

## 'Nonvertical' Triplet Energy Transfer to a Severely Non-planar 1,3-Diene: Proposal of a Mechanism based on Progressive Endothermicity of Vertical Transfer to Individual Single-bond Torsional Levels

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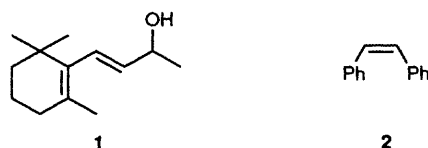
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The 1,3-diene unit in *trans*- $\beta$ -ionol exhibits extreme 'nonvertical' behaviour in accepting triplet energy from a series of donors, a result strongly supporting a mechanism herein presented, which depends on the modes of single-bond torsion available to non-planar molecules and the relative dispositions of their  $S_0$  and  $T_1$  surfaces with respect to such torsion.

We have recently presented evidence that 'nonvertical' triplet energy transfer as it applies to  $\pi$ -systems is a function of the degree of non-planarity of the particular system and results from the large number of single-bond torsional modes which are available to such molecules.<sup>1</sup> These conclusions contrast sharply with previous discussions of this phenomenon which have been centred on mechanisms involving torsion about the formal double bonds of the  $\pi$ -system.<sup>2</sup> In this communication we provide (i) the strongest support at a molecular level for the single-bond torsional mechanism and (ii) a simple rationale for the phenomenon based on the relationship between the  $S_0$  and  $T_1$  surfaces as a function of single-bond torsion and the effect that this has on Sandros<sup>3</sup> plots.

If single-bond torsion is the key to 'nonvertical' behaviour the ideal molecule to optimise such behaviour would have a minimum of  $\pi$ -delocalisation, *i.e.* be a 1,3-diene with an equilibrium central single-bond torsional angle of  $90^\circ$ , *i.e.* no  $\pi$ -bond order restricting rotation. Such a molecule would conversely have the maximum possible bond order across the formal double bonds making a mechanism based on double-bond torsion<sup>2</sup> at its most unlikely in terms of molecular structure. Although such a grossly twisted molecule is not currently available to us, we have been able to show that the central single bond in the diene system of *trans*- $\beta$ -ionol **1** has a very large torsional angle  $50$ – $60^\circ$ .<sup>†</sup> This diene therefore provides a close to optimum model to test the conclusions outlined above. With such considerations in mind we have



**Table 1** Donor triplet energies [ $E_T(D)$ /kcal mol<sup>-1</sup>] and rate constants ( $k_{et}$ /dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) for triplet energy transfer to *trans*- $\beta$ -ionol in benzene

Donor	$E_T(D)^a$	$k_{et}^c$
Acetophenone	73.6	$2.8 \times 10^9$
4'-Methoxyacetophenone	71.8	$2.5 \times 10^9$
Benzophenone	68.6	$1.4 \times 10^9$
Biphenyl	65.7	$7.2 \times 10^8$
Naphthalene	60.9	$2.5 \times 10^8$
2-Acetonaphthone	59.0	$1.8 \times 10^8$
Chrysene	56.6	$1.3 \times 10^8$
Fluoranthene	54.2	$6.0 \times 10^7$
1,2,5,6-Dibenzanthracene	52.2	$1.8 \times 10^7$
1,2,3,4-Dibenzanthracene	50.8	$3.3 \times 10^6$
Pyrene	48.2 <sup>b</sup>	$1.3 \times 10^5$

<sup>a</sup> Ref. 5 unless otherwise stated. <sup>b</sup> Ref. 6. <sup>c</sup>  $\pm 10\%$ .

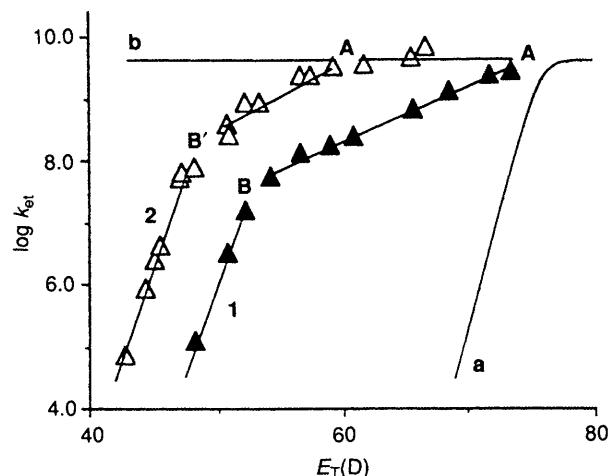
<sup>†</sup> The X-ray structure of the 1-naphthyl urethane of **1** shows a torsional angle of  $54^\circ$ . Energy minimisation calculations on **1** itself give a value of  $58^\circ$ .

determined rate constants for triplet energy transfer in benzene to **1**,  $k_{et}$ , for a series of donors with a wide range of available triplet energies,  $E_T(D)$ . Data were obtained by well-documented laser flash photolysis and pulse radiolysis techniques<sup>4</sup> and results are summarised in Table 1 and Fig. 1 which shows a Sandros plot<sup>3</sup> of the data. Experimental points show extreme deviation from vertical behaviour. For comparative purposes a similar plot is included in Fig. 1 for the archetypal 'nonvertical' acceptor *cis*-stilbene **2** based on published data.<sup>7</sup> We would make the following points concerning these plots.

