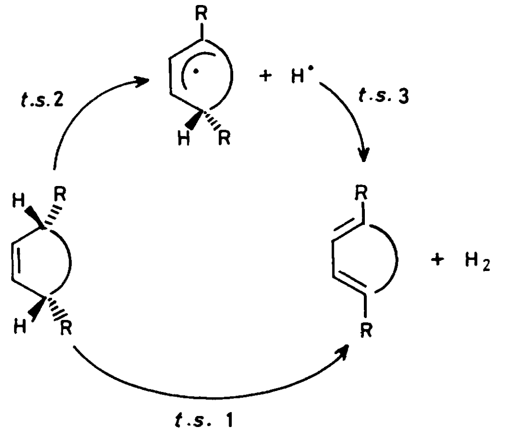
A Theoretical MNDO and AM1 SCF-MO Study of Dihydrogen Elimination Reactions

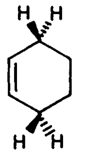
Dimitris K. Agrafiotis and Henry S. Rzepa*
Department of Chemistry, Imperial College, London SW7 2AY

Semiempirical SCF-MO calculations for the four-centre elimination of molecular hydrogen from substituted cyclohexadienes and cyclopentenes reveal the MNDO and AM1 enthalpic barriers to be too high by *ca.* 50 and 20 kcal mol^{-1} respectively compared with experiment, whereas the calculated entropies of activation are in good agreement with experiment. The alternative stepwise mechanism involving intermediate formation of a hydrogen atom and an alkenyl radical by C–H bond homolysis is significantly lower in energy than the concerted path at the MNDO level, but very similar at the AM1 level. Bis-α(oxy-anion) substituents are calculated to reduce the concerted barrier to hydrogen elimination by 22–26 kcal mol^{-1} compared to the neutral diol. Kinetic deuterium isotope effects calculated for the concerted reaction of cyclohexa-1,4-diene or cyclopentene agree very well with experimentally reported values. The importance of tunnelling contributions is discussed. The corresponding isotope effects for the two-centre stepwise reaction are calculated to be significantly greater.

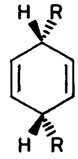
The gas-phase thermal elimination of molecular hydrogen from cyclic alkenes is a well established reaction.[1] Accumulated experimental data appear consistent with a first-order homogeneous intramolecular process, involving stereospecific elimination of molecular hydrogen from non-adjacent carbon atoms, postulated to occur *via* a six-electron symmetry-allowed cyclic mechanism (*t.s.* 1, Scheme). It has been suggested that the observed stereoselectivity of the reaction eliminates the possibility of alternative radical processes and this is further supported by kinetic experiments, which have demonstrated that the rates of decomposition of various substituted cyclopentenes and cyclohexenes were not sensitive to addition of typical radical-chain inhibitors such as propene, nitric oxide, *etc.* Measured deuterium isotope effects in the reaction of cyclohexa-1,4-diene (**2**; R = H)[2] and cyclopentene (**3**; R = H)[3] and a simple interpretation of zero-point energy differences in terms of a late transition-state model based on a resemblance to benzene have also been proposed[2] as supporting the concerted mechanism. However there is little analogy between the bond breaking–forming processes in dihydrogen eliminations and simple three-centre hydrogen transfers on which such transition-state models can be based. We report in this paper quantitative SCF-MO calculations based on the MNDO and AM1 methods[4] which indicate that these procedures are capable of providing more accurate models for such reactions.



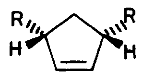
Scheme.



