

The Conformations of Cycloalkylmethyl Radicals and Barriers to Internal Rotation

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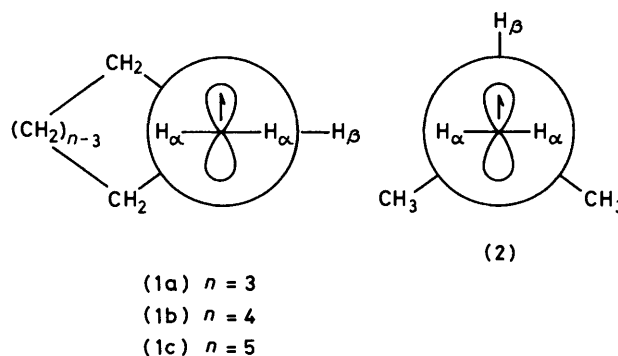
Cycloalkylmethyl radicals with C_4 , C_5 , C_6 , C_8 , and C_{11} rings have been studied by e.s.r. spectroscopy. The preferred conformation for cyclobutylmethyl and cyclopentylmethyl radicals is the bisected form with H_β in the nodal plane of the semi-occupied orbital; the radicals with larger rings adopt the eclipsed conformation. It is suggested that the conformational preferences of the radicals are governed by steric factors, except for cyclobutylmethyl where the bisected conformation is favoured by C-C hyperconjugation involving \dot{C} and the two $C_\alpha-C_\beta$ bonds. The cycloundecylmethyl radical exists in two different conformations at low temperatures but at $T > 230$ K interconversion is fast and a single e.s.r. spectrum is observed. The barriers to internal rotation in the cycloalkylmethyl radicals were calculated from the temperature dependence of the β -hyperfine splitting using the classical limit procedure. The internal rotation about the $\dot{C}-C_\alpha$ bond was also studied by the MNDO and INDO semi-empirical SCF MO methods.

E.s.r. spectroscopy has established the preferred conformations of the majority of alkyl radicals.¹ In the absence of a neighbouring π -system which can delocalize the unpaired electron, alkyl radicals appear to prefer those conformations in which steric interactions have been reduced to a minimum. However, the cycloalkylmethyl radicals present a fascinating and, as yet, unresolved problem. For the cyclopropylmethyl radical the magnitude of the hyperfine splitting (h.f.s.) by the single tertiary hydrogen (H_β) is much smaller (*viz.*,² 0.255 mT at 123 K) than is usual for a β -H (*e.g.* 2.69 mT for ethyl¹). It can be deduced from this¹ that the plane of the $\dot{C}H_2$ group bisects the cyclopropane ring since this conformation places H_β in the nodal plane of the $\dot{C} 2p_z$ semi-occupied orbital, as shown in structure (1a). Similarly, for the cyclobutylmethyl radical both the magnitude and the positive temperature coefficient¹ of the H_β h.f.s. [*i.e.* $a(H_\beta)$ increases with an increase in temperature] prove that this radical prefers the bisected conformation (1b).^{3,4} The cyclobutenylmethyl radical also adopts the bisected conformation.⁵ The only other cycloalkylmethyl radical to have been detected by e.s.r. spectroscopy is cyclopentylmethyl.⁶⁻¹⁰ A similar conformation (1c) is implied by the magnitude of $a(H_\beta)$ (*viz.*,⁶ 2.13 mT at 183 K). However, this has not been confirmed by a study of the temperature dependence of its H_β h.f.s. In contrast, with the isobutyl radical, which is the simplest structurally related acyclic species, the magnitude of $a(H_\beta)$ and its negative temperature coefficient [$a(H_\beta)$ decreases with an increase in temperature] prove that this radical prefers a conformation in which the $C_\alpha-H_\beta$ bond is eclipsed by the $\dot{C} 2p_z$ orbital (2).^{1,11-15,†} This con-

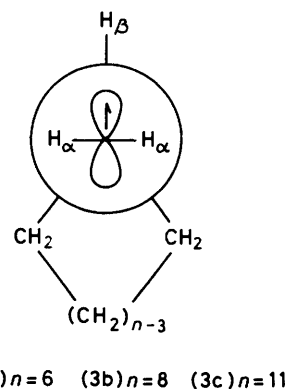
† Radicals adopting the bisected conformation (1) will, for reasons of symmetry, have a planar configuration. That is, the two H_α , \dot{C} , and C_α will all lie in one plane. Radicals which adopt the eclipsed conformation (2) and (3) may have a slightly non-planar configuration with the $H_\alpha\dot{C}C_\alpha H_\beta$ dihedral angle $< 90^\circ$,^{16,17} since this reduces steric strain. For the isobutyl radical the angle between the $\dot{C}-C_\alpha$ bond and the $H_\alpha\dot{C}H_\alpha$ plane has been calculated to be 8.6° .¹⁷ The slight non-planarity of radicals (2) and (3) does not affect the general arguments used within this paper.

formation for the isobutyl radical is supported by theoretical calculations.¹⁷

It is not at all obvious why cycloalkylmethyl radicals should adopt a bisected conformation when isobutyl



adopts the eclipsed conformation. Presumably ring size is, in some way, involved since one might expect that with a sufficiently large ring in which 'ring-effects' *per*



se were undetectable, a cycloalkylmethyl radical would adopt an eclipsed conformation (3) like isobutyl.

