A Theoretical Investigation of the Structures and Properties of Classical and Bridged β-Substituted Ethyl Radicals

Maurizio Guerra

Contribution from the Istituto dei Composti del Carbonio contenenti Eteroatomi e loro Applicazioni, CNR, Via della Chimica 8, Ozzano Emilia (Bologna), Italy. Received June 24, 1991

Abstract: The structural parameters of β-substituted ethyl radicals $H_nM–CH_2–CH_2{}^{\bullet}$ ($H_nM = H_3C$, H_2N, HO, F, H_3Si, H_2P, HS, Cl) have been determined by ab initio calculations including electron correlation. At the UMP2/DZP+BF level of theory, the absolute energy minimum is found in all radicals for a classical structure **1a** in which the radical center C_α is slightly pyramidal. Substituents containing second-row heteroatoms adopt a gauche conformation ($\omega = 60°$) with respect to the singly occupied 2p carbon orbital (SOMO). Rotation about the $C_\alpha–C_\beta$ bond is nearly free. Substituents containing third-row heteroatoms adopt the eclipsed conformation ($\omega = 0°$), having a rotation barrier of about 2 kcal mol⁻¹. The symmetrically bridged structure **1b** is less stable than the classical structure **1a** by 40–60 kcal mol⁻¹ and 10–20 kcal mol⁻¹ in radicals bearing second- and third-row substituents, respectively. However, third-row heteroatoms form a very loose bridged complex except for M = Cl, the energy minimum being only ca. 0.3 kcal mol⁻¹ lower in energy relative to dissociation. The rotational motion about the $C_\alpha–C_\beta$ bond is always favored as against a shuttle motion of the substituent between the two carbon atoms. Shuttling is, however, likely only for the chlorine atom. There is no theoretical evidence of either static or dynamic asymmetric bridging from third-row substituents as proposed to explain the unexpectedly low values of the β-proton hyperfine coupling constant a_β observed in radicals bearing third-row substituents as well as the stereochemical control exerted by third-row elements in free-radical reactions. The values of a_β computed as a Boltzmann weighted average over the rotational states agree qualitatively with the experimental findings. Low values of a_β in the eclipsed conformation are due to a sizable reduction in spin density at H_β with increasing electronegativity of the heteroatom. The high population of the eclipsed conformation in radicals bearing third-row substituents in conjunction with the nonplanarity of the radical site and/or steric hindrance of the β-substituent could account for the observed stereochemical control.

Introduction

The structure of β-substituted ethyl radicals $R_nM–CH_2CH_2{}^{\bullet}$, with M an element from the second, third, fourth, and fifth rows of the periodic table, has been extensively investigated by ESR spectroscopy.[1,2] The preferred conformation of groups which are located in the β position to the radical center has been determined from the β-splitting by using the semiempirical relationship suggested by Heller and McConnell[3]

$$a_\beta(\theta) = A + B \cos^2 \theta \qquad (1)$$

where θ is the dihedral angle between the singly occupied $2p_z$ orbital (SOMO) at C_α and the $C_\beta–H_\beta$ bond (see **1a** in Figure 1), A is known to be small, about 3 G, and B is equal to about 48 G.[4] It was established from the β-splittings measured for a large number of substituents that the R_nM group adopts the staggered conformation ($\omega = 90°$, $\theta = 210°$, and $a_\beta = 39$ G) when M is a second-row element and the eclipsed conformation ($\omega = 0°$, $\theta = 120°$, and $a_\beta = 15$ G) when M is an element from higher rows.[5] However, the structure of the eclipsed conformation is a subject of controversy. The hypothesized structures are shown in Figure 1.

At first, Skell and co-workers[6] proposed a symmetric bridged structure **1b** (bridging hypothesis) for β-substituted alkyl radicals containing third- and higher-row elements to explain the unexpected retention of stereochemical configuration found in free-radical reactions involving β-chloro-, β-bromo-, and β-mercaptoalkyl radicals as intermediates. Kochi and Krusic[7] ruled out the symmetric bridged structure from the inequivalence of α- and