(1)



(2)



(3)

Computational Procedure.—The calculations were carried out using the MNDO/AM1 SCF-MO procedures[4] employing a standard s/p valence basis set with full optimisation of all geometric variables. Closed- and open-shell species were investigated at the single determinantal RHF SCF and spin-unrestricted UHF SCF levels respectively. Potential energy surfaces for the synchronous eliminations were constructed maintaining C_{2v} symmetry for (**2**) (Figure 1b), and C_s symmetry for (**1**) and (**3**) (Figures 1a,c). Saddle points in these potential surfaces were characterised as transition states by force-constant analysis. Thermodynamic properties and kinetic isotope effects were obtained using the rigid rotor, harmonic oscillator model, and the normal vibrational frequencies calculated from the force-constant matrix.[5]

Results and Discussion

1. *Energetics of Reaction.*—Contour maps constructed as described above reveal the elimination of hydrogen to be a concerted process at the closed-shell RHF level (Figure 2). Significant enthalpic barriers were predicted for the concerted elimination of molecular hydrogen from the cyclic alkenes (**1**)–(**3**) (R = H) at both the MNDO and AM1 levels (Table 1). These barriers appear grossly overestimated by the MNDO procedure, being 25–30 kcal mol^{-1} higher than the AM1 values, a situation that was also encountered for the closely

related dihydrogen transfer reactions.[6] The discrepancy is almost certainly related to the inaccuracies of the core-repulsion function (CRF) used by the MNDO method. This tends to overestimate nuclear repulsions at interatomic distances of 1.5 times the van der Waals distance of the atoms involved, a situation typical of the transition states involved in the concerted eliminations.

The elimination from (**2**; R = H) proceeds with the lowest activation energy (61.1 kcal mol^{-1} for AM1), as a result of the additional driving force associated with the incipient aromatic ring. It is noteworthy that the calculated extra stabilisation relative to (**1**) is *ca.* 7 kcal mol^{-1}, compared with the reported experimental value of 20 kcal mol^{-1} (Table 1). The calculated result reflects the out-of-plane distortion imposed on the system as the transition state is attained, which suggests that the transition state is stabilised by less than half the possible benzene resonance energy. The experimental data[1–3] imply a very late transition state stabilised by full benzene resonance, and which is therefore not supported by the present calculations.

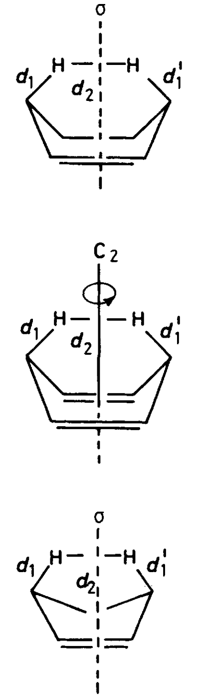


Figure 1. Reaction co-ordinates used for the construction of the potential energy surfaces for the concerted H_2 elimination from a, (**1**; R = H); b, (**2**; R = H); and c, (**3**; R = H) where d_2 is half the H–H distance

Although the AM1 figures manifest a dramatic improvement in the treatment of such systems, they are still considerably higher by 7–25 kcal mol^{-1} than those determined by experiment (Table 1). This error is not insignificant for the relatively well parametrised hyrocarbon series, and probably reflects the difficulty in reproducing entire potential surfaces *via* a parametrisation based exclusively on ground-state properties. We have noted previously[6] that the AM1 parametrisation may be qualitatively incorrect for nitrogen for similar reasons. It may also be possible that such reactions require significant electron correlation energy corrections in addition to the 'average' correction allowed for in the semiempirical AM1 parametrisation. Similar comments were made for the related dihydrogen transfer reactions from species such as hydroxymethylene (HOCH).[6]

The calculated transition state geometric data (Table 2) reveal that the concerted elimination is essentially synchronous at the RHF level, but with considerable out-of-plane distortion of the incipient benzene product (Figure 3).

The alternative radical route involves initial homolysis of the C–H bond to form an alkenyl radical and a free hydrogen atom (*t.s.* 2, Scheme), followed by biradical coupling (*t.s.* 3, Scheme). The MNDO and AM1 methods predict similar barriers for *t.s.* 2, with the former distinctly favouring the stepwise pathway. The two mechanisms are finely balanced at the AM1 level, even though the open-shell reaction does not necessitate any distortion of the cyclic system in the transition state. The transition state is a very late one, with very small reverse barriers corresponding to recombination of the intermediate radicals to reform the reactants at the AM1 level (<2.0 kcal mol^{-1}), but less so at the MNDO level. The reaction is completed by a fast disproportionation of the intermediate radical pair which also requires very little activation (<1.0 kcal mol^{-1}) at the AM1 level. Whereas the small finite AM1 barriers may be entirely due