In order to check on this last point and to gain further insight into the conformational problem which it poses,

we have examined cycloalkylmethyl radicals with ring sizes C_4 , C_5 , C_6 , C_8 , and C_{11} , plus the isobutyl radical by e.s.r. spectroscopy in hydrocarbon solvents over as wide a range of temperatures as possible.* In all cases, the values of $a(H_\beta)$ show a very large variation with temperature. This allows the barriers to hindered rotation about the $\dot{C}-C_\alpha$ bond to be determined using suitably modified but existing theories of rotational averaging. In addition, the geometry and energetics of selected radicals have been investigated using semi-empirical SCF MO methods.

RESULTS

E.s.r. Spectra.—The cycloalkylmethyl and isobutyl radicals were generated by photolysis of the parent bromide, triethylsilane, and di-*t*-butyl peroxide in the cavity of an

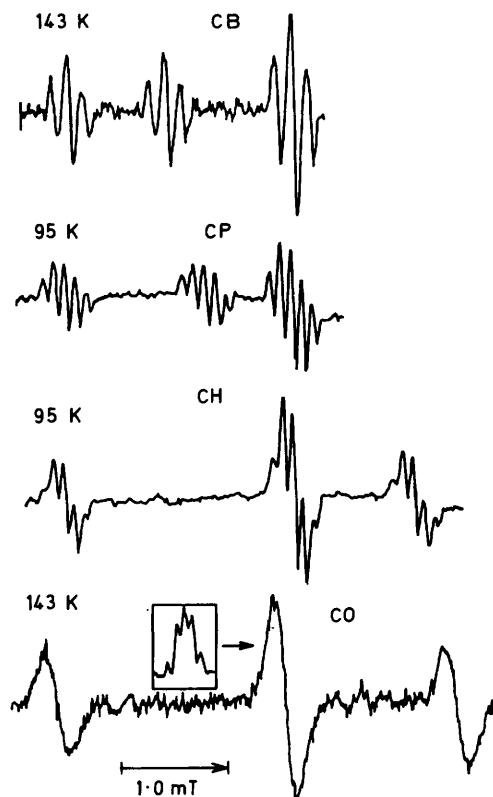


FIGURE 1 Low field halves of the e.s.r. spectra of cycloalkylmethyl radicals at 9.4 GHz, CB = cyclobutylmethyl, CP = cyclopentylmethyl, CH = cyclohexylmethyl, and CO = cyclo-octylmethyl. The inset above the CO spectrum shows the central line with second derivative presentation at 95 K

e.s.r. spectrometer using *n*-propane, cyclopropane, or isopentane as solvents for the low temperature work and *t*-butylbenzene as solvent for temperatures above ambient.

Cyclobutylmethyl radical (1b) has an e.s.r. spectrum which consists of a double triplet, each component of which is split into a further triplet by coupling with *two* γ -hydrogens (see Figure 1). The e.s.r. spectral parameters, which are in agreement with previous work,^{3,4} are listed in Table 1 for a

* The cyclopropylmethyl radical was not examined because of the very low temperature (*ca.* -120°C) at which it undergoes ring-opening to form the but-3-enyl radical.^{2,18}

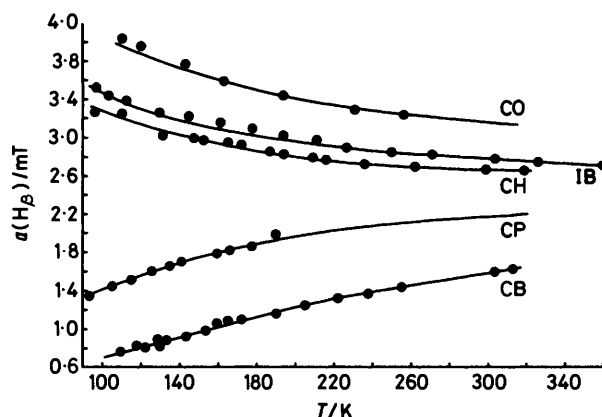


FIGURE 2 Temperature dependence of $a(H_\beta)$ for cycloalkylmethyl and isobutyl radicals. CB = cyclobutylmethyl, CP = cyclopentylmethyl, CH = cyclohexylmethyl, CO = cyclo-octylmethyl, IB = isobutyl. Filled circles experimental points; full lines calculated from equation (1)

temperature of *ca.* 140 K. The H_α and H_γ h.f.s. are essentially invariant with temperature but the H_β h.f.s. increases from 0.76 mT at 110 K to 1.61 mT at 313 K (see Figure 2). At higher temperatures only the ring-opened pent-4-enyl radical can be detected.⁴

Cyclopentylmethyl radical (1c) has an e.s.r. spectrum in which the double triplet is split (at $T < 175$ K) into a pentet which arises from coupling to *four* equivalent γ -hydrogens (see Figure 1 and Table 1). The β -H h.f.s. increases from 1.35 mT at 92 K to 1.97 mT at 186 K (see Figure 2). At higher temperatures the β - and α -H h.f.s. were too similar to be resolved and the spectrum simplified to a quartet [$a(3H) 2.13$ mT], as previously reported.⁶⁻⁸