β-splittings in $R_nMCH_2CH_2{}^{\bullet}$ radicals containing third- and higher-row elements and suggested that the R_nM group moves toward the radical center and the β-hydrogens move away from it (**1c**, asymmetric bridging hypothesis) since the experimental β-splittings were found to be usually lower than the minimum value expected for the ethyl radical according to eq 1 ($a_\beta = A + B/4 = 15$ G). This hypothesis was supported by INDO calculations on the ethyl[7] and β-chloroethyl[8] radicals. Then, Skell and co-workers[9,10] recognized that the stereochemical control exerted by third- and higher-row elements in free-radical reactions could be explained with a dynamic asymmetric bridging **1d** as well. In this model the substituent oscillates rapidly between the two carbon atoms (shuttle motion). This hypothesis was supported by MRD–CI calculations on β-haloethyl radicals.[11] Furthermore, Ingold and co-workers[12] concluded on the basis of kinetic studies that the anchimeric assistance in the formation of β-substituted alkyl radicals by third- and higher-row elements is a general phenomenon associated with asymmetric bridging. On the other hand, Lloyd and Wood,[13] performing INDO calculations on ethyl, reached the conclusion that low values of a_β in the eclipsed conformation can arise from a large deviation from planarity at the radical site. This, in turn, suggested that a high barrier to rotation could account for the observed stereochemical control. On the contrary, Symons and co-workers[14] suggested that low values of a_β could be due to a reduction of the electron-releasing power from the $C_\beta H_\beta$ bond toward the radical center (electronic hypothesis). This hypothesis was supported by INDO calculations performed on β-silyl- and β-thiylethyl radicals in this laboratory.[15] Subsequently, Pedulli and co-workers[16] challenged the electronic

(1) Sullivan, P. D.; Menger, E. M. *Adv. Magn. Reson.* **1977**, *9*, 1.
(2) Neugebauer, F. A. In *Magnetic Properties of Free Radicals*; Fischer, H., Ed.; Landolt-Börnstein New Series, Vol. II/17b; Springer-Verlag: Berlin–Heidelberg, 1987.
(3) Heller, C.; McConnell, H. M. *J. Chem. Phys.* **1960**, *32*, 1535.
(4) Fisher, H. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, Chapter 19.
(5) Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6715 and references therein.
(6) Skell, P. S. *Chem. Soc. Spec. Publ.* **1965**, *19*, 131.
(7) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 846.

(8) Biddles, I.; Hudson, A. *Chem. Phys. Lett.* **1973**, *18*, 45.
(9) Skell, P. S.; Shea, J. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, Chapter 26.
(10) Skell, P. S.; Traynham, J. G. *Acc. Chem. Res.* **1984**, *17*, 160.
(11) Engels, B.; Peyerimhoff, S. D. *J. Mol. Struct. (THEOCHEM)* **1986**, *138*, 59.
(12) Jackson, R. A.; Ingold, K. U.; Griller, D.; Nazran, A. S. *J. Am. Chem. Soc.* **1985**, *107*, 208.
(13) Lloyd, R. V.; Wood, D. E. *J. Am. Chem. Soc.* **1975**, *97*, 5986.
(14) Lyons, A. R.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans. 2* **1972**, 622.
(15) Lunazzi, L.; Placucci, G.; Grossi, L.; Guerra, M. *J. Chem. Soc., Perkin Trans. 2* **1982**, 43.
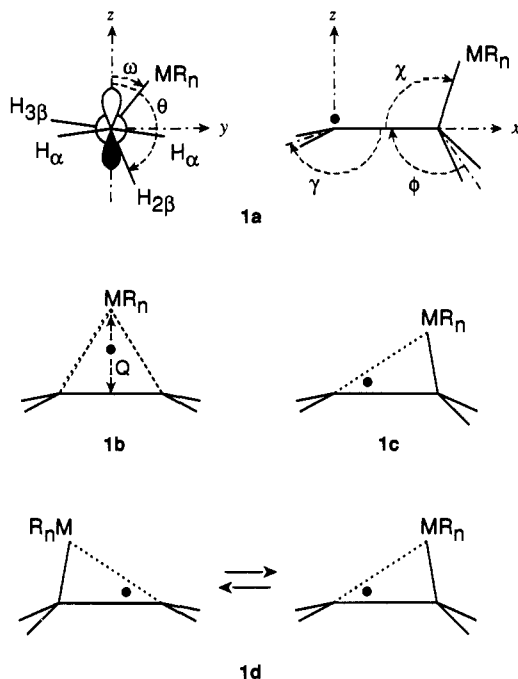
Figure 1. Hypothesized structures for β-substituted ethyl radicals: classical **1a**, bridged **1b**, asymmetric bridged **1c**, dynamic asymmetric bridged **1d** structures.

