An Electron Paramagnetic Resonance and Theoretical Study of the Radical Cationic $C_8H_8^{+\bullet}$ System

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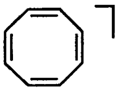
EPR spectroscopy shows that the radical cation of cyclooctatetraene (**1**), as formed by γ-radiolysis in solid freon matrices at 77 K, is converted by visible (blue) light (400–600 nm) to the isomeric bicyclo[3.3.0]octa-2,6-diene-4,8-diyl isomer (**2**). On subsequently irradiating with red light (>570 nm), **2** is converted to a third isomer with couplings (a = 13.5 G) to two protons which are α- to the SOMO, as may be judged from the g and A anisotropy. Restricted HF AM1 calculations establish the structure **11** for this isomer and provide a rationale for the conversion of **2** to **11** in the clear correlation that is found between the two highest occupied orbitals of excited **2*** and **11**. Other local minima are located by extensive exploration of the $C_8H_8^{+\bullet}$ potential energy surface, and possible conversions between selected examples of these are calculated to compare with published experimental results.

The electronic ground states and propensities of $C_8H_8^{+\bullet}$ radical cations to cross the $C_8H_8^{+\bullet}$ potential energy surface, leading to other $C_8H_8^{+\bullet}$ isomers, have recently attracted attention.[1–7] We,[1] and the Williams[2] group have communicated independently that the radical cation of cyclooctatetraene (**1**), as observed by EPR spectroscopy in solid freon matrices, is photolabile, being transformed on irradiation with visible light to the bicyclo[3.3.0]octa-2,6-diene-4,8-diyl (1,4-bishomobenzene) isomer (**2**). Clearly **2** would appear to be a favourable energy minimum for the $C_8H_8^{+\bullet}$ system since it is achieved from various starting points, as observed in studies of the other isomers, semibullvalene,[3] cubane[4] and cuneane.[4] In the present paper, we report our further and more complete studies of the properties of **1** and **2**, and also RHF AM1 calculations that aim to probe the electronic details of these different transformations.



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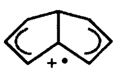

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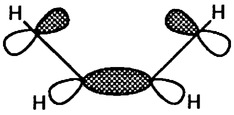
Experimental

Samples of cyclooctatetraene were purchased from Aldrich and Fluka and were used without further purification. Trichlorofluoromethane was obtained from BDH, and was purified by double filtration through short columns of activated silica. 1,1,2-Trichlorotrifluoroethane was a sample from Aldrich which was distilled and then passed through silica. Dilute solutions of cyclooctatetraene (0.1–1.0%) were prepared in the freon solvents and frozen in liquid nitrogen. It was found particularly advantageous to remove oxygen from the $CF_2ClCFCl_2$ solutions since otherwise strong signals from $ROO^{\bullet}$ radicals were observed, especially after annealing. The frozen solutions were γ-irradiated to a nominal dose of 1 Mrad, using a ^{60}Co source, prior to EPR measurements which were made on a Varian E9 spectrometer. Sample annealing was carried out by decanting the liquid nitrogen coolant from the insert Dewar and allowing warming, while continuously monitoring the EPR signal for changes, then recooling to 77 K for a final measurement when such were observed. Subsequent irradiations with visible light were performed, also at 77 K, using a 300 W halogen lamp fitted with Oriel filters to select particular wavelength ranges. RHF calculations were carried out using AM1, MNDO or PM3 Hamiltonians, in methods implemented in Version 5.0 of MOPAC [J. J. P. Stewart, QCPE No. 455].

