Rotational Barriers in Substituted Ethyl Radicals

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Summary *Ab initio* molecular orbital theory indicates that barriers to rotation about the C_{α}–C_{β} bond in several ethyl radicals with β first row substituents are considerably smaller than in the corresponding cations.

RECENTLY, the e.s.r. spectra of a number of substituted ethyl radicals ($XCH_2\dot{C}H_2$ and $X_2CH\dot{C}H_2$) have been measured[1] and used to determine preferred conformations and barriers to rotation about the C_{α}–C_{β} bond. These were noted[1b] to be markedly different in several instances from conformations and rotational barriers for the corresponding cations as determined by M.O. calculations.[2] The rotational barriers in the radicals were found to be considerably smaller than in the cations.

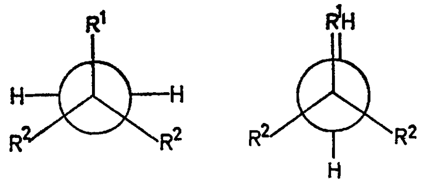
In order to examine these observations more closely, we have carried out *ab initio* unrestricted M.O. calculations[3] on some representative radicals with the STO-3G basis set.[4] Standard values of bond lengths and angles as specified elsewhere[5] are used with additional values C_α–C_β = 1·52 Å, C_α–H = 1·08 Å taken from the optimized geometry of the ethyl radical.[6] The radical centre is assumed to be planar.† Calculated total energies and relative energies‡ are listed in the Table and compared with experimental values and with theoretical results for corresponding cations.[2]

Table. Total relative and stabilization energies for radicals and cations

Radical	Conformation[a]	Total energy (hartrees) Radical	Relative energy[b] (kcal mol^{-1}) Radical calc.	Relative energy[b] (kcal mol^{-1}) Radical expt.[c]	Relative energy[b] (kcal mol^{-1}) Cation calc.[d]	Stabilization energy[f] (kcal mol^{-1}) Radical calc.	Stabilization energy[f] (kcal mol^{-1}) Radical expt.[g]	Stabilization energy[f] (kcal mol^{-1}) Cation calc.[d]
Ethyl	(I)	−77·66168	0		0	0	0	0
	(II)	−77·66168	0		0	0		0
n-Propyl	(I)	−116·24089	0	0	0	−0·3	+0·1	+4·6
	(II)	−116·24076	+0·1	−0·4	+2·5	−0·3		+2·1
Isobutyl	(II)	−154·82062	0	0	0	−0·4	−0·3	+7·5
	(I)	−154·82040	+0·1	−0·3	+2·7	−0·6		+4·8
Neopentyl	(I)	−193·40014	0		0	−0·7	−1·3	+8·5
	(II)	−193·40014	0		0	−0·7		+8·5
Cyclopropylmethyl ..	(II)	−153·60675	0	0	0	+1·8	+0·4±1·6[h]	+18·3
	(I)	−153·60418	+1·6	<3	+17·5	+0·2		+0·8
Cyclobutylmethyl ..	(II)	−192·20318	0		0	+0·2		+12·2
	(I)	−192·20288	+0·2		+4·1	0·0		+8·2
2-Fluoroethyl	(II)	−175·10687	0[e]		0	−0·9		−10·3
	(I)	−175·10684	0[e]		+9·3	−0·9		−19·6
2-Cyanoethyl	(I)	−168·20552	0		0	−0·6		−20·9
	(II)	−168·20537	+0·1		−2·0	−0·7		−19·0
2-Hydroxyethyl	(II)	−151·48452	0		0	−0·7		−2·6
	(I)	−151·48431	+0·1		+7·7	−0·8		−10·3

[a] The conformations considered are either symmetric orthogonal or symmetric eclipsed as in (I) and (II), respectively, with appropriate substituents R^1 and R^2. [b] Energy relative to conformation of lower energy. [c] From ref. 1. [d] From ref. 2. [e] From ref. 9. [f] Energy of the formal reaction: $R\text{-}CH_2(+ \text{ or } \cdot) + CH_3\text{-}CH_3 \longrightarrow R\text{-}CH_3 + CH_3\text{-}CH_2\ (+ \text{ or } \cdot)$. [g] Unless otherwise noted, calculated using heats of formation for radicals from J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465 and for neutral molecules from F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953. [h] D. F. McMillen, D. M. Golden, and S. W. Benson, *Internat. J. Chem. Kinetics*, 1971, **3**, 359.