Cyclohexylmethyl radical (3a) has an e.s.r. spectrum in which the double triplet is split (at $T < 170$ K) by the four

TABLE I
E.s.r. parameters for cycloalkylmethyl radicals at *ca.* 140 K^a

Radical	Expt.	h.f.s.	INDO h.f.s. ^b
$c\text{-C}_3\text{H}_5\text{CH}_2\cdot$ ^c	($2H_\alpha$)	2.074	
	(H_β)	0.255	
	($2H_\gamma$)	0.298	
	($2H_\gamma$)	0.201	
$c\text{-C}_4\text{H}_7\text{CH}_2\cdot$	($2H_\alpha$)	2.15	-2.08
	(H_β)	0.90	0.99
	($2H_\gamma$)	0.143	($2H_\gamma$) _{cis} -0.20, ($2H_\gamma$) _{trans} +0.02
$c\text{-C}_5\text{H}_9\text{CH}_2\cdot$	($2H_\alpha$)	2.13	-2.06
	(H_β)	1.68	1.08
	($4H_\gamma$)	0.075	($2H_\gamma$) _{cis} -0.20, ($2H_\gamma$) _{trans} -0.06
$c\text{-C}_6\text{H}_{11}\text{CH}_2\cdot$	($2H_\alpha$)	2.15	-2.08
	(H_β)	3.04	4.6
	($4H_\gamma$)	0.07	($2H_\gamma$) _{ax} -0.24, ($2H_\gamma$) _{eq} -0.16
$c\text{-C}_8\text{H}_{15}\text{CH}_2\cdot$	($2H_\alpha$)	2.16	
	(H_β)	4.01	
	($4H_\gamma$)	0.08	
$c\text{-C}_{11}\text{H}_{21}\text{CH}_2\cdot$ ^d	($2H_\alpha$)	2.14	
	(H_β)	3.11	
$c\text{-C}_{11}\text{H}_{21}\text{CH}_2\cdot$ ^e	($2H_\alpha$)	2.14	
	(H_β)	3.83	
$c\text{-C}_{11}\text{H}_{21}\text{CH}_2\cdot$ ^f	($2H_\alpha$)	2.14	
	(H_β)	2.98	

^a H.f.s. in mT. ^b INDO calc. h.f.s. with $a(H_\beta)$ averaged according to equation (3) (see text); *cis* means *cis* to the $\text{CH}_2\cdot$ group, *etc.* ^c Data from ref. 2 at 123 K. ^d Cyclohexylmethyl-like radical. ^e Cyclo-octylmethyl-like radical. ^f At 270 K.

γ -hydrogens (see Figure 1 and Table 1). The β -H h.f.s. decreases from 3.23 mT at 110 K to 2.65 mT at 319 K (see Figure 2). Both the absolute magnitude of $a(\text{H}_\beta)$ and the negative sign of $\partial a(\text{H}_\beta)/\partial T$ show that this radical adopts conformation (3).

Cyclo-octylmethyl radical (3b) has an e.s.r. spectrum similar to that of cyclohexylmethyl but in this case the presence of four equivalent γ -hydrogens can be revealed only by making use of a second derivative presentation (see insert in Figure 1). The β -H h.f.s. decreases from 4.01 mT at 110 K to 3.25 mT at 256 K (see Figure 2).

$\partial a(\text{H}_\beta)/\partial T$ has a positive sign (see Figure 2) for the cyclobutylmethyl and cyclopentylmethyl radicals proves¹ that these radicals prefer the bisected conformation (1). For cyclohexylmethyl, cyclo-octylmethyl, and cyclo-undecylmethyl radicals the absolute magnitude of $a(\text{H}_\beta)$ and the negative sign of $\partial a(\text{H}_\beta)/\partial T$ prove that these radicals, like isobutyl (2), prefer the eclipsed conformation (3). We initially assumed that these different conformations were a consequence of steric factors since such is the case even when a hydrogen atom in an acyclic alkyl

TABLE 2

Calculated H-H distances (Å) for cycloalkylmethyl and isobutyl radicals^a

	Cyclobutylmethyl ^b		Cyclopentylmethyl		Cyclohexylmethyl		Isobutyl	
	E	B	E	B	E	B	E	B
$\text{H}_\alpha\text{-H}_\beta$	2.80	2.42	2.77	2.38	2.76	2.38	2.79	2.42
$\text{H}_\alpha\text{-H}_\beta$	2.80	3.13	2.77	3.11	2.76	3.11	2.79	3.12
$\text{H}_\alpha\text{-H}_\gamma$	2.92	2.80	2.33	2.60	2.67	2.69	2.71	2.70
$\text{H}_\alpha\text{-H}_\gamma$	2.92	2.80	2.33	2.60	2.67	2.69	2.71	2.70
$\text{H}_\alpha\text{-H}_\gamma$					2.77		2.71	3.19
$\text{H}_\alpha\text{-H}_\gamma$					2.77		2.71	3.19

^a For structural parameters and assumptions see text. The preferred conformation of each radical, *viz.*, eclipsed (E) or bisected (B) is indicated in bold face. The dominant repulsive H-H interactions, *i.e.*, short H-H distances, for each conformer are indicated in italics. H-H distances > 3.20 Å are not recorded. There are actually 12 $\text{H}_\alpha\text{-H}_\gamma$ interactions in isobutyl and 8 in the cycloalkylmethyl radicals. ^b For a planar cyclobutyl ring the dominant H-H interactions in the eclipsed conformation are two $\text{H}_\alpha\text{-H}_\gamma$ distances; the dominant interaction in the bisected conformation remains $\text{H}_\alpha\text{-H}_\beta$.