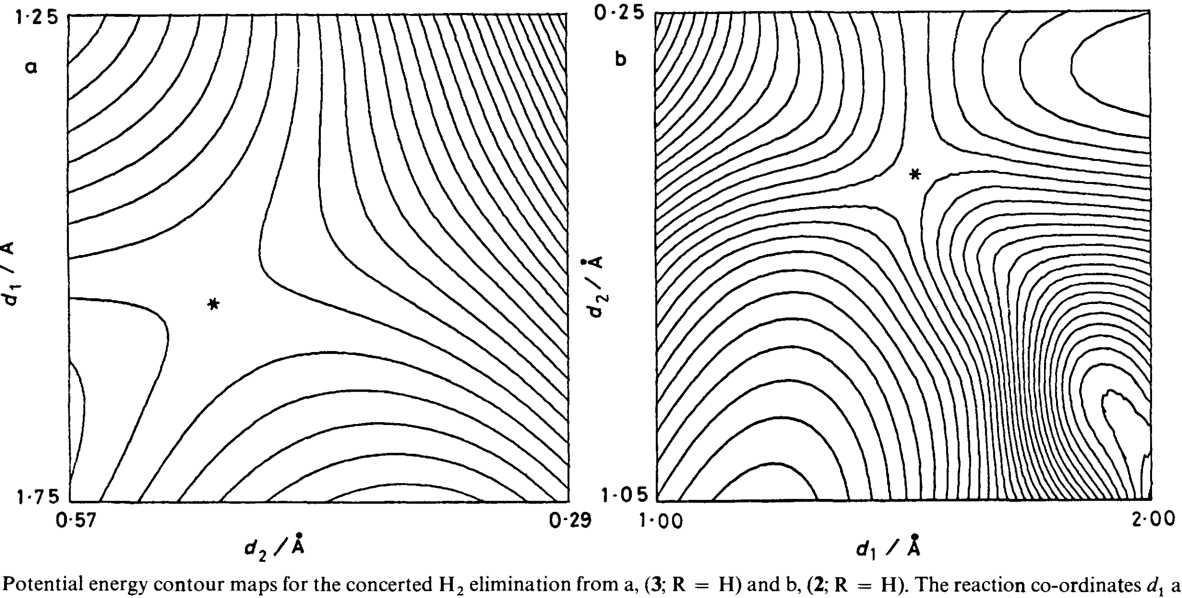


Figure 2. Potential energy contour maps for the concerted H_2 elimination from a, (**3**; R = H) and b, (**2**; R = H). The reaction co-ordinates d_1 and d_2 are as defined in Figure 1. The transition state is marked with an asterisk

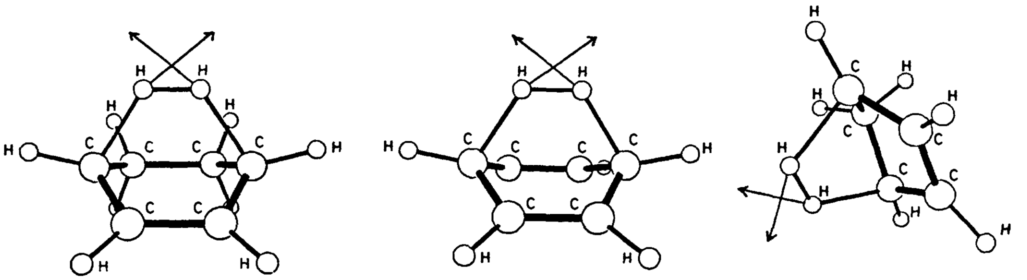


Figure 3. Transition state structures for the concerted H_2 elimination from (1)–(3) (R = H). Arrows indicate the calculated form of the single imaginary frequency derived from the Hessian matrix

Table 1. MNDO, AM1, and experimental enthalpies of activation for the concerted and stepwise pathways for dihydrogen elimination reactions

