'Nonvertical' Triplet Energy Transfer to Cyclooctatetraene: Support for the Single-bond Torsion Mechanism

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The severely non-planar π-system of cyclooctatetraene exhibits extreme 'nonvertical' behaviour in accepting triplet energy from a series of donors, a fact strongly supporting the proposal that 'nonvertical' behaviour is a consequence of single-bond torsional modes on the ground-state surface.

We have recently proposed that the 'nonvertical' or non-classical behaviour of certain flexible π-systems with respect to apparently endothermic triplet energy transfer is a function of the degree of non-planarity of the particular π-system and results from the large number of single-bond torsional modes which are available to such molecules.[1,2] In this communication we report data for cyclooctatetraene (COT; **1**) which strongly support this view. We would argue that the larger the measured torsional angle between adjacent double bonds of a conjugated π-system the smaller will be the π-bond order across the formal *single bond*, the more extreme will be the amplitude of the *single-bond* torsional modes and the more extreme therefore should be the 'nonvertical' behaviour. Were, on the other hand, *double-bond* torsion on the ground-state surface the key to such behaviour as has been widely accepted,[3] the increasing π-bond order across the formal double bonds as a result of increasing non-planarity would make 'nonvertical' behaviour *less* likely. COT appears to be an excellent candidate for testing this hypothesis for the following reasons: (*a*) The torsional angle between adjacent double bonds in its tub-like structure **1** is large, 43.5 ± 2.9°.[4] This increases double bond localisation and provides a clear opportunity to test the considerations outlined above. (*b*) All the single bonds and all the double bonds are identical, thus eliminating ambiguity concerning more than one type of torsional arrangement. (*c*) The absence of conformers other than of the type depicted in structure **1** excludes potential problems due to the presence of two or more species with their own particular triplet energy accepting characteristics.

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With such considerations in mind we have determined rate constants for triplet energy transfer in benzene to COT, 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[5] and results are summarised in Table 1. In Fig. 1 is shown a Sandros plot[8] of these data together with a theoretical line for vertical triplet energy transfer to an acceptor where that transfer becomes less than the optimum at about the same magnitude of $E_T(D)$ as does transfer to COT (*ca.* 60 kcal mol^{-1}; 1 cal = 4.184 J). The COT molecule clearly exhibits gross 'nonvertical' behaviour. In addition this behaviour covers a huge donor triplet energy range approaching 20 kcal mol^{-1}, since the experimental points in Fig. 1 barely become parallel at low $E_T(D)$ values to the theoretical line shown for vertical

Table 1 Donor triplet energies [$E_T(D)$/kcal mol^{-1}] and rate constants (k_{et}/l mol^{-1} s^{-1}) for triplet energy transfer to cyclooctatetraene in benzene

Donor	$E_T(D)^a$	k_{et}
Benzophenone	68.6	7.4×10^9
Fluorene	68.0	9.5×10^9
Biphenyl	65.7	8.4×10^9
Naphthalene	60.9	7.9×10^9
2-Acetonaphthone	59.0	6.3×10^9
Chrysene	56.6	6.2×10^9
Fluorenone	53.0	4.6×10^9
Pyrene	48.2^b	1.9×10^9
Acridine	45.0	8.1×10^8
Anthracene	42.7	4.2×10^8
9,10-Dichloroanthracene	40.5	8.9×10^7

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

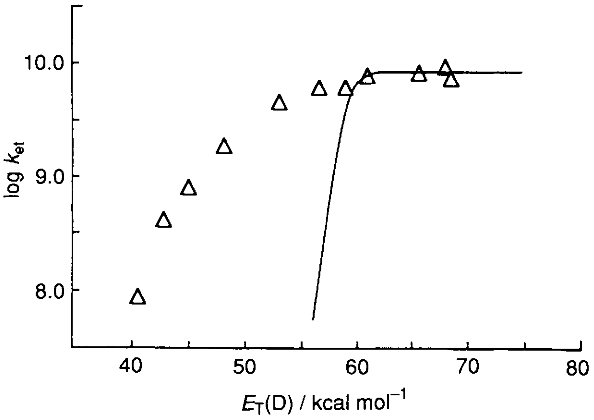

Fig. 1 Plot of log k_{et} *vs.* E_T(D) for triplet energy transfer from donors to COT (*cf.* Table 1). The solid line is that expected for a vertical acceptor with a triplet excitation energy requirement of 59 kcal mol^{-1}, *i.e.* where energy transfer begins to become less than the optimum at E_T(D) *ca.* 60 kcal mol^{-1}.[8]

transfer. This range is considerably larger than anything hitherto published, that for the archetypal 'nonvertical' acceptor *cis*-stilbene being 6–7 kcal mol^{-1}.[9] The data for COT therefore strongly support the contention[1] that the key to 'nonvertical' behaviour lies with single-bond torsional modes within flexible, non-planar π-systems.

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