Cycloundecylmethyl radical (3c) was unique in that the e.s.r. spectrum at $T < 230$ K showed that two distinct radicals were present. This was not due to an impurity in the starting cycloundecylmethyl bromide. The two radicals had identical g -factors, both showed coupling to two equivalent α -H and to one β -H, the γ -hydrogens being unresolved in both cases. The low temperature spectra of the two radicals (see Figure 3) differ only in the magnitude of the β -H h.f.s. (see Table 1). For both radicals $a(\text{H}_\beta)$ decreases with increasing temperature. At 230 K the lines due to the two radicals coalesce to give a single spectrum with rather broad lines. At somewhat higher temperatures the lines sharpen and the spectrum of a single cycloundecylmethyl radical is observed (see Figure 3).

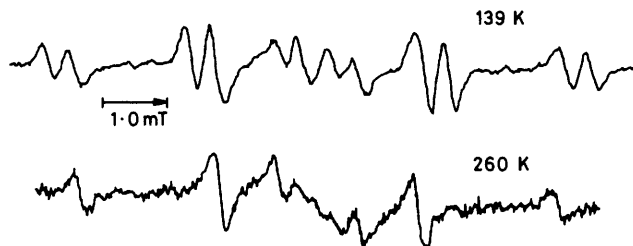


FIGURE 3 E.s.r. spectra of cycloundecylmethyl radicals at 9.4 GHz

Isobutyl radical (2) has a well known e.s.r. spectrum which was recorded in the present study over a wider range of temperature than heretofore. The variation in the β -H h.f.s. with temperature is shown in Figure 2.

DISCUSSION

Conformations of Cycloalkylmethyl Radicals.—The absolute magnitude of the β -H h.f.s. and the fact that

radical is replaced by deuterium^{12,19} or muonium,²⁰⁻²² For this reason we searched for the more important steric effects by calculating the distances between the α -hydrogens and the β - and γ -hydrogens for cyclobutylmethyl, cyclopentylmethyl, cyclohexylmethyl, and isobutyl radicals in the bisected [B *i.e.* (1)] and eclipsed [E *i.e.* (3)] conformations. Such an apparently simple task turned out to be surprisingly difficult. There are a number of imponderables which make the necessary accuracy unachievable by anything less than *ab initio* SCF calculations at the very highest level.^{16,17} These imponderables include $\dot{\text{C}}\text{-C}_\alpha$ bond lengths,* the degree of puckering of the cyclobutyl and cyclopentyl rings,† the precise configuration (planarity or otherwise) of the radical centre in the eclipsed conformations,^{16,17} *etc.* For these reasons, we report in Table 2 only the more important (*i.e.* shorter) H-H interatomic distances we have calculated using simplified structures and 'rationalized' geometries, *viz.*, a planar conformation for all radical centres with $\dot{\text{C}}\text{-H}_\alpha$ 1.08, $\dot{\text{C}}\text{-C}_\beta$ 1.48, $\text{C}_\alpha\text{-H}_\beta$ 1.12, and $\text{H}_\alpha\dot{\text{C}}\text{H}_\alpha$ 120°; a chair cyclohexyl ring, a planar cyclopentyl ring, and a puckered cyclobutyl ring with an acute angle of 35° between the $\text{C}_\beta\text{C}_\alpha\text{C}_\beta$ and $\text{C}_\beta\text{C}_\gamma\text{C}_\beta$ planes. (A puckered ring is preferred because only two γ -hydrogens are observed in the e.s.r. spectrum; see Figure 1.)

An examination of Table 2 shows that in the bisected conformations, the shortest H-H distance for all radicals is the unique (eclipsed) $\text{H}_\alpha\text{-H}_\beta$ at 2.38–2.42 Å. For cyclohexylmethyl and isobutyl this $\text{H}_\alpha\text{-H}_\beta$ repulsive

* MNDO calculations predict different $\dot{\text{C}}\text{-C}_\alpha$ bond lengths for different cycloalkylmethyl radicals.

† MNDO calculations predict both rings to be planar, though cyclobutane itself has a dihedral angle in the ring of 35°.

interaction dominates all others* and causes these two radicals to adopt the eclipsed conformation. For cyclopentylmethyl the bisected conformation is favoured because repulsion due to the single 2.38 Å $H_\alpha-H_\beta$ distance is outweighed by repulsion due to the double 2.33 Å $H_\alpha-H_\gamma$ distance of the eclipsed conformation. Although in the puckered cyclopentyl ring (dihedral angle 14°), in the eclipsed conformation, the double $H_\alpha-H_\gamma$ distance is calculated to increase to 2.47 Å this may still produce sufficient repulsion to outweigh that due to the 2.38 Å $H_\alpha-H_\beta$ distance in the bisected conformation.

