# Semi-empirical MNDO SCF-MO Study of Ion Radicals derived from Tricyclo[3.3.3.0]undecane, and from Some Related Alkanes

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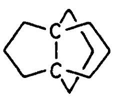
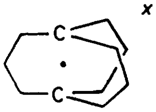
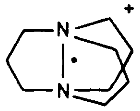
Molecular geometries have been calculated, using the MNDO method, for the cation and anion radicals derived from tricyclo[3.3.3.0]undecane ([3.3.3]propellane), for the corresponding neutral alkane and its dication, and for the cation radicals derived from the related series of acyclic alkanes: $Me_3CH$, $Me_3CMe$, and $Me_3CCMe_3$. Hyperfine coupling constants have also been calculated for these radicals. The two radicals derived from [3.3.3]propellane have very similar molecular and electronic structures, and differ principally in the character of the unique C–C bond, a one-electron σ bond in the cation and a three-electron σ* bond in the anion. Both the cations $Me_3CMe^+$ and $Me_3CCMe_3^+$ are calculated to be unstable as isolated species to dissociation into $Me_3C^+$ and $CH_3^{\bullet}$ or $Me_3C^{\bullet}$ respectively, a conclusion supported by experimental gas-phase data; the observed hyperfine couplings allow deductions to be made about their structures in frozen solution. Two isomeric structures have been calculated for the cation $Me_3CH^+$, having calculated proton hyperfine couplings in reasonable agreement with those observed experimentally.

The γ-radiolysis of alkanes in electron-scavenging media can yield the corresponding molecular cation radicals.[1–8] The $CH_4^+$ cation has not yet been identified (although the isoelectronic $BH_4$ has recently been reported[9]), but many other simple alkane cation radicals have been unambiguously detected. Of particular interest, as a closely related series all with potential three-fold symmetry, are the cations derived from $Me_3CH$,[8] $Me_4C$,[8] $Me_6C_2$,[1,2,8] and [3.3.3]propellane (tricyclo[3.3.3.0]undecane)[5] (**1**).


(1)


(2) $x = +$
(4) $x = 2+$
(5) $x = -$


(3)

Two isomeric forms of the $Me_3CH^+$ cation radical have been detected,[8] one at 4 K, the other at 77 K, but nothing is as yet known about their detailed geometric structures. The cation radical (**2**) derived from [3.3.3]propellane is characterised by hyperfine coupling to six protons only, the the e.s.r. spectrum was assigned[5] primarily by comparison with the spectrum of the di-aza σ* cation-radical (**3**) where selective deuteriation has been used to establish the assignment.[10]

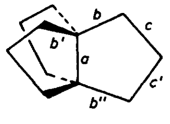
The cation (**2**) is closely related to the acyclic cation radical $Me_3CCMe_3^+$: it has been suggested[11] that both this cation, and the $Me_4C^+$ ion, owe their survival in halogenocarbon matrices primarily to cage effects, since according to MNDO calculations these cations dissociate to $Me_3C^+$ and $Me_3C^{\bullet}$ or $CH_3^{\bullet}$ respectively. A central C–C distance of *ca.* 2.5 Å was estimated from the e.s.r. data in frozen $CBr_4$. For the cyclic analogue (**2**), no such dissociation is possible.

In this work we report the results of some MNDO[12,13] calculations on the geometries of (**1**) and (**2**), and on the corresponding dication (**4**) and monoanion (**5**) derived from (**1**), together with calculations of the $A(^1H)$ values, using the INDO method;[14] on the structures and *A* values for the two isomeric forms of $Me_3CH^+$; and on the *A* values calculated from a number of MNDO optimisations of the geometries of $Me_4C^+$ and $Me_6C_2^+$, at a range of fixed values of the unique C–C distance. These calculations serve not only to support the assignments of the experimental e.s.r. spectra, but to determine molecular geometries, and to amplify the comparisons between the cations $Me_3X^+$ (X = H, $CH_3$, $CMe_3$) and ([3.3.3]propellane).

## Calculations

All calculations of molecular geometry and energy were made using the MNDO method[12,13] with a VAX 11/780 computer. UHF wavefunctions were used for all open-shell species, and geometries were completely optimised unless stated otherwise. Hyperfine splittings were calculated by the INDO method,[14] using the geometries calculated by the MNDO technique.

