Evidence that 'Nonvertical' Triplet Energy Transfer to Flexible π-Systems is a Function of Single-bond as opposed to Double-bond Torsion: Comparison of 2,3-Diphenylnorbornene and *cis*-Stilbene

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2,3-Diphenylnorbornene and *cis*-stilbene exhibit essentially identical 'nonvertical' triplet excitation behaviour, in agreement with a mechanism requiring torsion about formal single bonds on the ground-state surface.

The 'nonvertical' or non-classical behaviour of certain flexible π-systems with respect to endothermic triplet energy transfer has been a subject of considerable mechanistic discussion[1] which has centred around the *cis*-stilbene molecule. In this communication we report that 2,3-diphenylnorbornene **1**, a molecule with essentially the same π-system geometry as *cis*-stilbene, but with a central double bond which cannot undergo significant torsion on either the ground state or triplet state surfaces, exhibits virtually identical 'nonvertical' triplet excitation behaviour. This is a clear indication that the 'nonvertical' phenomenon, as it relates to flexible π-systems, reflects single-bond as opposed to double-bond torsion. The result is in complete accord with expectations based on the effects of single-bond torsion on the vertical triplet energies of conjugated π-systems.

2,3-Diphenylnorbornene was synthesised *via* standard procedures and the geometry of its non-planar π-system shown to be very similar to that of *cis*-stilbene.‡ The molecule was prepared because the rigidity of its σ-framework was expected severely to restrict geometry changes on both S_0 and T_1 which result from formal *double-bond* torsion. Strong experimental support for this expectation was obtained by pulse radiolysis experiments which demonstrated a triplet lifetime of 65 μs for **1**,§ three orders of magnitude larger than that of 61 ns[4] for the perpendicular stilbene triplet which is essentially isoenergetic with S_0 at that geometry. There is therefore no doubt that the σ-framework of **1** prevents the approach of its S_0 and T_1 surfaces along the central double bond torsional coordinate. Molecule **1** and *cis*-stilbene could therefore hardly be expected to exhibit similar 'nonvertical' behaviour if that behaviour was consequent upon double-bond torsion as has been generally assumed.

In Table 1 are shown rate constants, k_{et}, for triplet energy transfer to **1** determined by a combination of pulse radiolysis and pulsed laser excitation.§ A Sandros plot[5] of these data, together with those originally published for *cis*-stilbene, is shown in Fig. 1. Not only are both molecules clearly 'nonvertical' acceptors of triplet energy but their sensitivities to donor triplet energy are essentially identical. Such a result clearly indicates that the key torsional coordinate resulting in 'nonvertical' behaviour by these systems is not that involving the central double bond. However, as outlined below such behaviour is readily and simply explained on the basis of single-bond torsion.

All that is required for observation of 'nonvertical' behaviour is that the vertical triplet excitation energy requirement of the acceptor be reduced as a consequence of ground-state geometric distortion during the lifetime of the encounter complex. Gross changes in the ground-state geometries of flexible π-systems occur, certainly at ambient temperatures, *via* single-bond as opposed to double-bond torsion, the classic consequence in sterically unconstrained situations being s-*cis* ⇄ s-*trans* isomerisation. For molecules such as **1** and *cis*-stilbene which possess π-systems with non-planar equilibrium geometries, single-bond torsion towards a more planar

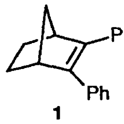

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Table 1 Donor triplet energies (E_T/kcal mol^{-1}; 1 cal = 4.184 J) and rate constants (k_{et}/l mol^{-1} s^{-1}) for triplet energy transfer to 2,3-diphenylnorbornene in benzene

Donor	E_T[a]	k_{et}
4'-Methoxyacetophenone	71.8	5.0×10^9
Benzophenone	68.6	3.6×10^9
Biphenyl	65.7	3.0×10^9
Naphthalene	60.9	3.0×10^9
Chrysene	56.6	1.4×10^9
Benzil	50.9[b]	2.9×10^8
Benzo[*b*]triphenylene	50.8	1.7×10^8
Pyrene	48.2[c]	2.7×10^7
Acridine	45.0	3.0×10^6

[a] Ref. 5 unless otherwise stated. [b] Ref. 6. [c] Ref. 7.