For the cyclobutylmethyl radical it is clear that simple steric arguments break down because they predict that the eclipsed conformation should be preferred irrespective of whether or not the ring is puckered. We therefore propose that the conformation of the cyclobutylmethyl radical is determined by electronic effects: specifically, following our earlier suggestion,⁴ by C-C hyperconjugation involving \dot{C} and the two $C_\alpha-C_\beta$ bonds. That is, in cyclobutane the C-H bonds are stronger and have more *s*-character while the C-C bonds are weaker and have more *p*-character than is the case for unstrained rings and acyclic hydrocarbons.^{4,23} Hyperconjugation with the $C_\alpha-C_\beta$ bonds is therefore favoured because of their π character while hyperconjugation with $C_\alpha-H_\beta$ is disfavoured, all of which leads to a preference for the bisected conformation. The potential role of $C_\alpha-H_\beta$ hyperconjugation in favouring eclipsed conformations for the cyclohexylmethyl and isobutyl radicals is uncertain since these conformations (and that of the cyclopentylmethyl radical) are so much more readily explained by steric factors (as has been tentatively suggested previously for the isobutyl radical by Danen²⁴). In this connection, it should be noted that the usual assumption that C-H hyperconjugation with an adjacent electron-deficient centre is stronger than C-C hyperconjugation in unstrained systems, has no basis in fact. The reverse has been shown to be true for strongly electron-deficient centres both theoretically²⁵ and experimentally.²⁶ The relative ordering of C-H and C-C hyperconjugation with respect to a neighbouring radical centre is uncertain, but in unstrained systems the difference is probably quite small. However, it seems highly probable that C-C hyperconjugation will be the more important in cyclobutylmethyl and in cyclopropylmethyl²⁴ radicals because of the increased *p*-character of the C-C bonds in the rings. The C-C bonds in cyclopropane have considerably more *p*-character than those in cyclobutane and we believe it is for this reason that the bisected conformation appears to be even more strongly favoured by the cyclopropylmethyl radical, at least as far as can be judged by the β -H h.f.s., *viz.* 0.255 mT² for cyclopropylmethyl *versus* 0.88 mT for cyclobutylmethyl at 133 K.

The cycloundecylmethyl radical prefers the eclipsed

* Note that for the cyclohexylmethyl radical the next largest steric repulsion will be that due to two $H_\alpha-H_\gamma$ interactions which are of almost equal magnitude in the eclipsed (2.67 Å) and bisected (2.69 Å) conformations. For the isobutyl radical all H-H distances other than the one $H_\alpha-H_\beta$ distance are ≥ 2.70 Å in both conformations.

conformation but the ring itself exists in two different conformations at low temperature. The magnitude of the β -H h.f.s. of these two conformers (see Table 1) implies that the local geometries can be described as 'cyclohexylmethyl-like' and 'cyclo-octylmethyl-like'. At the temperature of maximum line broadening, *viz. ca.* 230 K, the rate constant for the process which makes the β -H in the two conformers magnetically equivalent is given by $k = 6.22 \times 10^7 \Delta a \text{ s}^{-1}$,²⁷ where Δa (in mT) is the difference between the two H_β -h.f.s., which is *ca.* 0.7 mT. Hence $k = 4.4 \times 10^7 \text{ s}^{-1}$ at this temperature. Values of k calculated²⁷ at other temperatures are $2.1 \times 10^8 \text{ s}^{-1}$ (260 K), $1.3 \times 10^8 \text{ s}^{-1}$ (237 K), $1.5 \times 10^7 \text{ s}^{-1}$ (215 K), $1.5 \times 10^7 \text{ s}^{-1}$ (204 K), and $1.7 \times 10^7 \text{ s}^{-1}$ (194 K). Despite some scatter these rate constants give a reasonable fit to an Arrhenius equation having a pre-exponential factor of 10^{13} s^{-1} (the 'expected' value) and an activation energy around 23 kJ mol⁻¹. Since it is almost solely the dihedral angle between the $\dot{C} 2p_z$ orbital and the $C_\alpha-H_\beta$ bond which determines the magnitude of $a(H_\beta)$ it is obvious that a 23 kJ mol⁻¹ barrier cannot reflect hindered rotation about the $\dot{C}-C_\alpha$ bond (*vide infra*). Some ring motion must be involved, perhaps one in which the radical centre moves from the 'inside' to the 'outside' of the undecyl ring.

