Competition between Concerted and Non-concerted Modes in a π-Diradical

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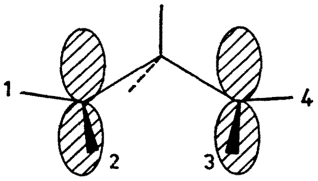
Summary In diradicals with degenerate molecular orbitals of opposite symmetry there is no preferred motion for re-closure, nonconcerted modes being equally probable as the two concerted modes.

ALTHOUGH the rules for allowed electrocyclic reactions of closed-shell conjugated reactants are well established,[1] the behaviour of open-shell systems in this respect has not been investigated.

Consider, as an example, the quasi-planar trimethylene intermediate suggested by Hoffmann.[2] Let us assume an idealized situation in which the starting geometry is such that the symmetric π orbital (π_+, say[3]) and the antisymmetric π orbital (π_-, say) are rigorously degenerate in energy. The lowest singlet wave function can then be written, in abbreviated fashion, as



$$\psi_0 = \frac{1}{\sqrt{2}}(\pi_+^2 - \pi_-^2)$$

with equal weights of the two configurations built on either orbital.[4] Since configuration π_+^2 would lead exclusively to disrotatory closure and configuration π_-^2 exclusively to conrotatory motion, it can be expected (and will be confirmed) that the two motions are equally probable here. The question arises, however, whether an intermediate *non-concerted* process would not be equally favourable.

A simple answer can be provided within the framework of the perturbational theory[5] in which the displacement co-ordinates induce mixing with low-lying excited states, and thereby are favoured to the extent that electronic relaxation is introduced. The relevant singlet excited states here[6] arise from $\pi \rightarrow \sigma^*$ or $\sigma \rightarrow \pi^*$ excitations.[5d] Typical functions occur in degenerate pairs, for instance the excited configurations

$$\begin{cases} \psi_C = \pi_-[(\sigma_1^* - \sigma_2^*) + (\sigma_4^* - \sigma_3^*)] \\ \psi_D = \pi_+[(\sigma_1^* - \sigma_2^*) + (\sigma_4^* - \sigma_3^*)] \end{cases}$$

where σ_j^* is the antibonding orbital in the CH_j bond and $\sigma_j^* - \sigma_{j+1}$ is the antibonding combination of two such orbitals for neighbouring bonds belonging to one methylene group. The subscripts C and D indicate that these are precisely the states which relax the pure conrotatory or the pure disrotatory motions for ground configurations π_-^2 (or π_+^2).

Now let Q_C be the internal symmetry co-ordinate for conrotatory twisting of the terminal methylenes, and Q_D that for disrotatory motion. Then a typical pair of non-concerted co-ordinates Q and Q' is defined by

$$\begin{cases} Q_C = aQ + \sqrt{1 - a^2}\,Q' \\ Q_D = -\sqrt{1 - a^2}\,Q + aQ' \end{cases}$$

(For $a = 1/\sqrt{2}$, Q and Q' correspond to the motion of a single methylene group).

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The relaxation energy for a motion along Q, say, is

$$\Delta E = \frac{-\left\langle \psi_0 \left| \frac{\partial V}{\partial Q} \right| \psi_C \right\rangle^2 - \left\langle \psi_0 \left| \frac{\partial V}{\partial Q} \right| \psi_D \right\rangle^2}{E_{C,D} - E_0}$$

(V, potential energy operator). Using the relation

$$\frac{\partial V}{\partial Q} \equiv a \frac{\partial V}{\partial Q_C} - \sqrt{1 - a^2}\, \frac{\partial V}{\partial Q_D}$$

and the fact that

$$\left\langle \psi_0 \left| \frac{\partial V}{\partial Q_C} \right| \psi_C \right\rangle \text{ and } \left\langle \psi_0 \left| \frac{\partial V}{\partial Q_D} \right| \psi_D \right\rangle$$

are the only non-vanishing matrix elements (with a common value b, say), we obtain

$$\Delta E = -\frac{b^2}{E_{C,D} - E_0}$$

The total relaxation energy is independent of the parameter a. It is clear that $Q_C(a \equiv 1)$ and $Q_D(a \equiv 0)$ are equally favoured; moreover any *non-concerted* mode is as probable as the pure concerted ones.

We conclude that in diradicals for which accidentally degenerate (or nearly degenerate) molecular orbitals would separately favour opposite concerted modes, *there is no preferred motion, any combination of the pure concerted co-ordinates being equally probable.* This conclusion will, of course, be invalidated if one of the following conditions prevails:

(1) The weights of the two m.o. configurations in ψ_0 are significantly different.

(2) The weights are equal but one concerted motion is accompanied by other geometrical changes—such as, here, the bending at the central carbon—which favour strongly the corresponding configuration in ψ_0.[7]

(3) Specific steric constraints of asymmetric nature modify the "classical" force constants[5b,d] in a manner which strongly favours one of the concerted modes.

The application of these results to such interesting systems as the biallyl radical and its collapse products[8] is straightforward.

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[1] R. B. Woodman and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.

[2] R. Hoffmann, *J. Amer. Chem. Soc.*, 1968, **90**, 1475.

[3] This orbital is delocalized into the central methylene group.[2]

[4] The calculated weights at the actual equilibrium configuration of this diradical are 46% π_+^2 and 54% π_-^2 (L. Salem, unpublished calculations).

[5] (a) R. F. W. Bader, *Mol. Phys.*, 1960, **3**, 137; (b) L. Salem, *Chem. Phys. Letters*, 1969, **3**, 99; (c) R. G. Pearson, *J. Amer. Chem. Soc.*, 1969, **91**, 1252; (d) L. Salem and J. S. Wright, *ibid.*, p. 5947.

[6] The ground state is a triplet, but we assume that the motions occur essentially in the singlet manifold.

[7] R. J. Crawford and A. Mishra, *J. Amer. Chem. Soc.*, 1966, **88**, 3963, footnote **24**.

[8] B. G. Odell, R. Hoffmann, and A. Imamura, in the press.