	1^a		2^b		3^c		
	MNDO	AM1	MNDO	AM1	MNDO	AM1	Exp.
(1)	97.4	68.5	68.5	67.9	6.5	0.5	61.6[1d]
(2; R = H)	90.8	61.1	62.3	61.6	4.9	0.4	41.4[2]
(2; R = OH)	78.0	59.0	55.6	61.6	5.7	1.2	
(2; R = O^-)	58.7	36.6	38.5	43.5	0.1	0.1	
(3; R = H)	109.4	83.7	71.4	72.9	7.6	1.1	58.3[3]
(3; R = OH)	94.4	79.4	62.2	65.5	7.4	2.2	
(3; R = O^-)	68.9	51.0	43.7	47.3	0.0	0.0	

[a] Energy barrier for *t.s.* 1 relative to reactants. All energies in kcal mol^{-1}. [b] Barrier for *t.s.* 2. [c] Barrier for *t.s.* 3 relative to the intermediate radical pair. [d] Arrhenius activation energy E_a.

Table 2. MNDO and AM1 (in italics) calculated geometric parameters for the synchronous transition states for dihydrogen elimination reactions (bond lengths in Å, as defined in Figure 1)

	d_1	d_2'	$2 \times d_2$
(1)	1.57	1.57	0.91
	1.55	*1.55*	*0.89*
(2; R = H)	1.54	1.54	0.98
	1.51	*1.51*	*0.97*
(2; R = OH)	1.53	1.53	0.98
	1.50	*1.50*	*0.98*
(2; R = O^-)	1.52	1.52	1.12
	1.45	*1.45*	*1.12*
(3; R = H)	1.58	1.55	0.94
	1.55	*1.53*	*0.95*
(3; R = OH)	1.56	1.55	0.96
	1.53	*1.53*	*0.96*
(3; R = O^-)	1.55	1.54	1.09
	1.49	*1.49*	*1.11*

to the approximate UHF formalism employed in the calculations, the much higher MNDO results are clearly qualitatively incorrect. They do appear however to be substantially lower than the disproportionation barriers reported in the study of the dihydrogen transfer reactions,[6] and it is likely that this discrepancy is also related to the CRF treatment in the MNDO approximation.

2. *Entropy of Reaction.*—The rigidity of the synchronous transition state is responsible for the relatively large negative entropies of activation ($\Delta S^{\ddagger}_{tot}$, Table 3) predicted for this process, which appear in reasonable agreement with the value of -7.09 cal mol^{-1} K^{-1} derived from kinetic data reported for the decomposition of cyclohexa-1,4-diene at temperatures between 577 and 616 K.[1a] The homolysis of the C–H bond in the dihydrogen elimination reactions progresses with a simultaneous *increase* in the vibrational freedom and consequently, the entropy of the system, which is totally inconsistent with experiment. Clearly however, if the reverse barrier, and hence the characterised transition state, is an AM1 or MNDO artifact, then classical transition state theory does not apply and such classical entropies cannot be calculated by this means.

3. *Kinetic Hydrogen Isotope Effects.*—These reactions involve quite complex reorganisation of bonds involving hydrogen, and hence hydrogen kinetic isotope effects might be expected to be quite sensitive probes of the transition-state structure. Such an alternative probe is important, since the kinetic data for (1) and (2) appear to indicate a particularly late transition state. We have calculated the harmonic rate ratios for the concerted and stepwise dihydrogen elimination reactions from perdeuterio- and 1,2,3,4,5,6-hexadeuterio-(2) (R = H), as well as perdeuterio- and 1,2,3,4,4,5,5-heptadeuterio-(3) (R = H) at both the MNDO and AM1 levels (Tables 4 and 5), since direct comparison could be made with available experimental data on these systems. The calculated rate ratios for the concerted D_2 and HD elimination from $C_6H_2D_6$ were typical of a large primary effect, dominated by the zero-point energy contribution. The isotope effects also display a close geometric rather than arithmetic relationship between the rates for elimination of H_2, HD, and D_2, which is typical of a concerted synchronous reaction. However, the deuterio-substitution at the vinylic and allylic (α to the cleaving C–H bonds) positions induces an inverse secondary effect, due to the increased restriction in the bending freedom of these atoms in the distorted boat-like transition state as compared with the unstrained planar reactant (Table 4).