Calculation of Barriers to Rotation about the $\dot{C}-C_\alpha$ Bond.—The angular dependence of $a(H_\beta)$ can be represented by $a(H_\beta) = A + B \cos^2 \theta$ where θ is the dihedral angle between the $\dot{C} 2p_z$ orbital and the $C_\alpha-H_\beta$ bond. For the radicals considered in this paper certain θ values are preferred but the populations of different conformers vary with the temperature, thereby making $a(H_\beta)$ temperature dependent. The potential barrier to rotation about the $\dot{C}-C_\alpha$ bond, V_θ , can be estimated by fitting the observed temperature dependence of $a(H_\beta)$ with calculated values. A classical limit approach^{1,13} has been shown to give essentially the same results for small primary alkyl radicals as a more cumbersome quantum-mechanical procedure.¹² The integrals involved in the classical limit procedure have been evaluated numerically.¹³ However, an analytical expression can be given for these integrals and the equation for $a(H_\beta)$ is then (1)

$$\langle a(H_\beta) \rangle = A + \frac{1}{2}B + \frac{1}{2}B \cos 2\theta_0 \left[\frac{I_1(\lambda)}{I_0(\lambda)} \right] \quad (1)$$

where $I_1(\lambda)$ and $I_0(\lambda)$ are modified (hyperbolic) Bessel functions, $\lambda = V_\theta/kT$, and θ_0 is the value of θ at the potential minimum. Equation (1) may be approximated by a power series in λ [equation (2)]. For $\lambda < 1$ it

$$\langle a(H_\beta) \rangle = A + \frac{1}{2}B + \frac{1}{2}B \cos 2\theta_0 \left[\frac{\lambda}{2} - \frac{\lambda^3}{16} + \frac{\lambda^5}{96} - \dots \right] \quad (2)$$

is sufficient to take the first two terms in the series, *i.e.* in the temperature range 100–300 K equation (2) may be used if $V_\theta < ca.$ 2.4 kJ mol⁻¹. The barrier height is determined by fitting equation (2) to the observed $a(H_\beta)$ values and varying A , B , and V_θ so as to get the best fit.

In principle, this equation could also be used for higher barriers by employing more terms in the power series. However, it is difficult to estimate the coefficients of the terms in λ^5 , etc. with sufficient accuracy by curve fitting, and it is therefore better to use equation (1).

The preferred conformation for the isobutyl, cyclohexylmethyl, and cyclo-octylmethyl radicals is (3) and therefore $\theta_0 = 0$. For the isobutyl radical an analysis of the data, using equation (2) and the terms in λ and λ^3 only, leads directly to the values A 0.018 mT, B 4.641 mT, and V_0 1.94 kJ mol⁻¹. The full expression [equation (1)] gives an excellent fit to the experimental points with essentially the same parameters, viz., A 0, B 4.70 mT, and V_0 1.85 kJ mol⁻¹ (see Table 2). The solid line shown in Figure 2 for the isobutyl radical was obtained from these parameters. Our barrier is somewhat greater than that found by Fessenden¹² using the quantum-mechanical approach, viz.,¹² V_0 1.23 kJ mol⁻¹ with A 0 and B 5.37 mT; and than that found by Krusic and Kochi¹³ using Fessenden's experimental data and their classical limit method, viz.,¹³ V_0 1.27 kJ mol⁻¹ with A 0.15 mT and B 5.06 mT. For both these studies the number of experimental data points and the temperature range were more restricted and much poorer fits to the data points were achieved than that shown in Figure 2. An *ab initio* SCF study of isobutyl¹⁷ has given V_0 1.17 kJ mol⁻¹.

TABLE 3
Values of A , B , and V_0 used to obtain curves shown in Figure 2

Radical	θ_0 (°)	A	B	V_0 / kJ mol ⁻¹
(CH ₃) ₂ CHCH ₂	0	0	47	1.85
c-C ₆ H ₁₁ CH ₂	0	0	46	1.60
c-C ₈ H ₁₅ CH ₂	0	0	52	2.30
c-C ₆ H ₉ CH ₂	90	2	50	2.00
c-C ₄ H ₇ CH ₂	90	2	50	4.90

Good fits to the experimental points were also obtained for the cyclohexylmethyl and cyclo-octylmethyl radicals with A 0 and appropriate values of B and V_0 using equation (1). The values used to construct the solid lines in Figure 2 are recorded in Table 3. It should be noted that these values do not represent unique solutions. Equally good fits could be obtained with small negative values for A and slightly larger B values.

Cyclobutylmethyl and cyclopentylmethyl radicals prefer conformation (1) with θ_0 90°. The calculated curves for these two radicals are shown in Figure 2 and values of A , B , and V_0 are listed in Table 3. Although the 'fits' to the experimental points are somewhat 'soft' it should be noted that no fit could be obtained with A 0. Positive A values are necessary but equally good fits to those shown in Figure 2 could be obtained with larger A and smaller B values. Most notably, we point out that V_0 for the cyclobutylmethyl radical is clearly larger than the V_0 value for any of the other cycloalkylmethyl radicals (and the isobutyl radical) listed in Table 2. Since the cyclobutylmethyl radical should have the least steric hindrance to rotation about the \dot{C} -C_α bond [because the C_β(H)₂ groups are firmly ' tied-

back'—see Table 2] it is clear that effects other than those of purely steric origin are operative in this radical.