Results and Discussion

Cyclooctatetraene in $CFCl_3$.—Fig. 1(*a*) shows a spectrum recorded from cyclooctatetraene (**1**) which has been γ-irradiated in a $CFCl_3$ matrix at 77 K. This is recorded with the intense central feature, which is a structureless single peak, offscale in order to reveal weaker features that flank this in the wing regions. There seems little doubt that the central line is from cyclooctatetraene radical cations, given that the couplings measured from this species in the liquid phase[8] [a(8 H) = 1.5 G] are readily accommodated within its breadth but are not resolved because the solid-state linewidths are expected to be of the order of 3 G for this cation. We had considered the possibility that the 'flattening' of the ring from the neutral geometry, as predicted from MINDO/2 calculations,[9] might be retarded by the solid matrix, as was apparently the case with hexamethyl(Dewar)benzene radical cations;[10] however, this does not appear to be so, because the SOMO should then resemble the $5a_1$ HOMO of the neutral molecule **3**,[11] from which it might be expected that the EPR spectrum would show relatively large (positive) couplings to four of the protons and rather smaller couplings to the remaining four. It is the flattening of the ring that gives rise to only very small couplings, which are not resolved in the solid state, because the protons are then coupled *via* both the mechanisms of spin polarisation and hyperconjugation which partially cancel each other because they deliver negative and positive spin densities respectively, and in similar amounts. In the present example, we infer that the solid matrix exerts little influence on the cation geometry. In accord with our inter-



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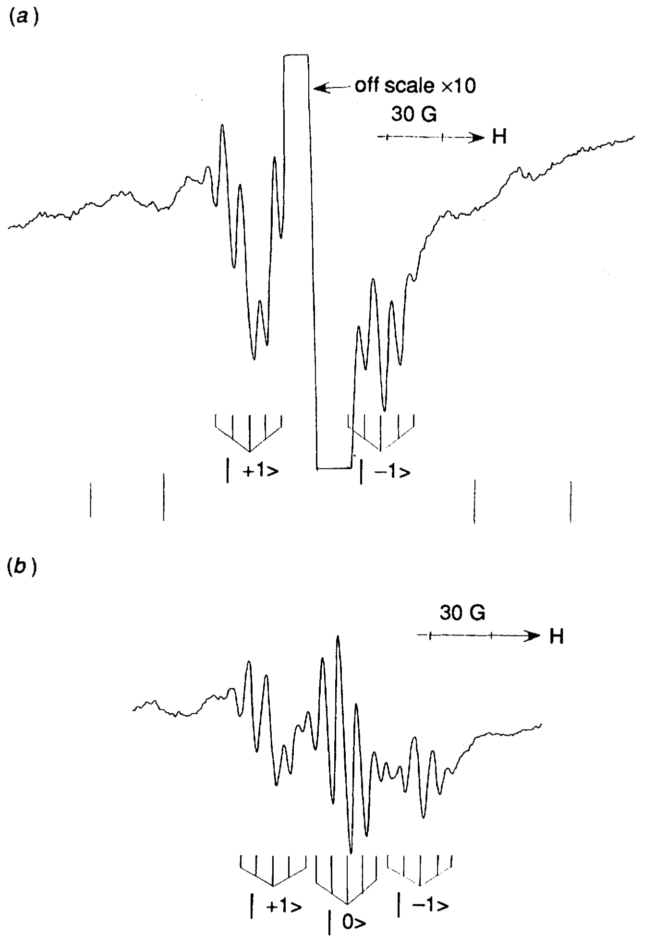
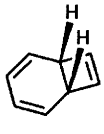


Fig. 1 (*a*) EPR spectra recorded from cyclooctatetraene radical cations (**1**) in a solid $CFCl_3$ matrix at 77 K; (*b*) sample in (*a*) after irradiation with blue light (400–600 nm) showing features from cations **2**

pretation of the nature of the central line, but also given the disparity in the intensities of this and the wing features, it is most unlikely that both belong to the same radical. We can eliminate the possibility that the latter arise from impurities because GC–MS showed that the cyclooctatetraene is >99% in purity: therefore, under the present conditions, they must be derived from cyclooctatetraene radical cations (**1**). The absence of any concentration dependence of the relative intensities of the central and wing features argues against the species responsible for the latter being formed through an ion–molecule reaction, and suggests an intramolecular rearrangement.

