# Ring Inversion in the Cyclohexenyl Radical

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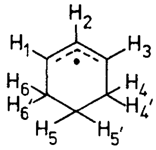
*Summary* Activation parameters for ring inversion in the cyclohexenyl radical ($\Delta H^{\ddagger} = 6{\cdot}81 \pm 0{\cdot}58$ kcal mol$^{-1}$, $\Delta S^{\ddagger} = -0{\cdot}04 \pm 2{\cdot}40$ cal K$^{-1}$ mol$^{-1}$, and $\Delta G^{\ddagger}_{298} = 6{\cdot}82 \pm 0{\cdot}98$ kcal mol$^{-1}$) have been determined by variable temperature e.s.r. spectroscopy.

A KNOWLEDGE of the conformational properties of cyclohexane derivatives containing $sp^2$ hybridized ring carbon atoms is fundamental in organic chemistry. Consequently, we report the first experimental determination of the activation parameters for ring inversion in the cyclohexenyl radical (I). As in our previous work on related systems,[1]



(I)

samples were prepared by room temperature $X$-irradiation of a solid pellet of carefully purified [$^2H_{16}$]adamantane containing a small amount of cyclohexene and studied using a Varian E4 spectrometer equipped with a calibrated variable temperature controller.

The low-field portion of the $X$-band e.s.r. spectrum of (I) at selected temperatures is shown in the Figure. At 200 K and below, the entire spectrum consists of 162 well resolved lines which may be assigned to the nine protons of the molecule with $a^{H}_{1,3} = 14{\cdot}63$, $a^{H}_{2} = 3{\cdot}57$, $a^{H}_{4,6} = 26{\cdot}49$, $a^{H}_{4',6'} = 8{\cdot}44$, and $a^{H}_{5,5'} = 0{\cdot}89$ G.[2] These hyperfine splittings (h.f.s.) are characteristic of an allylic free radical with two pairs of magnetically inequivalent $\beta$ protons ($H_{4,6}$ and $H_{4',6'}$) and one pair of equivalent $\gamma$ protons ($H_{5,5'}$).[3] At higher temperatures, those lines arising from transitions between states in which the spin components of geminal $\beta$ protons are different broaden selectively and are no longer observed above 300 K. This behaviour, which is completely reversible, may be attributed to a conformational change which averages the magnetic environments of the interacting $\beta$ protons, *i.e.*, ring inversion.

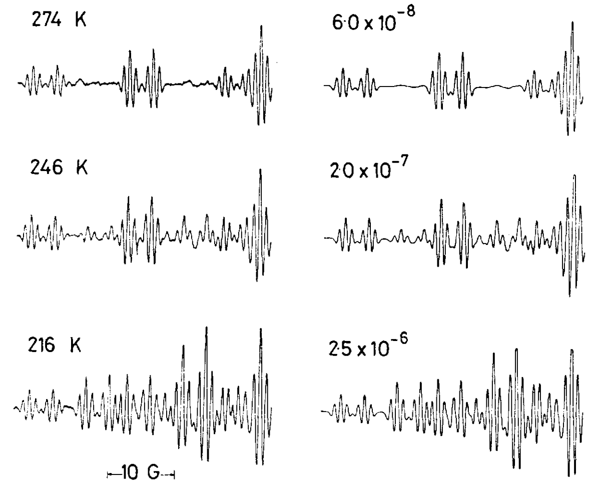


FIGURE. Expanded scale portions of the e.s.r. spectrum of the cyclohexenyl radical in [$^2H_{16}$]adamantane at selected temperatures (left) with their respective computer simulations (right).

TABLE. Hyperfine splittings (G) and conformational lifetimes of cyclohexenyl radical.