hypothesis since they found no correlation between the β-splittings and the group electronegativity of R_nM in β-substituted 1,1-diphenylethyl radicals where the R_nM group was supposed, against experimental evidence, to be locked in the eclipsed conformation in consequence of steric hindrance around the radical center. More recently, the importance of electronic interactions in determining the trends in β-splittings was supported by a theoretical study on the angular dependence of a_β.[17] In fact, it was found that eq 1 is valid only for the unsubstituted ethyl radical and that a third parameter, related to the electronegativity of the heteroatom M, must be added to correctly reproduce the theoretical a_β value at any rotational angle:

$$a_\beta(\theta,\omega) = A + B \cos^2\theta + C \cos\theta \cos\omega \qquad (2)$$

In order to establish the relative importance of geometric and electronic factors, the structural parameters of β-substituted ethyl radicals have been evaluated by means of ab initio calculations including electron correlation. The rotational barriers about the C_α–C_β bond as well as the energies and structural parameters of the symmetric bridged structure have also been determined to obtain qualitative information about the two competitive dynamical processes which can take place in these radicals, that is, rotation about the C_α–C_β bond and shuttling of the R_nM group between the two carbon atoms.

Methods and Computational Details

Ab initio unrestricted Hartree–Fock (UHF) calculations have been performed on β-substituted ethyl radicals $H_nM-CH_2-CH_2^\bullet$ ($H_nM = H_3C, H_2N, HO, F, H_3Si, H_2P, HS, Cl$) with the GAUSSIAN82 system of programs.[18] Structural parameters of the classical **1a** and bridged **1b** structures have been evaluated by means of the Fletcher–Powell algorithm,[19] employing a quite flexible basis set and taking into account electronic correlation. The basis set (DZP+BF) consists of Dunning's full double-zeta (DZ) contraction of Huzinaga's primitives: (4s)/[2s] for hydrogen, (9s5p)/[4s2p] for second- and (12s8p)/[6s4p] for third-row atoms supplemented with a polarization d-function (P) on heavy atoms

(16) Leardini, R.; Tundo, A.; Zanardi, G.; Pedulli, G. F. *J. Chem. Soc., Perkin Trans. 2* **1983**, 285; *Ibid.* **1985**, 1117.

(17) Guerra, M. *Chem. Phys. Lett.* **1987**, *139*, 463.

(18) Binkley, J. S.; Frisch, M. J.; Raghavechari, K.; De Frees, D. J.; Schlegel, H. B.; Whiteside, R. A.; Fluder, E.; Seeger, R.; Pople, J. A. *GAUSSIAN82*, Department of Chemistry, Carnegie-Mellon University: Pittsburgh, PA, 1983.

(19) Fletcher, R.; Powell, M. J. D. *Comput. J.* **1963**, *6*, 163.

($\alpha_C = 0.75$, $\alpha_N = 0.80$, $\alpha_O = 0.85$; $\alpha_F = 0.90$, $\alpha_{Si} = 0.3247$, $\alpha_P = 0.37$, $\alpha_S = 0.532$, $\alpha_{Cl} = 0.60$).[20] Since the bridged structure implies a partial bond between the carbon atoms and the heteroatom M, a bond function (BF) formed by an s-function has been located midway between C_α (C_β) and M. The exponent has been chosen as 1.3 and 1.2 for radicals containing second- and third-row atoms, respectively.[11] Electron correlation energy has been computed by using second-order Moller–Plesset perturbation theory (UMP2).[21] The UMP2 wave function correctly describes the doublet state, since its contamination by higher spin multiplets is quite small, being the $\langle S^2\rangle$ value on the order of 0.76 both for classical and bridged structures.

Theoretical hyperfine coupling constants have been estimated at the UHF/DZP+BF//UMP2/DZP+BF level from a statistical averaging of the computed $a_\beta(\theta,\omega)$ values over the thermally populated rotational states:[22]

$$\langle a_\beta(T)\rangle = \sum_m \langle\psi_m|a_\beta(\theta,\omega)|\psi_m\rangle e^{-E_m/KT}/\sum_m e^{-E_m/KT} \qquad (3)$$

The eigenfunctions ψ_m and eigenvalues E_m have been taken as solutions of the hamiltonian H for the hindered rotor

$$H = -h^2\partial^2\psi_m/8\pi^2 I\partial^2\omega + V(\omega) \qquad (4)$$

where h is the Planck constant and I is the reduced moment of inertia for rotation about the C_α–C_β bond.