In order to try to promote this rearrangement, we annealed the sample close to the melting point of the $CFCl_3$ matrix, *ca.* 160 K, but found no increase in the wing signals at the expense of the central line: although an overall decrease in intensity occurred, the relative intensities of the two sets of signals were essentially unchanged. In marked contrast, however, we found that following irradiation of the initially deep-red sample with visible (blue) light (400–600 nm) the wing features had gained considerable intensity and the central signal from **1** had disappeared, clearly disclosing the central |0> component of a 36.4 G triplet [Fig. 1(*b*)]; the additional structure is from a 7.8 G (4 H) quintet splitting. (Similar results were obtained using the $CF_2ClCFCl_2$ matrix, except that the lines were somewhat sharper.) It is certain that the process is a photochemical rather than a thermal reaction, and to account for the small yield of the rearranged radical observed prior to light-irradiation, we propose a degree of 'inadvertent' photolysis: it is probably significant that the sample vials sometimes show a deep-blue fluorescence when viewed in a darkened room immediately following γ-irradiation, which may account for this.

In order to make an assignment of the rearranged cyclooctatetraene radical cation, we considered the photochemical behaviour of the neutral compound. There are two rearranged products, **4** and **5**, that have been reported from the photolysis of cyclooctatetraene,[12,13] and while the EPR spectrum of Fig. 1(*b*) cannot be easily reconciled with a cation derived from the former structure, it may readily be interpreted as arising from the formation of the radical cation **2** which is analogous to the biradical **6**, proposed as an intermediate in the formation of semibullvalene (**5**).[13] While this work was in progress, Williams *et al.* reported studies that confirm this assignment:[2,3] most incisive is their observation that radiolytic oxidation of **5** leads to the same species **2** *via* C–C bond cleavage of the cyclopropane ring.[3]

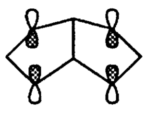


4

5

6

In **2**, the unpaired electron is equally distributed between the two interacting allylic units in the b_2 π-SOMO (**7**). Therefore, the 7.8 G coupling, at roughly half that measured for the *exo* protons in allyl itself,[14] is assigned to the four equivalent allylic protons and the 36.4 G coupling to the bridgehead protons. In order to comment on the dihedral angles (θ) between these and the SOMO p_z directions, it is necessary to use the Heller–McConnell formula[15] [eqn. (1)] with a value for *B* that is appropriate for cationic systems, and modified [eqn. (2)] as proposed by Whiffen[16] to account for the quantum mechanical reinforcement of hyperconjugation involving two interacting sites of appreciable spin density.



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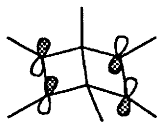

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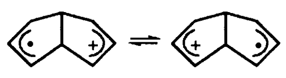


9

$$a = B\cos^2\theta \qquad (1)$$

$$a = B(c_1 + c_2)^2\cos^2\theta \qquad (2)$$

In order to try to confirm that **2** is symmetrically delocalised, Williams[3] has used this approach with a *B* value of 48 G, but this is almost certainly too low for a radical cation, in which hyperconjugation must be enhanced by the positive charge,[17] despite the apparently good agreement obtained. In order to overcome this difficulty, we made recourse to our data[10] for the $^2B_2$ hexamethyl(Dewar)benzene radical cation (**8**) which shows a coupling of 9.5 G to the four methyl groups at the olefinic positions: thus a value of $B = 76$ G is obtained (for unit spin density and a proton with $\theta = 0°$). (In further support of this estimate, we note that a very similar value of 75 G was used by Bock in his extensive liquid phase studies of aromatic radical cations.)[18] In which case, the further assumption made by Williams that the dihedral angles subtended by the bridgehead C–H bonds with the adjacent SOMO p_z orbital axes are 30° now leads to predicted *a* values of 28.5 G for equilibrating spin-localised structures **9**, and 57 G for the fully delocalised b_2 structure **7**, assuming that the spin populations at the adjacent allylic positions are 0.25 or 0.5 for **7** or **9**. This is particularly worrying because the experimental value is now *closer* to that