The kinetics of the gas-phase decomposition of $[^2H_6]$-(2) have revealed[2] an experimental isotope effect corresponding to a difference in the Arrhenius E_a parameter of 2.1 and 2.4 kcal mol^{-1} for the inter- and intra-molecular competitive elimination of H_2 or D_2, respectively. The value for the competitive intramolecular elimination of H_2 and HD from $[^2H_6]$-(2) was 1.2 kcal mol^{-1}. Least-squares fitting of the calculated AM1 and MNDO harmonic rate ratios in the range 550–750 K (the approximate range of temperatures where the isotopic experiments were carried out) predicts AM1 isotope effects corresponding to 2.52 and 2.56 kcal mol^{-1} for the

Table 3. Calculated thermodynamic properties at 605 K for the molecular hydrogen elimination from (**2**) and (**3**) (R = H). Enthalpies and Gibbs free energies in kcal mol^{-1}, entropies in cal mol^{-1} K^{-1}

	(**2**; R = H)				(**3**; R = H)			
	Concerted		Stepwise		Concerted		Stepwise	
	MNDO	AM1	MNDO	AM1	MNDO	AM1	MNDO	AM1
$\Delta H^{\ddagger}$	90.8	61.1	62.3	61.6	109.4	83.7	71.4	72.9
$\Delta S^{\ddagger}_{\text{vib}}$	−3.89	−5.01	5.80	5.90	−2.09	−2.81	6.12	10.51
$\Delta S^{\ddagger}_{\text{rot}}$	−0.21	−0.20	1.41	1.43	1.21	1.24	1.45	1.59
$\Delta S^{\ddagger}_{\text{int}}$	−4.10	−5.21	7.21	7.33	−0.88	−1.57	7.57	12.10
$\Delta S^{\ddagger}_{\text{tr}}$	0	0	0	0	0	0	0	0
$\Delta S^{\ddagger}_{\text{tot}}$	−4.10	−5.21	7.21	7.33	−0.88	−1.57	7.57	12.10
$\Delta G^{\ddagger}$	93.3	64.2	58.0	57.2	109.9	84.6	66.9	65.6

Table 4. Calculated harmonic rate ratios for the molecular hydrogen elimination from (**2**; R = H)

	k_{H_2}/k_{H_2}[a] $(C_6H_8/C_6H_2D_6)$				$k_{H_2}/k_{D_2}(C_6H_8/C_6D_8)$			
	Concerted		Stepwise		Concerted		Stepwise	
T/K	MNDO	AM1	MNDO	AM1	MNDO	AM1	MNDO	AM1
298.0	0.93	0.91	1.18	1.18	15.10	8.14	21.86	18.85
350.0	0.94	0.92	1.14	1.14	10.19	6.08	12.90	11.41
400.0	0.95	0.93	1.11	1.10	7.66	4.92	8.89	8.01
450.0	0.95	0.93	1.08	1.08	6.12	4.16	6.69	6.12
500.0	0.95	0.94	1.07	1.06	5.10	3.63	5.35	4.95
550.0	0.95	0.94	1.05	1.05	4.39	3.24	4.48	4.18
600.0	0.95	0.94	1.04	1.04	3.87	2.95	3.87	3.65
650.0	0.95	0.94	1.03	1.03	3.47	2.72	3.43	3.25
700.0	0.96	0.95	1.03	1.03	3.17	2.54	3.10	2.96
750.0	0.96	0.95	1.02	1.02	2.92	2.39	2.85	2.73

[a] Secondary isotope effect for $C_6H_2D_6$ eliminating H_2.

