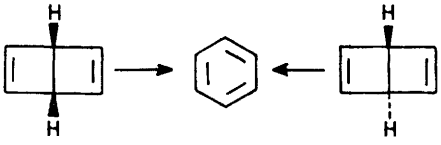
# Electrocyclic Ring Opening of 1α,4α- and 1α,4β-Bicyclo[2.2.0]hexa-2,5-dienes (*cis* and *trans* Dewar Benzenes): MNDO (Modified Neglect of Diatomic Overlap) Semiempirical Molecular Orbital Calculations

By Michael J. S. Dewar,* George P. Ford, and Henry S. Rzepa
(*The University of Texas at Austin, Austin, Texas* 78712)

*Summary* *trans*-Dewar benzene is calculated by the semiempirical SCF–MO method MNDO to have a barrier of 21 kJ mol$^{-1}$ towards the allowed conrotatory electrocyclic ring opening to benzene, suggesting that the species may have a transient existence at low temperatures, while the forbidden disrotatory opening of *cis*-Dewar benzene is correctly predicted to involve passage over a much higher barrier *via* a transition state of $C_{2v}$ symmetry.

Although the conversion of 'normal' (*cis*) Dewar benzene (**1**) into benzene (**2**) is exceedingly exothermic, the activation energy for this process is quite high (96 kJ mol$^{-1}$ in $C_2Cl_4$[1]). Woodward and Hoffmann[2] have attributed this to the 'forbidden' nature of the requisite disrotatory ring opening and have predicted on this basis that the corresponding conversion of *trans*-Dewar benzene (**3**) into (**2**) should require little or no activation, this reaction being both 'allowed' and even more exothermic than (**1**) → (**2**). We have now studied both these reactions, using a new semiempirical SCF MO treatment (MNDO[3]) recently developed here.



(1) (2) (3)

While (**3**) → (**2**) was indeed predicted to be extremely exothermic ($\Delta H$, 617 kJ mol$^{-1}$), (**3**) nevertheless represented a local minimum on the MNDO potential surface. The transition state for the interconversion was located by our usual procedure (*cf.* ref. 4) and characterized by showing that its Hessian (force constant) matrix had one, and only one, negative eigenvalue.[5] The calculated entropy of activation was small (0·56 J mol$^{-1}$ K$^{-1}$) and the geometry of the transition state was reactant-like [Figure 1(a)], as would be expected for so exothermic a reaction. The imaginary vibration of $a_g$ symmetry (798 cm$^{-1}$) correlated with that at (calc.) 723 cm$^{-1}$ in (**3**) and with the in-plane $e_{2g}$ ring deformation of (**2**) at (calc.) 616 and (obs.) 606 cm$^{-1}$.

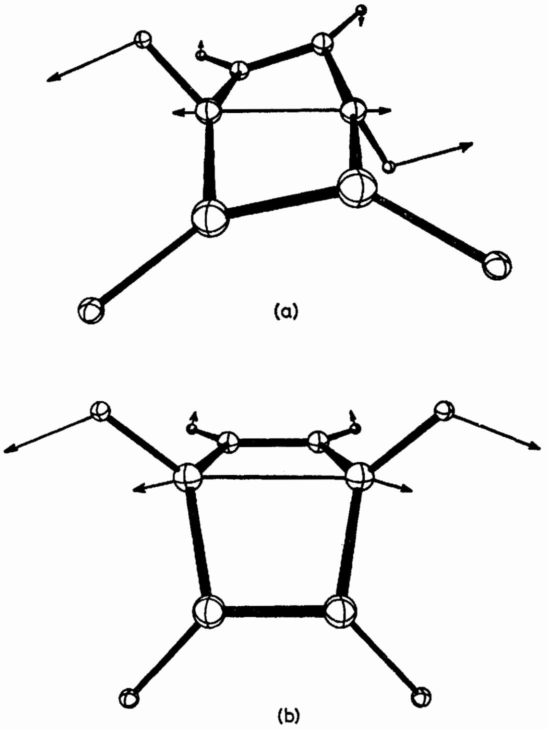


Figure 1. ORTEP plots of the calculated (MNDO) transition states for the conversion of (a) (**3**) → (**2**) and (b) (**1**) → (**2**). Arrows illustrate the form of the normal mode corresponding to the reaction co-ordinate in each case. Calculated 1,4 bond lengths: a, 1·820; b, 2·079 Å.