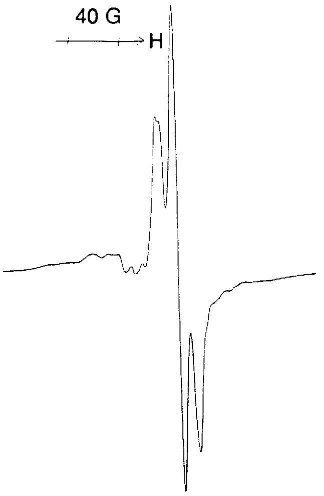


Fig. 2 EPR spectrum recorded from sample in Fig. 1(*b*) after a second irradiation with red light (> 570 nm), and assigned to cations **11**

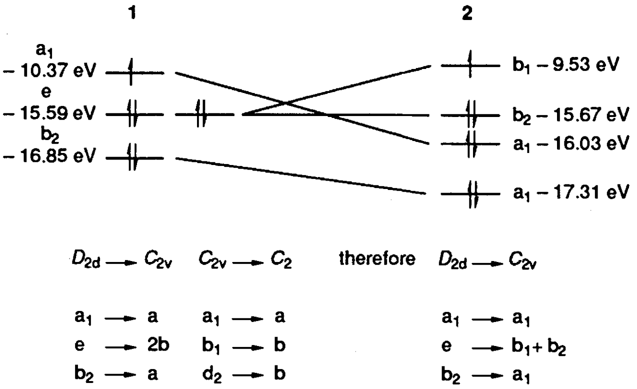
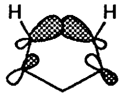


Fig. 3 Correlation diagram for the conversion **1** → **2**

expected for the equilibrating *localised* structures **9**. The situation is even worse when π–π spin polarisation, as must occur in allylic systems, is considered: the relevant spin populations must now be raised to 0.3 or 0.6,[3] because of negative spin densities at the 'nodal' allylic positions. In this case, we obtain predicted *a* values of 34.2 G and 68.4 G so that the experimental value is *now* almost *equal* to that expected for equilibrating localised structures **9**. However, we must recall that this is a strained system, and while the relevant dihedral angles are probably close to 30° for the cyclopentenyl system, the presence of the second ring might increase these angles, particularly if the transannular C–C bond is strongly bent (**10**). Solution of eqn. (2) for θ leads to dihedral angles of 46° or 51° depending on whether spin populations of 0.25 or 0.3 are taken. However, our MO calculations predict the symmetrical b_2 form **7** as the minimum, and the photochemical transformations involving this intermediate are best understood in terms of the symmetries of the orbitals that are imposed by the C_{2v} (as opposed to C_s) symmetry.

We note that changes were observed previously[19] in the electronic absorption spectrum of the cyclooctatetraene radical cation after bleaching with visible light, and it was suggested that a rearrangement of the primary species had occurred, although no firm assignment could be made. The present work establishes that this is the case, and clearly identifies the species thus produced.