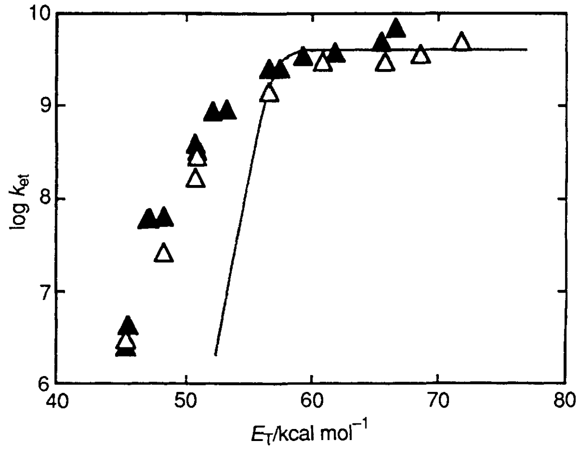

Fig. 1 Plot of log k_{et} for triplet energy transfer from sensitizer molecules to *cis*-stilbene (▲, data from ref. 1*b*) and to 2,3-diphenylnorbornene (△). The solid line is that expected[5] for a vertical acceptor with the vertical triplet energy of *cis*-stilbene (*ca.* 57 kcal mol^{-1}).[9]

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‡ Phenyl–alkene torsional angles determined by X-ray analysis are 34.3 and 44.0° for **1**, 36.6 and 39.5° for a *cis*-stilbene derivative.[2] Absorption maxima and extinction coefficients are: λ_{max}/nm 286 (ε 10 340), 224 (22 560) and 204 (25 700) for **1**, 277 (10 400), 224 (22 000) and 202 (25 000) for *cis*-stilbene. The S_0–T_1 absorption spectra of **1** and *cis*-silbene, measured at 100 atmospheres of oxygen in carbon tetrachloride, were extremely similar with onsets in both cases close to 550 nm, a clear indication that these molecules have similar spectroscopic triplet energies.

§ The time-resolved techniques employed in this work have been described in detail.[3] The identity of the triplet state was confirmed by its ability to transfer triplet energy to perylene (k_{et} = 3.5×10^9 l mol s^{-1}). The rate constant for quenching by oxygen (k_{ox} = 2.5×10^9 l mol^{-1} s^{-1}) was a factor of about three smaller than the corresponding value for stilbene triplet,[4] as would be expected for a molecule whose S_0 and T_1 surfaces are kept far apart.

geometry within the encounter complex will increase π-conjugation. This will in turn lower the vertical triplet energy requirement and enhance the rate constant for triplet energy transfer, *i.e.* 'nonvertical' behaviour will be observed. Their essentially identical behaviour in this respect is readily understandable on the basis of the very similar single-bond torsional angles in the ground state. An additional corollary of this analysis is that flexible π-systems with essentially planar equilibrium geometries will not exhibit 'nonvertical' behaviour because single-bond torsion from a planar to a non-planar arrangement can only raise the vertical triplet energy requirement. This distinction between planar systems which behave vertically and non-planar systems which behave 'nonvertically' is exactly what we have also observed for simple dienes[10] and trienes.[3]

In summary, we propose that 'nonvertical' triplet energy transfer, certainly as it applies to flexible π-systems, is a direct consequence of single-bond torsion within a significantly non-planar acceptor during the lifetime of the encounter complex. This proposal is clearly not in accord with virtually all previous work in this area which has concluded that the key torsional coordinates are those involving formal double bonds. It should be emphasised, however, that these results are in complete accord with the known 'nonvertical' behaviour of biphenyl,[1c] a non-planar molecule for which only single-bond torsion is available. In this respect it is not unreasonable to consider **1** and *cis*-stilbene as vinylogous biphenyls.

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