In both the ethyl cation and radical, conformations (I) and (II) ($R^1 = R^2 = H$) have approximately the same energy and the barriers to rotation about the C_α–C_β bond are therefore close to zero.[7] For β-substituted ethyl cations, it is found that the β-substituents change the energies of (I) and (II) by different amounts leading to a strong conformational preference and hence a large rotational barrier.[2,8,9] These conformational preferences are accompanied by a strong hyperconjugative interaction between the bonds at the β-carbon and the formally vacant 2*p* orbital at the positive carbon[2,9] (measured by the electron population of that orbital).



(I) (Symmetric orthogonal) (II) (Symmetric eclipsed)

The corresponding 2*p* orbital in the radicals is no longer vacant and the hyperconjugative interaction is much weaker. Consequently, the rotational barriers, insofar as they depend on the differential hyperconjugation of C–X and C–H bonds, should be smaller in the radicals than in the cations. Thus the calculated barriers in the fluoroethyl and cyclopropylmethyl radicals are reduced to 0 and 1·6 kcal mol^{-1}, respectively, from the corresponding values (9·3 and 17·5 kcal mol^{-1}) in the cations.§ These results agree with experimental observations. For the fluoroethyl radical, there is evidence for slightly hindered rotation about the C_α–C_β bond.[1d] For cyclopropylmethyl, the barrier is estimated[b] to be less than 3 kcal mol^{-1}. Small barrier values (less than *ca.* 0·5 kcal mol^{-1}) are also suggested by the experimental results[1] for the n-propyl, isobutyl, cyanoethyl, and hydroxyethyl radicals. In contrast, the experi-

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† This approximation should be adequate for present purposes. Except for the conformations in which the CH_2 group lies in a molecular symmetry plane, *e.g.* (II), the radical centre cannot be exactly planar. Even in the former situation, the radical centre may be non-planar.

‡ These correspond approximately to the rotational barriers. More detailed calculations show that the potential minima or maxima do not always occur at the symmetric eclipsed (II) or perpendicular (I) conformations so that the barriers are not always exactly given by the energy difference between these forms. However, the barrier values are not greatly changed by this refinement.

§ Calculated rotational barriers for the cyclopropylcarbinyl cation and radical calculated using partially optimized geometries are 26·3 and 1·4 kcal mol^{-1}, respectively: W. J. Hehre, *J. Amer. Chem. Soc.*, 1972, **94**, 597 and personal communication.

mental barrier[10] for the dimethylcyclopropylmethyl cation is 13·7 kcal mol^{-1}.

The lowest energy conformation predicted by the theory agrees with that deduced from the experimental results for the cyclopropylmethyl radical.[1a] For the other radicals, this is not always the case (see, for example, n-propyl and isobutyl radicals, Table). However, here the theoretical energy differences are very small and are not considered particularly significant in view of the approximations implicit in the assumed geometries and use of a minimal basis set.

Further evidence that the rotational barriers should be small comes from the calculated stabilization energies (Table) evaluated as the energy change in reaction (1).

$$\text{R–}\dot{\text{C}}\text{H}_2 + \text{CH}_3\text{–CH}_3 \longrightarrow \text{R–CH}_3 + \text{CH}_3\text{–}\dot{\text{C}}\text{H}_2 \qquad (1)$$

The stabilization energies compare the stabilization of the methyl radical by R and by CH_3 (relative to corresponding effects in methane). These stabilization energies are uniformly small in contrast to the very large values obtained for the corresponding cations.[2] The small stabilization energies imply that the interaction of C–H, and of other C–X bonds involving first row elements with the radical centre are of similar magnitude; hence the rotational barriers should be small.

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[1] Leading references: (a) R. W. Fessenden, *J. Chim. phys.*, 1964, **61**, 1570; (b) P. J. Krusik, P. Meakin, and J. P. Jesson, *J. Phys. Chem.*, 1971, **75**, 3438; (c) T. Kawamura, D. J. Edge, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 1752; (d) D. J. Edge and J. K. Kochi, *ibid.*, 1972, **94**, 6485, 7695.

[2] L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1970, **92**, 6380, 6987; L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1972, **95**, 5935.

[3] J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, 1954, **22**, 571.

[4] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 1969, **51**, 2657.

[5] J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.*, 1967, **89**, 4253.

[6] W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 1971, **93**, 808.

[7] When optimized geometries are used,[6] the barrier values are increased slightly.

[8] D. T. Clark and D. M. J. Lilley, *Chem. Comm.*, 1970, 603.

[9] R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Amer. Chem. Soc.*, 1972, **94**, 6221.

[10] D. S. Kabakoff and E. Namanworth, *J. Amer. Chem. Soc.*, 1970, **92**, 3234.