| $T$/K | $a^{H}_{1,3}$ | $a^{H}_{2}$ | $a^{H}_{4,6}$ | $a^{H}_{4',6'}$ | $a^{H}_{5,5'}$ | $\tau$/s |
|---|---|---|---|---|---|---|
| 216 | 14·63 | 3·57 | 26·49 | 8·44 | 0·89 | $2{\cdot}5 \times 10^{-6}$ |
| 227 | 14·63 | 3·52 | 26·49 | 8·44 | 0·90 | $6{\cdot}5 \times 10^{-7}$ |
| 236 | 14·59 | 3·57 | 26·33 | 8·45 | 0·89 | $3{\cdot}3 \times 10^{-7}$ |
| 246 | 14·59 | 3·58 | 26·20 | 8·44 | 0·89 | $2{\cdot}0 \times 10^{-7}$ |
| 257 | 14·59 | 3·60 | 26·26 | 8·45 | 0·89 | $1{\cdot}2 \times 10^{-7}$ |
| 264 | 14·59 | 3·60 | 25·95 | 8·58 | 0·85 | $8{\cdot}2 \times 10^{-8}$ |
| 274 | 14·50 | 3·62 | 25·80 | 8·74 | 0·90 | $6{\cdot}0 \times 10^{-8}$ |

The Table lists the e.s.r. parameters and conformational lifetimes ($\tau$) of the cyclohexenyl radical as obtained from computer simulations of the observed spectra (*cf.*, Figure) over the temperature range 216—274 K using the program MEAKIN.[1,4] $a^{H}_{4,6}$ and $a^{H}_{4',6'}$ exhibit temperature coefficients of opposite sign, as expected for increasing torsional motion about the $C_\alpha$–$C_\beta$ bonds, and $\tau$ varies by nearly two orders of magnitude over this range. A plot of ln $(1/T\tau)$ *vs.* $(1/T)$ yields the activation parameters $\Delta H^\ddagger = 6{\cdot}81 \pm 0{\cdot}58$ kcal mol$^{-1}$, $\Delta S^\ddagger = -\ 0{\cdot}04 \pm 2{\cdot}40$ cal K$^{-1}$ mol$^{-1}$, and $\Delta G^\ddagger_{298} = 6{\cdot}82 \pm 0{\cdot}98$ kcal mol$^{-1}$.† The corresponding activation energies for cyclohexane,[5] cyclohexyl radical,[6,7] and oxocyclohexyl radical[1,7] are 10·2, 4·9, and 3·7 kcal mol$^{-1}$, respectively. Thus, an increase in the number of $sp^2$ centres from one or two to three substantially enhances the barrier to ring inversion.

If we assume that all heavy atoms of (I) except C-5 are coplanar, as suggested by microwave studies of similarly hybridized systems,[8] then the conformational change affecting its e.s.r. spectrum probably involves movement of C-5 above and below this plane. In agreement with this, the measured activation energy is only slightly larger than that predicted for a 'planar' transition state in which there are twice as many eclipsing interactions as in ethane ($V_3 = 2{\cdot}93$ kcal mol$^{-1}$).[9] The excess *ca.* 1·0 kcal mol$^{-1}$ presumably reflects additional contributions to the barrier from angle strain within the six-membered ring.

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† 1 cal = 4·184 J.

[1] D. M. Camaioni and D. W. Pratt, *J. Amer. Chem. Soc.*, 1972, **94**, 9258; D. M. Camaioni, H. F. Walter, and D. W. Pratt, *ibid.*, 1973, **95**, 4057; D. M. Camaioni, H. F. Walter, J. E. Jordan, and D. W. Pratt, *ibid.*, p. 7978; J. E. Jordan, D. W. Pratt, and D. E. Wood, *ibid.*, 1974, **96**, 5588.

[2] Nearly identical h.f.s. are observed in fluid solutions at low temperature: see J. K. Kochi and P. J. Krusic, Chem. Soc. Specl. Publ. No. 24, 1970, p. 157.

[3] We estimate, based on a comparison of $a^{H}_{4,6}$ and the value $a^{H}_{Me} = 14{\cdot}01$ G for *cis*-1-methylallyl radical (J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 1968, **90**, 7157), that the dihedral angle between the C–H-4 (C–H-6) bond and the axis of the $\pi$ orbital on C-3 (C-1) is 10 ± 5°. A small inequivalence of the $\gamma$-proton h.f.s, which might be expected at very low temperatures, has not been observed.

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[7] D. W. Pratt, unpublished results.

[8] See, for example, the data of S. A. Manley and J. K. Tyler, *Chem. Comm.*, 1970, 382, on cyclohex-2-enone.

[9] S. Weiss and G. E. Leroi, *J. Chem. Phys.*, 1968, **48**, 962.