According to the symmetry properties of $V(\omega)$ ($V(\omega) = V(-\omega) = V(\pi \pm \omega)$), the potential $V(\omega)$ has been expanded in periodic even functions of the angle ω

$$V(\omega) = \tfrac{1}{2}\sum_k V_{2k}(1 + \cos 2k\omega) \qquad k = 0, 1, ..., n \qquad (5)$$

The coefficients V_{2k} have been determined by means of a least-squares fitting of the ab initio rotation–energy curves displayed in Figure 2. An expansion up to the fifth term ($k = 4$) is sufficient to fit the energy curves with accuracy.

The hamiltonian H has been set up in the basis of the even ϕ^e and odd ϕ^o eigenfunctions of the free rotor

$$\phi_0^e = (2\pi)^{-1/2} \qquad (6)$$

$$\phi_\lambda^e = \pi^{-1/2}\cos 2\lambda\omega \qquad (7)$$

$$\phi_\lambda^o = \pi^{-1/2}\sin 2\lambda\omega \qquad (8)$$

According to the parity inversion properties of $V(\omega)$, the matrix H can be partitioned into the even H^e and odd H^o blocks whose elements are reported in ref 23. Thus, ψ_m can be separated in the even ψ_m^e and odd ψ_m^o expansions by diagonalizing the H^e and H^o matrices, respectively.

Using some simple trigonometric manipulations, the angular dependence of $a_\beta(\theta,\omega)$ (eq 2) can be rewritten in terms of only the angle ω as

$$a_\beta(\omega) = b_0 + b_2^e \cos 2\omega \pm b_2^s \sin 2\omega \qquad (9)$$

where

$$b_0 = A + B/2 - C/4 \qquad (10)$$

$$b_2^e = -(B + C)/4 \qquad (11)$$

$$b_2^s = 3^{1/2}(B - C)/4 \qquad (12)$$

and the plus and minus signs refer to $H_{2\beta}$ and $H_{3\beta}$, respectively (**1a** in Figure 1). However, higher terms in the Fourier series expansion of the periodic function a_β

$$a_\beta(\omega) = \sum_k b_k^e \cos 2k\omega \pm b_k^s \sin 2k\omega \qquad k = 0, 1, ... \qquad (13)$$

have to be considered to account for the change in the a_β value caused by the inversion motion about the radical site. An expansion up to the 6-fold terms ($k = 3$) is sufficient to accurately reproduce the computed a_β values by means of a least-squares procedure. Only expectation values of even-fold terms

$$\langle\psi_m^i|\cos 2k\omega|\psi_m^i\rangle = 2^{1/2}c_{m0}^i c_{mk}^i \delta_{ie} +$$
$$\sum_\lambda \sum_{\mu=1}^{... -1} c_{m\lambda}^i c_{m\lambda+k}^i + (\delta_{ie} - \tfrac{1}{2})\sum_{\lambda=1}^{k-1} c_{m\lambda}^i c_{mk-\lambda}^i \qquad i = e, o \quad (14)$$

contribute to $\langle a_\beta(T)\rangle$ since the matrix elements of odd-fold terms vanish due to symmetry. An expansion up to the 60th term ($\lambda_{max} = 60$) is sufficient to obtain complete convergence.

(20) Dunning, T. H.; Hay, J. P. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1976.

(21) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

(22) Fessenden, R. W. *J. Chim. Phys. Phys.-Chim. Biol.* **1964**, *61*, 1570.

(23) Alberti, A.; Guerra, M.; Martelli, G.; Bernardi, F.; Mangini, A.; Pedulli, G. F. *J. Am. Chem. Soc.* **1979**, *101*, 4627.