**Table 1.** Calculated geometrical data for (**1**), (**2**), (**4**), and (**5**)



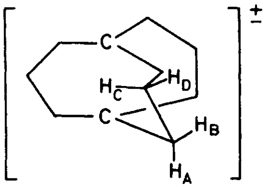
| Distances (Å) | (**1**) | (**2**) | (**4**) | (**5**) |
|---|---|---|---|---|
| *a* | 1.608 | 2.372 | 2.754 | 2.335 |
| *b* | 1.559 | 1.513 | 1.505 | 1.498 |
| *c* | 1.539 | 1.547 | 1.558 | 1.545 |
| Angles (°) | | | | |
| $a\hat{}b$ | 106.3 | 94.1 | 80.0 | 94.6 |
| $b\hat{}b'$ | 112.4 | 119.5 | 120.0 | 119.4 |
| $b\hat{}c$ | 108.4 | 113.5 | 115.6 | 113.8 |
| $c\hat{}c'$ | 107.7 | 113.7 | 119.1 | 113.1 |
| Dihedral[a] | 18.7 | 32.8 | 34.1 | 30.5 |
| $\Delta H_f^{\ominus}$/kJ mol$^{-1}$ | −136.2 | +788.6 | +2 030.8 | −23.1 |

[a] Defined as angle between normals to the planes *bab″* and *cc′*.

## Results and Discussion

[3.3.3]*Propellane and its Ions.*—The optimised molecular geometries of (**1**), (**2**), (**4**), and (**5**) all have manxane-like conformation of $C_{3h}$ symmetry (Table 1), as found experimentally for (**4**)[15] and for bicyclo[3.3.3]undecane-1,5-diol,[16]

**Table 2.** $A(^1H)$ values for (**2**) and (**5**)



| $A/G^{a,b}$ | $(\mathbf{2})_{calc}$ | $(\mathbf{2})_{obs}$ | (**5**) |
|---|---|---|---|
| $H_A(\times 6)$ | 12.0 | 17 | 20.9 |
| $H_B(\times 6)$ | 2.4 | *c* | 2.0 |
| $H_C(\times 3)$ | 1.0 | *c* | 3.0 |
| $H_D(\times 3)$ | 0.8 | *c* | 1.5 |

[a] $G = 10^{-4}$ T. [b] Atom labelling as in ref 5. [c] Not resolved.

and as determined[17] by molecular mechanics for the neutral parent of (**3**). In neutral (**1**) the unique C–C distance is calculated to be long (1.61 Å) although with a bond order of 0.95, and the HOMO and LUMO are both concentrated in this bond, being $\sigma$ and $\sigma^*$, of $A'$ and $A''$ symmetry respectively. Whereas in (**1**) the quaternary carbons are only modestly distorted from tetrahedral, in the cation-radical (**2**) these carbons are separated by 2.37 Å and are almost planar, and in the dication (**4**), the unique C–C distance is calculated to be 2.75 Å, with the cationic carbons exactly planar. The geometry of the $\sigma^*$ anion-radical (**5**), which has a three-electron C–C bond, is very similar (Table 1) to that of the $\sigma$ cation-radical (**2**), which has a one-electron C–C bond.

The calculated hyperfine coupling constants are given in Table 2 for (**2**) and (**5**). For both (**2**) and (**5**), the major coupling is that involving $H_A$:* although the calculated value for (**2**) is only *ca.* 2/3 the observed value, it is nonetheless very much bigger than the other couplings, which were unresolved experimentally.[5] The calculated direction cosines between the C–$H_A$ and C–$H_B$ bonds and the SOMO in (**2**) are 0.75 and 0.25, whereas the bonds to both $H_C$ and $H_D$ are orthogonal to the SOMO; these geometric features account in large measure for the variations in the observed couplings. Similarly in (**5**) the bonds C–$H_A$ and C–$H_B$ make direction cosines of 0.75 and 0.26 with the SOMO: not only are C–$H_C$ and C–$H_D$ orthogonal to the $\sigma^*$ SOMO, but in (**5**) both $H_C$ and $H_D$ lie in one of its nodal planes.