Table 5. Calculated harmonic rate ratios for the molecular hydrogen elimination from (**3**; R = H)

	$k_{H_2}/k_{D_2}(C_5H_8/C_5D_8)$				$k_{H_2}/k_{D_2}(C_5H_8/C_5HD_7)$				$k_{HD}/k_{D_2}(C_5HD_7)$			
	Concerted		Stepwise		Concerted		Stepwise		Concerted		Stepwise	
T/K	MNDO	AM1	MNDO	AM1	MNDO	AM1	MNDO	AM1	MNDO	AM1	MNDO	AM1
298.0	17.57	10.62	25.84	24.72	17.00	10.23	22.94	21.58	4.06	3.10	17.59	15.58
350.0	11.40	7.49	14.72	14.72	11.12	7.28	13.44	12.71	3.31	2.65	10.90	9.84
400.0	8.33	5.81	9.89	9.50	8.19	5.69	9.21	8.76	2.86	2.36	7.78	7.13
450.0	6.51	4.76	7.30	7.03	6.44	4.69	6.90	6.60	2.55	2.16	6.01	5.57
500.0	5.34	4.05	5.75	5.55	5.30	4.01	5.51	5.28	2.33	2.02	4.91	4.60
550.0	4.54	3.55	4.75	4.60	4.52	3.53	4.59	4.42	2.16	1.90	4.18	3.94
600.0	3.96	3.18	4.07	3.95	3.96	3.17	3.96	3.83	2.03	1.81	3.66	3.47
650.0	3.53	2.89	3.58	3.49	3.54	2.89	3.50	3.40	1.92	1.73	3.27	3.13
700.0	3.20	2.67	3.21	3.14	3.21	2.68	3.16	3.08	1.84	1.67	3.98	2.86
750.0	2.94	2.50	2.94	2.88	2.95	2.50	2.90	2.83	1.76	1.62	2.76	2.66

concerted inter- and intra-molecular elimination of H_2 and D_2 respectively, and 1.90 kcal mol^{-1} for the intramolecular HD elimination, which agrees quite well with the experimental data. The three corresponding MNDO values (2.93, 2.96, and 2.10 kcal mol^{-1}) are noticeably higher. Thus, the experimental results are consistent with a concerted synchronous four-centre model for the elimination mechanism in which benzene aromaticity is only partially attained. It seems to be unnecessary to postulate a late transition state as a model for this reaction. The calculated AM1 isotope effect on E_a for the stepwise homolysis mechanism is higher (3.01 or 2.90 kcal mol^{-1} for D_2 or HD elimination). Similar overall conclusions emerged from the study of the cyclopentene system (Table 5), although the experimental ΔE_a reported by Knecht[3] (2.50 and 1.25 kcal mol^{-1} for D_2 and HD elimination, respectively) might be in error because of an impurity (C_5HD_7) in the perdeuteriocyclopentene sample.

These isotope effects were all calculated with no allowance for hydrogen tunnelling. The calculated imaginary frequencies are all very high, and indeed are much higher than those normally calculated for three-centre hydrogen transfers where tunnelling can be important.[7,8] The simple Bell correction for a small degree of unimolecular tunnelling could not be applied in our case at the temperature range of interest since it gave non-convergent results. Clearly however, the degree of agreement between experiment and theory at the AM1 level will not be improved by the addition of such a correction, which can only *increase* the calculated isotope effect. Since tunnelling *is* a well established effect, and *should* exist quantum mechanically, it is tempting to assume at least some cancellation of errors occurs in which the deficiencies in the potential surface compensate for the neglect of tunnelling corrections. Such simple reactions can be studied fairly rigorously at the *ab initio* correlated level, and may indeed prove to be valuable 'benchmarks' for assessing the importance of tunnelling in more complex hydrogen-transfer reactions.[8]