Table I. Optimized Structural Parameters[a] of β-Substituted Ethyl Radicals ($H_nM-CH_2-CH_2$·) at the UMP2/DZP+BF Level

H_nM	$r(C_\alpha-C_\beta)$	$r(C_\beta-M)$	$\angle H_\alpha C_\alpha H_\alpha$	$\angle H_\beta C_\beta H_\beta$	$r(C_\alpha-H_\alpha)$	$r(C_\beta-H_\beta)$	$\angle C_\alpha C_\beta M$	γ	ϕ	ω
H	1.500	1.103	117.5	108.4	1.087	1.097	111.5	191.0	128.2	0.0
H_3C^b	1.501	1.534	117.5	106.0	1.088	1.102	112.6	168.7	123.7	60.5
H_2N^c	1.505	1.473	117.6	106.0	1.089	1.101	115.6	167.3	124.5	59.5
HO^d	1.499	1.432	118.5	107.2	1.088	1.101	112.7	165.8	126.1	59.5
F	1.491	1.402	119.2	108.7	1.086	1.099	110.1	167.9	129.4	61.2
H_3Si^e	1.496	1.901	117.8	107.6	1.087	1.100	110.4	191.3	126.8	0.4
H_2P^f	1.489	1.896	117.4	107.5	1.088	1.098	114.0	196.3	127.8	0.2
HS^g	1.489	1.852	117.7	108.4	1.088	1.096	111.7	196.1	129.0	3.7
Cl	1.484	1.826	118.1	110.1	1.087	1.093	109.9	195.3	131.2	0.1

[a] Bond lengths are given in angstroms, dihedral and bond angles in degrees. The optimized parameters of the H_nM group are the following. [b] $\angle C_\beta CH = 110.8$, $r(CH) = 1.098$, $\angle HCH = 109.5$, $\tau(C_\alpha C_\beta CH) = 60.9$. [c] $\angle C_\beta NY = 122.8$, $r(NH) = 1.022$, $\angle HNH = 106.1$, $\tau(C_\alpha C_\beta NY) = 3.3$; Y is the projection of hydrogens on the $C_\alpha C_\beta M$ plane. [d] $\angle C_\beta OH = 106.6$, $r(OH) = 0.972$, $\tau(C_\alpha C_\beta OH) = 53.2$. [e] $\angle C_\beta SiH = 110.2$, $r(SiH) = 1.491$, $\angle HSiH = 109.4$, $\tau(C_\alpha C_\beta SiH) = 59.8$. [f] $\angle C_\beta PH = 99.7$, $r(PH) = 1.426$, $\angle HPH = 93.7$, $\tau(C_\alpha C_\beta PY) = 0.4$. [g] $\angle C_\beta SH = 95.2$, $r(SH) = 1.343$, $\tau(C_\alpha C_\beta SH) = 61.6$.

Table II. Optimized Structural Parameters[a] of β-Substituted Ethyl Radicals ($H_nM-CH_2-CH_2$·) in the Eclipsed Conformation I ($\omega = 0°$) at the UMP2/DZP+BF Level

H_nM^b	$r(C_\alpha-C_\beta)$	$r(C_\beta-M)$	$\angle H_\alpha C_\alpha H_\alpha$	$\angle H_\beta C_\beta H_\beta$	$r(C_\alpha-H_\alpha)$	$r(C_\beta-H_\beta)$	$\angle C_\alpha C_\beta M$	γ	ϕ
H_3C^c	1.501	1.543	117.2	107.2	1.088	1.099	112.3	193.2	124.3
H_2N^d	1.503	1.486	117.2	107.4	1.089	1.097	114.3	194.9	126.0
HO^e	1.499	1.445	117.7	108.4	1.088	1.097	112.5	192.9	126.4
F	1.492	1.415	117.9	109.8	1.087	1.095	110.3	192.8	129.6

[a] Bond lengths are given in angstroms, dihedral and bond angles in degrees. [b] For M from the third row, see Table I. The optimized parameters of the H_nM group are the following. [c] $\angle C_\beta CH = 110.7$, $r(CH) = 1.098$, $\angle HCH = 109.5$, $\tau(C_A C_\beta CH) = 59.8$. [d] $\angle C_\beta NY = 122.2$, $r(NH) = 1.023$, $\angle HNH = 105.8$, $\tau(C_\alpha C_\beta NY) = 0.0$; Y is the projection of hydrogens on the $C_\alpha C_\beta M$ plane. [e] $\angle C_\beta OH = 106.8$, $r(OH) = 0.973$, $\tau(C_\alpha C_\beta OH) = 53.3$.