Finally we note, that for the ethyl radical, in which rotation is completely unhindered on the e.s.r. time scale (*i.e.* V_0 ca. 0), that $a(H_\beta) = A + \frac{1}{2}B = 2.69$ mT.¹ It has generally been assumed^{1,12,14} that $A + \frac{1}{2}B$ has a constant value for primary alkyl radicals and for this reason 2.69 mT was forcibly imposed for this quantity in previous calculations of barriers to internal rotation. Our current results clearly demonstrate that if a good fit is to be obtained between the experimental and theoretical temperature dependencies of β -H h.f.s., *i.e.* if theory is to be a valid description of fact, then $A + \frac{1}{2}B$ is *not* a constant. Specifically, if $A = 0$, B would have to be 5.38 mT, but we find smaller values than this for all the radicals studied in this work (see Table 2). Moreover, if B were 5.38 mT then A would have to be negative for isobutyl, cyclohexylmethyl [note that $a(H_\beta) < 2.69$ mT at high temperatures, see Figure 2], and cyclo-octylmethyl, though the data for cyclobutylmethyl and cyclopentylmethyl radicals *cannot be fitted* with negative A values. We draw attention to these facts not because we can provide answers to the questions they raise but in the hope that others may be stimulated to provide such answers.

Semi-empirical SCF MO Calculations.—The cyclobutylmethyl, cyclopentylmethyl, cyclohexylmethyl, and isobutyl radicals were examined using the MNDO method of Dewar and Thiel.^{28,29} Geometries were fully optimised with respect to all bond lengths, bond angles, and dihedral angles in preliminary calculations. It was found that the C-H bond lengths and H-C-C bond angles for atoms further from the radical centre than C_β were not sensitive to the dihedral angle about \dot{C} -C_α and they were subsequently held constant. Planarity was also enforced at \dot{C} . The enthalpies of formation of the radicals were then calculated for a series of values of the dihedral angle about the \dot{C} -C_α bond. The MNDO calculations predicted planar cyclobutyl and cyclopentyl rings, but a chair conformation for the cyclohexyl ring. Calculations were carried out for radicals with both planar rings, and rings with enforced puckering. The optimum H_α- \dot{C} bond lengths were all 1.082 ± 0.002 Å and the H_α- \dot{C} -C_α angles were 120 ± 2°. The optimum \dot{C} -C_α bond lengths were 1.460, 1.474, 1.481, and 1.482 Å for cyclobutylmethyl, cyclopentylmethyl, cyclohexylmethyl, and isobutyl respectively, and the optimum C_α-H_β bond lengths were all 1.120 ± 0.003 Å. The MNDO calculations indicated a lengthening of the C_α-C_β bond lengths from the corresponding values in the hydrocarbons from which the radicals were derived. The optimum geometrical parameters given above changed very little with variation of the dihedral angle about \dot{C} -C_α. The optimum calculated conformations and the barriers to rotation are given in Table 4. It is apparent that although the MNDO method gives barriers of approximately the right magnitude, only in the cyclopentylmethyl case is the preferred conformation correctly predicted. The energy difference between the E and B conformers

is very small in all cases so the problem provides a severe test of any theory and the failure of MNDO to reproduce exactly the experimental result is not surprising. It should be noted that in the cyclobutylmethyl case the calculated \dot{C} - C_α bond length is particularly short, the C_α - C_β bond (1.57 Å) is appreciably longer than the C_β - C_γ bond (1.54 Å) and the calculated barrier is higher than for the other radicals. There was little change in the above parameters whether the C_4 ring was constrained to be puckered with an acute angle of 35° between the $C_\beta C_\alpha C_\beta$ plane and the $C_\beta C_\alpha C_\beta$ plane, or whether it was planar. The MNDO results give an indication that there is significant interaction of the \dot{C} $2p_z$ orbital with the orbitals forming the ring C_α - C_β bonds (C-C hyperconjugation).

Calculations were also carried out using the INDO method of Pople and his co-workers.^{30,31} Geometries were not optimised but were based on the optimum structures obtained with MNDO. Rings were considered puckered with the $\dot{C}H_2$ group equatorial; bond lengths and angles for atoms beyond C_α were taken directly from the MNDO geometries. The radical centre was assumed planar with \dot{C} - H_α 1.08 Å, C_α - H_β 1.12 Å, angle H_α - \dot{C} - C_α 120° . The INDO calculations predicted the correct conformations for all the radicals taking tetrahedral bond angles about C_α and \dot{C} - C_α = 1.50 Å (Table 4). However, the total energies of the radicals and the preferred conformations were very sensitive to the geometrical parameters about C_α . *E.g.* with cyclopentylmethyl radicals having angle \dot{C} - C_α - C_β greater than

all values of θ are allowed. The INDO-calculated h.f.s. are shown in Table I where the $a(H_\beta)$ values were averaged at 140 K by the use of equation (3) with h.f.s. and E_θ

$$\langle a(H_\beta) \rangle_{av} = \frac{\sum_{\theta=0}^{90} a(H_\beta)_\theta \exp(-E_\theta/kT)}{\sum_{\theta=0}^{90} \exp(-E_\theta/kT)} \quad (3)$$

values taken at 10° intervals. The INDO-calculated h.f.s. are in quite good agreement with experiment, the worst discrepancy being for $a(H_\beta)$ of cyclohexylmethyl radicals. In part this is due to the assumed geometry and in part to the size of the rotational barrier; better agreement would be obtained with a lower barrier. Of particular note is the calculated decrease in $a(2H_\gamma)_{trans}$ with ring size; thus INDO successfully predicts a triplet γ -structure for cyclobutylmethyl because the 0.02 mT splitting would not be resolved (see Figure 1).