The eigenvector [Figure 1(a)] for the imaginary vibration also had the form expected. There is therefore no doubt that this species indeed represents the required transition state; the corresponding activation energy for (**3**) → (**2**) was 21 kJ mol$^{-1}$.

The validity of these results rests on the validity of the MNDO method which has as yet been applied only to a few reactions. It therefore seemed imperative to check it by a similar calculation for the analogous conversion of (**1**) into (**2**), which has been studied kinetically.[1] This reaction is also of interest in connection with theories of orbital isomerism[7] and chemiluminescent pericyclic processes.[8]

Dewar and Kirschner[9] performed calculations on the reaction (**1**) → (**2**) by the MINDO/3[10] method but this work was carried out before the McIver–Komornicki procedure for characterising transition states was implemented here. We therefore first re-examined (by MINDO/3) the transition state they reported for the reaction. While this indeed proved to be a saddlepoint on the potential surface, the Hessian matrix having just one negative eigenvalue, the corresponding eigenvector (Figure 2) did not have the correct form. Note in particular that one methine group is rotating in the direction opposite to that expected for the conversion of (**1**) into (**2**). This error illustrates in a striking way the need for thorough evaluation of putative transition states by the McIver–Komornicki procedure[5] or some equivalent.

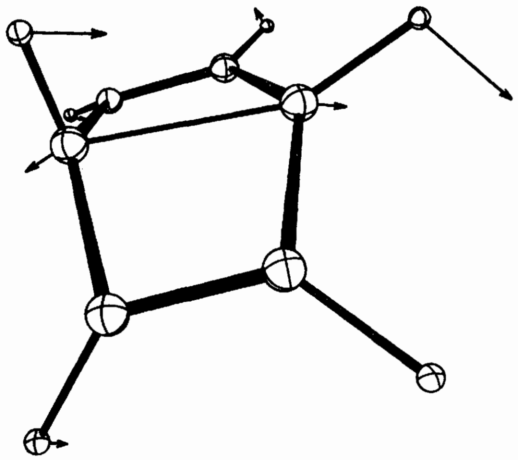


Figure 2. ORTEP plot of the stationary point on the single configuration restricted Hartree–Fock MINDO/3 energy surface (see text) previously assumed (ref. 9) to be the transition state for the conversion (**1**) → (**2**). The arrows illustrate the form of the vibration corresponding to the negative root of the force-constant matrix.

Further study showed this discrepancy to be due to use of the restricted single-configuration version of MINDO/3. A 'forbidden' reaction involves a HOMO–LUMO crossing, and in such regions of the potential surface it is necessary[7] to include limited configuration interaction (CI$_0$).[11] We have therefore studied the conversion of (**1**) into (**2**) by MNDO with CI$_0$. The results are shown in Figure 1(b). Since the calculation of second derivatives of the energy involves excessive computer time if CI$_0$ is included, they were found using an unrestricted[12] version of MNDO. The Hessian matrix had just one negative eigenvalue. The form of the corresponding eigenvector [Figure 1(b)] of $a_1$ symmetry ($\nu$, 995 cm$^{-1}$) was that expected for the (**1**) → (**2**) transition state. This correlated with a CH bending vibration in (**1**) at (calc.) 1064 and (obs.)[13] 929 cm$^{-1}$ and an $e_{2g}$ out-of-plane deformation of benzene at (calc.) 1038 and (obs.[6]) 975 cm$^{-1}$. While the calculated enthalpy of activation (124 kJ mol$^{-1}$) was somewhat higher than the value (96 kJ mol$^{-1}$) reported by Breslow *et al.*[1] for the reaction in $C_2Cl_4$ solution, the calculated entropy of activation (4·4 J mol$^{-1}$ K$^{-1}$) was close to that for similar reactions[14] and fell in the range of their somewhat uncertain estimate ($-21 \pm 29$ J mol$^{-1}$ K$^{-1}$).