Formation of the Tetracyclo[3.3.0.0.^{2,8}.0^{4,6}]*octane*-3,7-*diyl Radical Cation.*—In the paper, referred to earlier, by Shida and Iwata,[19] it was reported that a second bleaching with red light is possible for the cyclooctatetraene radical cation, leading to yet a different product. In order to investigate this by EPR spectroscopy, which is more decisive from the structural viewpoint than is optical spectroscopy, we carried out a second bleaching of the sample containing cations **2** with visible light filtered to transmit only > 570 nm. As is clear from Fig. 2, this caused a second dramatic change in the EPR spectrum, the sample changing in appearance from a sky-blue to a 'peach' colour. The spectrum is now very simple and reflects coupling (a = 13.5 G) to only two equivalent protons: the low field line is split into $\parallel$ and $\perp$ components arising from the g and A anisotropy that is characteristic of protons that are bound alpha to the SOMO, so that this low field line is from the $| -1 >$ transition because the isotropic coupling is of negative sign. The assignment of the species present is not immediately obvious, and, in order to make further elucidation of this matter, we explored the $C_8H_8{}^{+\bullet}$ potential energy surface by means of RHF AM1 calculations to locate possible minima and to determine the spin-density distributions in the structures corresponding to them. Two possible structures, **11** and **12**, had occurred to us as contenders for this species, although both are of high energy compared to **1** and **2**, (Table 1). Results for the cyclobutenyl radical[20] suggest that an unsymmetrical version of **12** with weakly interacting cyclobutenyl units could lead to only two appreciably coupled protons, if the electronic structure were distonic as drawn, because the remaining hydrogens would then effectively occupy the nodal region of the spin-localised SOMO. However, the calculations favour a symmetrical structure in which the SOMO comprises both rings equally (Scheme 1), and so **12** is eliminated because a *ca.* 7–8 G quintet pattern would be expected from it. In contrast, the SOMO for **11** (Scheme 1) agrees well with the EPR results since there are only two positions of high spin density, leading to the observed spectral form. No other minima were located that met this requirement.



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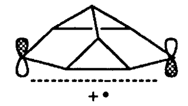

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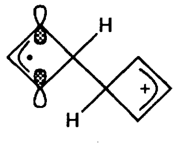

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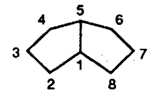

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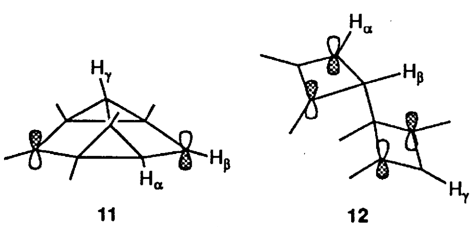


11 12

H(1s) coefs

α 0.0034 $\quad$ α 0.0081

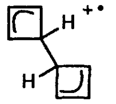
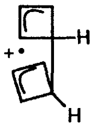
β 0.0352 $\quad$ $\beta \simeq \gamma \sim 0.$

$\gamma \sim 0.$

Scheme 1 SOMO for **11** and **12**

MO Calculations.—Our AM1 calculations indicate that, as expected, the cyclooctatetraene radical cation **1** has D_{2d} symmetry, and the top four occupied orbitals (largely arising from the C–C π-systems) are of symmetry types a_1, e and b_2 respectively (Fig. 3). The radical cation **2** has C_{2v} symmetry, as noted earlier, and the top four occupied orbitals are of symmetry types b_1, b_2, a_3 and a_1 respectively. If the conversion

Table 1 Calculations of $C_8H_8^{+\bullet}$ radical cations

	H_f^0/kJ mol^{-1}			Relative energies/kJ mol^{-1}		
	MNDO	AM1	PM3	MNDO	AM1	PM3
1	+997.1	+1037.6	+1084.4	0.0	0.0	0.0
2	+1019.3	+1056.1	+1053.7	+22.2	+18.5	−30.7
$\mathbf{5}^{+\bullet}$	Optimises to cation immediately above					
11	+1154.9	+1223.5	+1203.9	+157.8	+185.9	+119.5
$\mathbf{4}^{+\bullet}$	+1059.2	+1132.3	+1123.0	+62.1	+94.7	+38.6
	+1293.4	+1444.4	+1387.0	+296.3	+406.8	+302.6
	+1298.6	+1442.7	+1388.8	+301.5	+405.1	+304.4

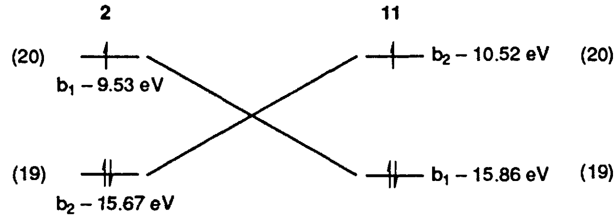


Fig. 4 Correlation diagram for the conversion $\mathbf{2} \longrightarrow \mathbf{11}$