EXPERIMENTAL

¹H N.m.r. spectra were recorded on a Bruker WP 80 instrument in $CDCl_3$ solutions at room temperature with tetramethylsilane as internal standard. Mass spectra were obtained with an A.E.I. MS 902 spectrometer. G.l.c. analysis was carried out using a Pye PU 4500 chromatograph fitted with 7 ft columns packed with 10% SE 30 on Chromosorb G, or 15% TTP on Chromosorb G. E.s.r. spectra were recorded with a Bruker ER 200D spectrometer.

Synthesis of Cycloalkylmethyl Bromides.—All the cycloalkylmethyl bromides were made from commercial cyclo-

TABLE 4
Conformations of cycloalkylmethyl and isobutyl radicals calculated by MNDO and INDO

Radical	MNDO		INDO	
	Conformation ^a	$V_0/kJ mol^{-1}$	Conformation ^a	$V_0/kJ mol^{-1}$
Cyclobutylmethyl	E	2.6	B	4.4
Cyclopentylmethyl	B	1.2	B	3.7
Cyclohexylmethyl	B	1.5	E	0.8
Isobutyl	B	2.3	E	3.1

^a Predicted stable conformation.

tetrahedral the eclipsed conformation was preferred, although the total energies were higher; on the other hand with \dot{C} - C_α 1.48 Å and the angle \dot{C} - C_α - C_β greater than tetrahedral the lowest total energies were calculated but the rotational energy function was then skewed. Similar sensitivity was observed with the other radicals. The calculated barriers to rotation are also of the right magnitude (Table 4) and the INDO calculations also predict the highest barrier for cyclobutylmethyl radicals.

The h.f.s. calculated by the INDO technique cannot be directly compared with experiment because they [particularly $a(H_\beta)$] vary with the dihedral angle θ . The average INDO h.f.s. $\langle a(H_\beta) \rangle_{av}$ may be calculated from the computed h.f.s. at a given dihedral angle [$a(H_\beta)_\theta$] and the corresponding energies E_θ , where E_θ is the energy of the radical relative to the energy at the bottom of the rotational potential well at the preferred conformation [equation (3)]. In fact there are only certain allowed values of θ and E_θ ¹² and equation (3) is an approximation equivalent to the classical limit approach in which

alkylmethanols using the same procedure. The cycloalkylmethanol (0.05 mol) and triethylamine (0.05 mol) in dry CH_2Cl_2 (150 ml) were stirred at $-10^\circ C$ and methanesulphonyl chloride (0.055 mol) was added over 15 min under nitrogen. After a further 20 min stirring, water was added and the CH_2Cl_2 layer separated, washed with 2M-HCl, 5% brine, and saturated $NaHCO_3$ solution, and dried (Na_2SO_4). The CH_2Cl_2 was removed on a rotary evaporator at room temperature. The mesylate and dry lithium bromide (7.0 g) were then refluxed in acetone (150 ml) for *ca.* 12 h. The precipitate was filtered off and the acetone removed by distillation. Water and then ether were added to the residue; the organic layer was separated and dried (Na_2SO_4) and the ether removed on a rotary evaporator. The residual oil was then distilled under reduced pressure in a Vigreux flask. The resulting cycloalkylmethyl bromides were examined by g.l.c. and in each case the product contained a single component with purity $\geq 99\%$.

Cyclobutylmethyl bromide was synthesised as described previously.⁴

Cyclopentylmethyl bromide was formed in 71% yield, b.p. $59^\circ C$ at 22 mmHg (lit.,³² 58 – $60^\circ C$ at 15 mmHg), M^+

(weak) 162, 164; δ_{H} 1.0—2.0 (8 H, m), 2.0—2.5 (1 H, m), and 3.32 (2 H, d, J 7 Hz).

Cyclohexylmethyl bromide was formed in 73% yield, b.p. 76 °C at 17 mmHg (lit.³³ 76—77 °C at 26 mmHg) (Found: M^+ , 176.0190. Calc. for $\text{C}_7\text{H}_{15}^{79}\text{Br}$: m/e , 176.0201); δ_{H} 0.75—2.00 (m, 11 H) and 3.27 (2 H, d, J 7 Hz).

Cyclo-octylmethyl bromide was formed in 73% yield, b.p. 123—124 °C at 20 mmHg (Found: M^+ , 204.0522. $\text{C}_9\text{H}_{17}^{79}\text{Br}$ requires m/e , 204.0514); δ_{H} 1.0—2.2 (15 H, m) and 3.27 (2 H, d, J 7 Hz).

Cycloundecylmethyl bromide was formed in 79% yield, b.p. 120—122 °C at 2.5 mmHg (Found: M^+ , 246.0974. $\text{C}_{12}\text{H}_{23}^{79}\text{Br}$ requires m/e , 246.0984); δ_{H} 1.1—1.7 (21 H, m) and 3.35 (2 H, d, J 7 Hz). G.l.c. analysis on two columns (see above) confirmed this as a single compound of purity ca. 99%.

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