4. *Oxy-anion Effects.*—We have also decided to investigate the effect of oxy-anionic substitution[9] in the elimination reactions, since such substituents have been demonstrated to promote enormous rate accelerations for a diversity of pericyclic processes. In the recent semi-empirical study of the related dihydrogen transfer reactions,[6] alkoxy-anions were shown to decrease the barriers by *ca.* 25 kcal mol^{-1} relative to the corresponding neutral alcohols, inducing a stepwise mechanism proceeding by initial hydride transfer to the alkene, followed by a proton transfer to form the enolate. Although hydroxy groups were estimated to have little effect on the activation enthalpies for species (**2**) and (**3**), bis-α(oxy-anion) substituents decreased the barriers by 22.4 and 28.4 kcal mol^{-1} for (**2**) and (**3**) ($R = O^-$) compared with the diols. The saddle points for the synchronous elimination displayed only one large negative eigenvalue in the calculated Hessian matrices with the correct associated displacement vectors, corresponding to genuine transition states. The stepwise pathways were affected equally for the two systems [18.1 and 18.2 kcal mol^{-1} for systems (**2**) and (**3**) respectively, Table 1], but to a lesser extent compared with the concerted route. Thus, unlike the dihydrogen exchange reactions, oxy-anion substitution is not accompanied by any qualitative changes in the potential energy surfaces, and concerted mechanisms are greatly favoured. It should be noted however, that metal counter-ions (which represent a much more realistic model of the system in a solution environment), are expected to attenuate the effect substantially.

Acknowledgements

We thank the University of London for time on the FPS 164 system at Imperial College. D. K. A. thanks the A. Onassis Foundation for financial support.

References

1 R. J. Ellis and H. M. Frey, *J. Chem. Soc. A*, 1966, 553; S. W. Benson and R. Shaw, *Trans. Faraday Soc.*, 1967, **63**, 985; S. R. Smith and A. S. Gordon, *J. Phys. Chem.*, 1961, **65**, 1124; D. W. Vanas and W. D. Walters, *J. Am. Chem. Soc.*, 1948, **70**, 4035; H. Tanzi, M. Uchiyama, A. Amano, and H. Tokuhisa, *Kogyo Kagaku Zasshi*, 1967, **70**, 307 (*Chem. Abstr.*, 1967, **67**, 72,975c); C. A. Wellington and W. D. Walters, *J. Am. Chem. Soc.*, 1961, **83**, 4888.

2 D. C. Tardy, A. S. Gordon, and W. P. Norris, *J. Phys. Chem.*, 1976, **80**, 1398.

3 D. A. Knecht, *J. Am. Chem. Soc.*, 1973, **95**, 7933.

4 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902; for the theoretical background to the MNDO method, see M. J. S. Dewar and W. J. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899; *Theor. Chim. Acta*, 1977, **46**, 89; *QCPE* Program No. 506, Bloomington, Indiana, USA.

5 S. B. Brown, M. J. S. Dewar, G. P. Ford, D. J. Nelson, and H. S. Rzepa, *J. Am. Chem. Soc.*, 1978, **100**, 7832; H. S. Rzepa, *J. Chem. Soc., Chem. Commun.*, 1981, 939; B. Anhede, N. A. Bergman, and L. Melander, *Acta Chem. Scand., Ser. A*, 1983, **37**, 843; J. P. Shea, S. D. Nelson, and G. P. Ford, *J. Am. Chem. Soc.*, 1983, **105**, 5451.

6 D. K. Agrafiotis and H. S. Rzepa, *J. Chem. Soc., Chem. Commun.*, 1987, 902; D. K. Agrafiotis and H. S. Rzepa, *J. Chem. Soc., Perkin Trans. 2*, in press. H. S. Rzepa, *J. Chem. Res.*, 1988, 224.

7 R. P. Bell, 'The Tunnel Effect in Chemistry,' Chapman and Hall, London, 1980.

8 See for example, M. J. Field, I. H. Hillier, S. Smith, M. A. Vincent, S. C. Mason, S. N. Whittleton, C. I. F. Watt, and M. Guest, *J. Chem. Soc., Chem. Commun.*, 1987, 84. We are particularly grateful to a referee for a most cogent discussion of this point.

9 M. L. Steigerwald, W. A. Goddard, and D. A. Evans, *J. Am. Chem. Soc.*, 1979, **101**, 1994; for MNDO calculations on this subject see, I. G. El Karim and H. S. Rzepa, *J. Chem. Soc., Chem. Commun.*, 1987, 193.

Received 28*th May* 1988; *Paper* 8/02092B