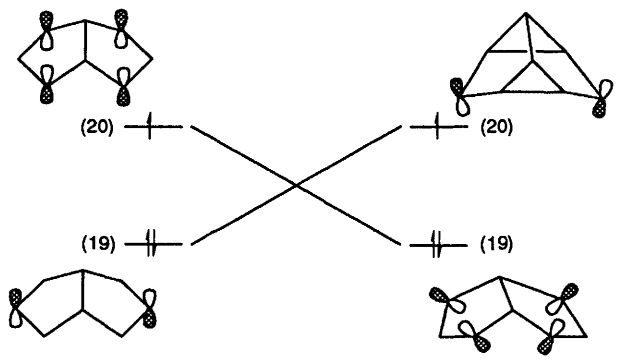


Fig. 5 Symmetry correlation diagram for SOMO and NHOMO in the conversion $\mathbf{2} \longrightarrow \mathbf{11}$

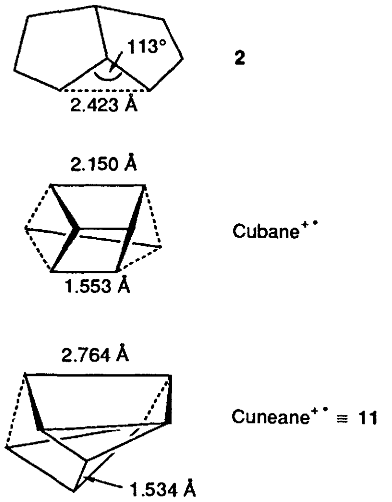
of **1** to **2** preserves a single C_2 axis throughout, then there is a complete correlation of these orbitals, with preservation of the *a*, *b* classification: a single excitation of **1** can thus lead smoothly to **2**, as described by Williams and co-workers;[2] conversion is symmetry forbidden in a thermal reaction.

Conversion of **2** *to* **11**.—The top two occupied orbitals in **2** have b_1 and b_2 symmetry in C_{2v}, while in **11** the order is reversed. Again, if C_{2v} symmetry is preserved throughout, the conversion is straightforward as photochemical but is forbidden as a thermal reaction (Fig. 4). A computational scan, driving the reaction by constraining the fold angle between the rings at a series of fixed values while allowing all other variables to optimise, indicates that C_{2v} symmetry is indeed preserved throughout. There is (Fig. 5) a clear symmetry correlation between orbitals 19 and 20 of **2** and 20 and 19 of **11**. A simple conversion of $\mathbf{2} \longrightarrow \mathbf{11}$ is thus:

$$\mathbf{2} \longrightarrow \mathbf{2^*} \longrightarrow \mathbf{11}$$

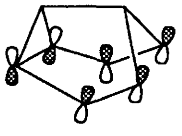
$..(19)^2(20)^1$ $..(19)^1(20)^2$ $..(20)^2(19)^1$ (in original numbering; LHS of Fig. 5)
$..(19)^2(20)^1$ (in numbering as RHS of Fig. 5)

The key to the transformation would appear to be, using the atom numbering in **13**, that orbital 20 of **2** is bonding between atoms 4 and 6, and between 2 and 8; when doubly occupied it induces bond formation and decreases the fold angle between the rings. Orbital 19 of **2** is antibonding between atoms 3 and 7, and hence when doubly occupied keeps atoms 3 and 7 apart, leading to a large inter-ring fold angle. Calculated geometric parameters for **2** and **11** are shown in Scheme 2, from which it is clear that, structurally, **2** and **11** do indeed differ mainly in the values of the fold angle between the rings.