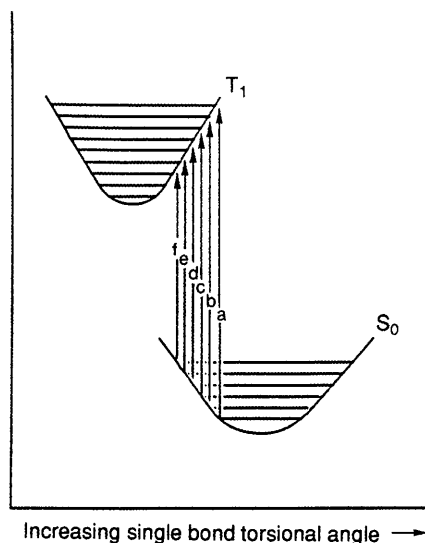
(i) At high  $E_T(D)$  the plot for **1** does not quite reach the optimum 'exothermic' value for our available range of sensitizers. This is simply a consequence of the anticipated high excitation energy requirements of a highly twisted diene. The line **a** is that for a vertical acceptor for which  $k_{et}$  would appear to become less than optimum at approximately the same value of  $E_T(D)$  as it would for **1**.

(ii) It would clearly appear that **1** and **2** show essentially the same behaviour towards donors. For each, there are three distinct regions, an optimum horizontal 'exothermic' region, not attained experimentally for **1** for reasons mentioned, a close to linear region **A** to **B** for **1** and **A'** to **B'** for **2** which we shall henceforth term the 'torsional progression' region and a normal activated region at the low  $E_T(D)$  end of the plots which is typical of the endothermic region of the plots for vertical acceptors, *cf.* line **a**.

(iii) Despite the aforementioned uncertainty in defining point **A** for **1**, it is absolutely clear that **A** to **B** covers a much greater  $E_T(D)$  range [ $\sim 22$  kcal mol<sup>-1</sup> (1 cal = 4.18 J)] than does **A'** to **B'** for **2**, strongly supporting the contention that



**Fig. 1** Plot of  $\log k_{et}$  vs.  $E_T(D)$  for triplet energy transfer from donors to *trans*- $\beta$ -ionol **1** (*cf.* Table 1) and *cis*-stilbene **2**.<sup>7</sup> Line **a** is that expected for a vertical acceptor with a triplet excitation energy requirement of  $75$  kcal mol<sup>-1</sup> and an optimum rate constant for exothermic transfer of  $4.0 \times 10^9$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. Line **b** is an extrapolation for this latter value to aid comparison.



**Fig. 2** Vertical transitions from single-bond torsional states of  $S_0$  to  $T_1$  for a significantly non-planar  $\pi$ -system. It is recognised that the average geometry for each torsional level will progress from that corresponding to the equilibrium geometry for the lowest level towards the extreme torsional geometries as one moves up the torsional ladder.

single-bond torsion is the key to the 'nonvertical' transfer mechanism.

Flexible conjugated  $\pi$ -systems, which would be severely sterically crowded in the planar configuration adopt non-planar arrangements by means of torsion about the formal single bonds of the  $\pi$ -system, **1** and **2** being prime examples. In Fig. 2 are shown schematically the  $S_0$  and  $T_1$  surfaces of such a  $\pi$ -system as a function of single-bond torsion together with occupied torsional excitation levels. The fact that the  $\pi$ -bond order across formal single-bonds is enhanced in the electronically excited  $T_1$  means that (i) the  $T_1$  minimum will be closer to the planar configuration than that of  $S_0$  and (ii) its potential surface will rise more steeply as a function of single-bond torsion. Assuming that the Boltzmann distribution within the torsional levels is not grossly different within the encounter complex for triplet transfer, levels of each type will make their own vertical contribution to the overall rate constant. For instance for **1**, at high  $E_T(D)$  transitions of all types (a–f in Fig. 2) are exothermic and the rate constant is optimum. As  $E_T(D)$  decreases through point A (Fig. 1) transitions of type a (Fig. 2) will become endothermic and their contribution to the overall rate constant will decrease rapidly (cf. line a in Fig. 1). Further lowering of  $E_T(D)$  results in sequential development of

endothermicity for transitions of types b–f. At point B all contributions have become endothermic and the slope of the plot becomes that for standard endothermic vertical transfer. The much wider 'torsional progression' region for **1** relative to **2** (Fig. 1) is to be expected on the basis of this mechanism. Firstly the relative displacements of the equilibrium geometries of  $S_0$  and  $T_1$  with respect to single-bond torsion will be largest for 1,3-dienes for bond-order reasons already mentioned, and secondly the larger the equilibrium single-bond torsional angle the flatter will be the  $S_0$  surface with respect to such torsion and the more pronounced the occupation of upper torsional levels.‡

Of course, bond-order considerations demand that a  $\pi$ -system which is planar on  $S_0$  is also planar on  $T_1$  with respect to single-bond torsion. Therefore, on the basis of the mechanism put forward here, approximately planar molecules will not exhibit significant 'nonvertical' behaviour, a conclusion that we have already reached experimentally.<sup>4,8</sup>

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‡ In the case of **1** the torsional progression region does appear to be more or less linear, the smaller range for **2** making such a conclusion less definite. It would appear clear that the detailed nature of this region will depend on individual non-planar structures and their particular torsional characteristics.