet excitation energy requirements of individual torsional levels (1–m; see Fig. 1). Thirdly, in contrast with the severely twisted system (see Fig. 1), it is transfer to the least populated torsional level which becomes endothermic first as $E_T(D)$ is decreased. The result is the relatively small deviation from classical behaviour. Having said this, we are unaware of any system, flexible or otherwise, for which, based on the Sandros equation, absolutely clear classical behaviour right through the isoenergetic region has been demonstrated.

In summary, the triplet energy accepting properties of styrene and appropriate derivatives appear to be in complete accord with a situation in which the relationship between the donor triplet energies and the rate constants for transfer to flexible π systems is a function of the occupancy of single-bond torsional levels and the relative positions of the ground and triplet state surfaces with respect to such torsion. It should be emphasized that if the coordinate for double-bond torsion was the key in this respect, one would expect the degree of non-classical behaviour to increase in the order $3 < 2 < 1$, i.e. that of decreasing π bond order across the formal vinyl double bond. As demonstrated herein, the reverse is the case. A paper has recently appeared in which the behaviour of the trans and cis isomers of β-methylstyrene has been reported [29]. As anticipated, "non-vertical" behaviour is observed only for the non-planar cis isomer.

Acknowledgements

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