Scheme 2 Molecular structures for **2**, cubane$^{+\bullet}$ and cuneane$^{+\bullet}$ (**11**)

Other Conversions to (**2**).—In the case of semibullvalene **5**, the HOMO of the neutral molecule is as in **14** from which it may be anticipated that the C(2)–C(8) bond will be weakened



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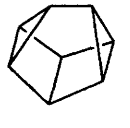

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Table 2 Calculations of neutral C_8H_8 isomers

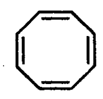
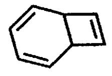
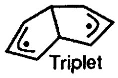
	ΔH_f^0/kJ mol^{-1}			Relative energies/kJ mol^{-1}		
Isomer	MNDO	AM1	PM3	MNDO	AM1	PM3
	+235.1	+265.6	+278.9	0.0	0.0	0.0
	+268.8	+342.4	+309.4	+33.7	+76.8	+30.5
	+303.3	+353.5	+311.2	+68.2	+87.9	+32.3
 Triplet	+229.1	+287.4	+261.0	−6.0	+22.8	−18.9
 Triplet	+398.9	+490.3	+446.5	+163.8	+224.7	+167.2

Table 3 AM1 calculations of neutral and radical cation forms of cubane, cuneane and barrelene

Molecule	Symmetry	H_f°/kJ mol^{-1}
Cubane	O_h	+632.7
Cubane$^{+\bullet}$	C_{2v}	+1514.4
Cuneane	C_{2v}	+560.4
Cuneane$^{+\bullet}$	C_{2v}	+1241.1
Barrelene	D_{3h}	+281.8
Barrelene$^{+\bullet}$	D_{3h}	+1147.3

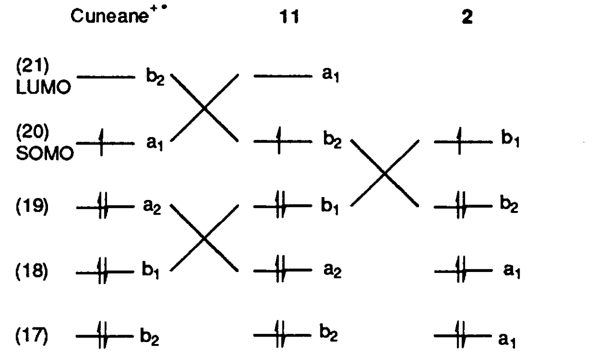
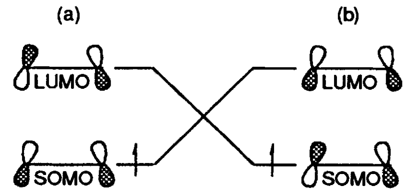


Fig. 6 Orbital correlation diagram for (vertically ionised) cuneane$^{+\bullet}$ (**11**) and **2**

on ionisation. Indeed, the Williams[3] group observed that, following radiolytic oxidation in freon matrices at 77 K, only the cation **2** was observed. Our AM1 calculations on $\mathbf{5}^{+\bullet}$ show only a smooth geometric conversion to **2** and so it is unlikely that $\mathbf{5}^{+\bullet}$ is an energy minimum; Table 2 makes clear that there is a considerable thermodynamic driving force of *ca.* 50–70 kJ mol^{-1} for the conversion of **5** to **6** and probably a similar quantity drives the reaction $\mathbf{5}^{+\bullet}$ to **2**, eqn. (2).

The radical cation of cubane has been the subject of three investigations:[4–6] given the triply degenerate t_{2g} manifold in the O_h symmetry of the neutral, a Jahn–Teller distortion is expected on ionisation. Conclusive liquid phase work by Trifunac,[5] using an FDMR technique, has established that all eight protons are equivalent with a coupling of 16.1 G, in approximate agreement with RHF AM1 calculations if it is assumed that a dynamic C_{2v} distortion occurs probably between the twelve equivalent minima of this type on the cubane$^{+\bullet}$ energy surface. This contradicts previous work[4,6] on cubane in solid matrices under ionising conditions, and it appears that cubane$^{+\bullet}$ has not been detected in the solid state. Whatever the true nature of the species formed from cubane on radiolysis in freon matrices at 77 K, it is most interesting that **2** is the sole product observed on annealing to 110 K.[4] On radiolytic oxidation of cuneane[4] (**15**) in solid freons, **2** was detected directly at 77 K without the observation of any intermediate that could be assigned to $\mathbf{15}^{+\bullet}$, and it is suggested that $\mathbf{15}^{+\bullet}$ might be a transient intermediate in the conversion, cubane$^{+\bullet} \longrightarrow$ **2**.