In (**5**) the $\sigma^*$ SOMO is much less tightly bound than the $\sigma$ SOMO in (**2**) [*I*(Koopmans') = 14.19 eV in (**2**), 1.97 eV in (**5**)], and the resultant increase in the diffuseness of the SOMO is consistent with the large coupling to $H_A$ calculated in (**5**).

$Me_6C_2^+$ *and* $Me_4C^+$.—We have suggested[11] previously, based upon MNDO calculations, that the cation radicals $Me_6C_2^+$ and $Me_4C^+$ are unstable, in halogenocarbon matrices, with respect to loss of $Me_3C^+$. Experimental gas-phase data support this contention.

The experimental gas-phase $\Delta H_f^{\ominus}$ values for neutral $Me_6C_2$ are[18] −22.57 and −167.4 kJ mol$^{-1}$, respectively, and the vertical ionisation energies are 10.37 and 10.90 eV, respectively:[19] the $\Delta H_f^{\ominus}$ values for the resultant, vertically ionised, cations are then +775 and +884 kJ mol$^{-1}$, respectively. The $\Delta H_f^{\ominus}$ sums for ($Me_3C^+$ + $Me_3C^{\bullet}$) and ($Me_3C^+$ + $CH_3^{\bullet}$) are[20,21] respectively 741 and 853 kJ mol$^{-1}$. Consequently the gas-phase, vertically ionised, cations are both unstable to dissociation by some 30 kJ mol$^{-1}$, in the sense found by the earlier MNDO calculations.[11] Consistent with this is the absence of molecular ion peaks in the electron-impact mass spectra of both $Me_4C$ and $Me_6C_2$.[22]

**Table 3.** Calculated and observed $A(^1H)$ values for $Me_6C_2^+$ and $Me_4C^+$

(a) $Me_6C_2$

| $d$(C–C)/Å | $A(^1H)/G^a$ (×6) | $A(^1H)$/G (×12) | Ratio |
|---|---|---|---|
| 2.3 | 32.2 | 4.6 | 7.0 |
| 2.4 | 31.8 | 4.9 | 6.5 |
| 2.5 | 31.4 | 5.1 | 6.2 |
| 2.6 | 31.1 | 5.4 | 5.8 |
| Observed[b] *A* | 29 | 4.2 | 6.9 |

(b) $Me_3C\text{–}CH_3^+$

| $d$(C–C)/Å | $A(^1H)$/G (×3) | $A(^1H)$/G (×6) | $A(^1H)$/G (×3)[c] |
|---|---|---|---|
| 1.90 | 44.5 | 4.9 | −3.2 |
| 1.95 | 42.4 | 4.9 | −5.7 |
| 2.00 | 40.1 | 4.9 | −6.7 |
| Observed[d] *A* | 42 | *e* | *e* |

[a] $G = 10^{-4}$ T. [b] Ref. 1. [c] Unique methyl group. [d] Ref. 3. [e] Not resolved.

The hydrogen spin densities calculated[11] by MNDO suggest that the unique C–C distances in $Me_6C_2^+$ and $Me_4C^+$, in halogenocarbon matrices, are *ca.* 2.5 and 2.0 Å, respectively. In Table 3 are collected the *A* values calculated by the INDO method, using the MNDO-optimised geometries, at a range of fixed values of the unique C–C distances. The INDO results are broadly in accord with the previous calculations, except that the observed ratio of hyperfine couplings in $Me_6C_2^+$ is reproduced, by MNDO at a C–C distance of 2.5 Å and by INDO at a distance of 2.3 Å.

In the radical (**2**) the symmetry of the $C_3CCC_3$ core is necessarily $D_{3h}$ rather than $D_{3d}$ as found in $Me_6C_2^+$, but the overall ring conformation of (**2**) is such that, like $Me_6C_2^+$, there are six hydrogen atoms outside the core, with $A(^1H)$ 17 G. In $Me_6C_2^+$, the calculated spin densities indicate[11] that the preferred conformation observed[1] is that with six hydrogens outside the core and twelve in close contact between the two terminal planes of methyl carbons. The application of a simple $\cos^2\theta$ law to the observed *A* values in (**2**) and in $Me_6C_2^+$ yields a value for the direction cosine of the C–$H_A$ bond in (**2**) of 0.77, essentially identical to the value of 0.75 obtained from the calculated structure. Consequently, although the calculated spin densities, and *A* values, derived for (**2**) are quantitatively in error, we can have confidence in the reliability of the calculated geometry for (**2**).