The reasonable results given by MNDO in this connection support its prediction that (**3**) should be a stable species, identifiable at low temperatures or if substituted with groups bulky enough to hinder rearrangement to (**2**).

These results are entirely consistent with the suggestions of Dewar, Kirschner, and Kollmar[8] concerning the chemiluminescence associated with (**1**) → (**2**). We find that a HOMO–LUMO crossing does indeed take place during this reaction but only after the transition state is passed.†

---

† In a single configuration treatment of a 'forbidden' reaction, the HOMO–LUMO crossing can be identified at once from the corresponding discontinuity in the eigenvectors. With CI$_0$, as here, the orbital crossing corresponds to the point when the two closed shell configurations have equal energies and hence equal weights in the CI$_0$ wave function.

We thank the Air Force Office of Scientific Research for support, the Robert A. Welch Foundation for a postdoctoral fellowship (to G.P.F.), and the S.R.C. and NATO for a postdoctoral fellowship (to H.S.R.). The calculations were carried out using the CDC 6400/6600 computer at the University of Texas Computer Center.

(*Received, 8th June* 1977; *Com.* 551.)

[1] R. Breslow, J. Napierski, and A. H. Schmidt, *J. Amer. Chem. Soc.*, 1972, **94**, 5906.

[2] R. B. Woodward and R. Hoffmann, 'Conservation of Orbital Symmetry,' Verlag Chemie, Academic Press, New York, 1970, p. 174.

[3] M. J. S. Dewar and W. Thiel, *J. Amer. Chem. Soc.*, 1977, **99**, 4899, 4907.

[4] J. W. McIver and A. Komornicki, *Chem. Phys. Letters*, 1971, **10**, 303.

[5] J. W. McIver, *Accounts Chem. Res.*, 1974, **7**, 72.

[6] T. Shimanouchi, 'Tables of Molecular Vibrational Frequencies Consolidated Vol. 1,' Nat. Stand. Ref. Data Ser., N.B.S. (U.S.) NSRDS–NBS 39, 1972.

[7] M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, 1974, **96**, 5244; M. J. S. Dewar, S. Kirschner, H. W. Kollmar, and L. E. Wade, *ibid.*, p. 5242; M. J. S. Dewar, S. Kirschner, and H. W. Kollmar, *ibid.*, p. 5240.

[8] M. J. S. Dewar, S. Kirschner, and H. W. Kollmar, *J. Amer. Chem. Soc.*, 1974, **96**, 1579; N. J. Turro, *ibid.*, 1975, **97**, 3859.

[9] M. J. S. Dewar and S. Kirschner, *J.C.S. Chem. Comm.*, 1975, 463.

[10] M. J. S. Dewar, R. C. Bingham, and D. H. Lo, *J. Amer. Chem. Soc.*, 1975, **97**, 1285, 1294, 1302, 1307.

[11] A minimum configuration CI (3 × 3) *cf.* R. E. Townshend, G. Ramunni, G. A. Segal, W. J. Hehre, and L. Salem, *J. Amer. Chem. Soc.*, 1976, **98**, 2190; M. J. S. Dewar and C. E. Doubleday, *ibid.*, submitted for publication.

[12] M. J. S. Dewar, S. Olivella, and H. S. Rzepa, *Chem. Phys. Letters*, 1977, **47**, 80.

[13] D. W. T. Griffith, J. E. Kent, and M. F. O'Dwyer, *Austral. J. Chem.*, 1975, **28**, 1397.

[14] M. J. S. Dewar and G. P. Ford, *J. Amer. Chem. Soc.*, accepted for publication.