In order to try to understand these phenomena, we have also investigated the above species by RHF AM1 calculations; our results are summarised in Table 3. For cubane$^{+\bullet}$, geometry optimisation leads to a C_{2v} structure opened out along one edge with one long C–C bond of 2.150 Å, and is consistent with a Jahn–Teller distortion that lifts the triple degeneracy of the t_{2g} manifold: the SOMO and LUMO are localised on this edge (Scheme 3). Optimisation of cuneane$^{+\bullet}$ leads also to a C_{2v} structure but which may be identified with **11**, rather than **2**. As is clear from Scheme 3, cubane$^{+\bullet}$ and **11** differ mainly by a twist of the two bottom carbon atoms from a position parallel to the long edge in cubane$^{+\bullet}$ to perpendicular to the long edge in cuneane$^{+\bullet}$ (**11**), and the SOMO and LUMO are localised on the 2.76 Å edge in **11**, similar to cubane$^{+\bullet}$. Scheme 3 shows that there is a symmetry correlation between the SOMO/LUMO pair for cubane$^{+\bullet}$ and **11**; in both, the next orbital down (NHOMO) has nearly zero contribution from the long edge.



Scheme 3 SOMO and LUMO for (*a*) cubane$^{+\bullet}$ and (*b*) cuneane$^{+\bullet}$ (**11**)

Fig. 6 shows the orbital correlations for vertically ionised cubane, and **11** and **2**. What is clear is that the energy of vertically ionised cuneane$^{+\bullet}$ is very high (ΔH_f° = +1498.2 kJ mol^{-1}) so that there is scope for substantial structural reorganisation on relaxation; furthermore, there is *no* minimum on the energy surface identifiable as cuneane$^{+\bullet}$, but only a convergence to **11**. While all the foregoing accords with experimental observation insofar as the instability of cuneane$^{+\bullet}$ is concerned,[4] the product **11** is not what is found in freon matrices, but **2**. One possible explanation is that, computationally, the convergence falls into the (local) minimum **11** as the nearest *geometrically* to cuneane, requiring only the elongation of one C–C bond, whereas in the real-life situation, relaxation and vibronic energy loss to the matrix leads to the much lower [by 140–160 kJ mol^{-1} (Table 1)] minimum **2**. Regarding the potential conversion of cubane$^{+\bullet}$ to cuneane$^{+\bullet}$ (**11**), as suggested by Trifunac as the first step in the conversion of cubane$^{+\bullet}$ to **2**, we find that there is (Scheme 3) a clear symmetry correlation between the frontier orbitals (SOMO/LUMO) of cubane$^{+\bullet}$ and cuneane$^{+\bullet}$ (**11**), both of which have C_{2v} symmetric structures. However, if the twist of the bottom two carbon atoms in cubane$^{+\bullet}$ (Scheme 2) is driven computationally, preserving C_2 symmetry throughout, the end point is the cyclooctatetraene radical cation (**1**). Thus the calculations do not fully explain all the experimental details, but as usual, the MO approach does not model transition state selectivities or energy losses that pertain for species isolated in a rigid, vibrating solid matrix.

The data for barrelene (Table 3) indicate that the molecule retains its D_{3h} symmetry following ionisation, and that the resulting radical cation is designated as A_2' as in the symmetry of the neutral HOMO. This accords with experimental work on this cation by Gerson and co-workers.[7]

Acknowledgements

We thank Dr. P. G. Clay (Imperial College, London) for providing access to facilities for ^{60}Co irradiation, and the University of London Central Research Fund for an equipment grant.

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Paper 2/01832B
Received 30*th March* 1992
Accepted 18*th May* 1992