*Isomers of* $Me_3CH^+$.—At 4 K the e.s.r. spectrum of $Me_3CH^+$, whether in halogenocarbon or $SF_6$ matrices, is characterised[8] by hyperfine coupling to the unique hydrogen, with *A* 15 G, and to two further hydrogens, with *A ca.* 55 G, the exact values depending upon the matrix employed. In contrast at 77 K, in halogenocarbon matrices, the e.s.r. spectrum is quite different, exhibiting hyperfine couplings of 250 G to the unique hydrogen, and of 48 G to three other, equivalent, hydrogens. The assignments were confirmed[8] by use of selective deuteriation.

MNDO calculations have revealed two quite distinct minima, whose structures are summarised in Table 4. The higher-energy form has $C_{3v}$ symmetry, with a SOMO strongly concentrated in the unique C–H bond. The calculated hyperfine couplings are in reasonable accord with those observed: the three hydrogens having *A* 48 G are those whose C–H bonds are parallel to the three-fold symmetry axis, and to the SOMO. The molecular and electronic structure of the $Me_3C$ portion in this isomer are very similar to those calculated for the $Me_3CCH_3^+$ cation, where the three-fold Me–C–Me angle is 116.3° (compared with 117.6° in $Me_3CH^+$) and the hyperfine couplings are *ca.* 40 G (×3) and 4.9 G (×6).

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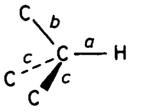
* The atom labelling follows that employed in ref 5: see also Table 2.

Table 4. Calculated parameters for the two isomers of $Me_3CH^+$



| | $C_{3v}$ isomer | $C_s$ isomer |
|---|---|---|
| Distances (Å) | | |
| $a$ | 1.1222 | 1.113 |
| $b$ | 1.525 | 1.916 |
| $c$ | $(\equiv b)$ | 1.507 |
| Angles (°) | | |
| $a\hat{}b$ | 98.9 | 89.6 |
| $a\hat{}c$ | $(\equiv a\hat{}b)$ | 114.6 |
| $b\hat{}c$ | 117.6 | 106.3 |
| $c\hat{}c'$ | $(\equiv b\hat{}c)$ | 119.9 |
| $\Delta H_f^{\ominus}$/kJ mol$^{-1}$ | 976.4 | 956.2 |
| $A(^1H)/G$[a] | 273($\times$ 1)<br>48.1($\times$ 3)<br>5.2($\times$ 6) | 25.5($\times$ 1)<br>54.0($\times$ 2)<br>8.3($\times$ 2)<br>6.2($\times$ 2)<br>$-4.7$($\times$ 3) |
| SOMO | $A_1$,(C–H)σ | $A'$,(C–C)σ |

[a] Observed $A$ values (ref. 8); $C_{3v}$ isomer: 250 G ($\times$ 1), 48 G ($\times$ 3); $C_s$ isomer: 15 G ($\times$ 1), 55 G ($\times$ 2)

The second minimum, of $C_s$ symmetry, has a single methyl group bonded to the central carbon by a very long bond (*ca.* 1.92 Å) which is approximately normal to the unique C–H bond of an almost planar $Me_2CH$ group. That this represents a genuine local minimum is confirmed, both by the force constant matrix, and by a series of refinements carried out at a range of fixed values of the long C–C distance. The SOMO is a bonding combination of $A'$ symmetry, localised primarily in the C–C bonds, particularly the unique long C–C bond. The calculated hyperfine couplings (Table 4) are in rough agreement with those found experimentally[8] at 77 K. The 54 G coupling arises from the two hydrogens, one in each methyl group of the $Me_2CH$ fragments whose C–H bonds are approximately parallel to the unique C–C bond and the SOMO. The other hydrogens in these methyl groups are all close to nodal planes of the SOMO.

In the $C_{3v}$ isomer the SOMO is normal to the plane defined by the three methyl carbons, while in the $C_s$ isomer it is approximately normal to a plane defined by two methyl carbons and the unique hydrogen, in the $Me_2CH$ fragment. All the differences between the e.s.r. spectra of the two isomers can be attributed to this apparent rotation of the SOMO.

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