Table III. Optimized Structural Parameters[a] of β-Substituted Ethyl Radicals ($H_nM-CH_2-CH_2$·) in the Staggered Conformation IV ($\omega = 90°$) at the UMP2/DZP+BF Level

H_nM	$r(C_\alpha-C_\beta)$	$r(C_\beta-M)$	$\angle H_\alpha C_\alpha H_\alpha$	$\angle H_\beta C_\beta H_\beta$	$r(C_\alpha-H_\alpha)$	$r(C_\beta-H_\beta)$	$\angle C_\alpha C_\beta M$	γ	ϕ
H	1.500	1.097	117.9	106.7	1.086	1.101	111.2	179.2	127.6
H_3C^b	1.502	1.532	117.9	105.5	1.088	1.103	112.7	179.9	123.6
H_2N^c	1.506	1.470	118.2	105.4	1.088	1.101	116.1	179.3	124.1
HO^d	1.500	1.430	118.8	106.5	1.087	1.102	113.1	171.0	125.8
F	1.492	1.400	120.0	108.3	1.085	1.100	109.9	179.4	129.2
H_3Si^e	1.506	1.887	117.2	104.8	1.088	1.104	113.7	180.0	124.2
H_2P^f	1.501	1.870	118.1	104.9	1.088	1.103	116.6	179.6	125.0
HS^g	1.500	1.825	118.8	105.9	1.087	1.101	114.0	176.0	126.3
Cl	1.496	1.793	119.6	107.7	1.086	1.099	111.4	179.7	128.6

[a] Bond lengths are given in angstroms, dihedral and bond angles in degrees. The optimized parameters of the H_nM group are the following. [b] $\angle C_\beta CH = 110.8$, $r(CH) = 1.098$, $\angle HCH = 109.5$, $\tau(C_\alpha C_\beta CH) = 60.1$. [c] $\angle C_\beta NY = 123.4$, $r(NH) = 1.022$, $\angle HNH = 106.4$, $\tau(C_\alpha C_\beta NY) = 0.0$; Y is the projection of hydrogens on the $C_\alpha C_\beta M$ plane. [d] $\angle C_\beta OH = 106.9$, $r(OH) = 0.972$, $\tau(C_\alpha C_\beta OH) = 62.3$. [e] $\angle C_\beta SiH = 110.4$, $r(SiH) = 1.491$, $\angle HSiH = 109.5$, $\tau(C_\alpha C_\beta SiH) = 60.0$. [f] $\angle C_B PY = 99.9$, $r(PH) = 1.426$, $HPH = 93.8$, $\tau(C_\alpha C_\beta PY) = 0.0$. [g] $\angle C_\beta SH = 95.5$, $r(SH) = 1.343$, $\tau(C_\alpha C_\beta SH) = 66.0$.

INDO calculations have also been carried out at the ab initio optimized structures to compute β-splittings also at this level of theory. The parametrization originally developed by Pople and co-workers[24] has been employed for second-row elements, and that proposed by Benson and Hudson[25] has been utilized for third-row elements.

The calculations have been performed on the FPS array processor attached to the VAX 11/780 computer of the Theoretical Chemistry Group in Bologna.

Results and Discussion

Asymmetric Structure. The structural parameters for the absolute energy minima are listed in Table I. Three variables (see **1a** in Figure 1) deserve to be mainly considered in the discussion: (i) the $C_\alpha C_\beta M$ bond angle, χ, which gives the measure of the degree of bridging; (ii) the dihedral angle ω which identifies the rotamers about the $C_\alpha-C_\beta$ bond; (iii) the angle γ which is related to the deviation from planarity at the radical site.

The most important aspect of the theoretical results is the small deviation of the $C_\alpha C_\beta M$ bond angle from the tetrahedral value found in all radicals. Consequently, the asymmetric bridging hypothesis should be ruled out since the arrangement of atoms around C_β is approximately tetrahedral. In addition, Table I shows that the change of M along a column of the periodic table has no significant effect on the optimum value of the $C_\alpha C_\beta M$ bond

angle, the major influence being related to the change of M along each row. On the contrary, the conformational preferences display different trends as observed experimentally. In particular, the substituent adopts a gauche conformation ($\omega = 60°$) with respect to the SOMO for M from the second row and the eclipsed conformation ($\omega = 0°$) for M from the third row. In both rotamers the radical center is slightly pyramidal with an out-of-plane angle ($|180° - \gamma|$) of about 10–15° as compared with 35° for the sp³ hybridization. The same result was previously obtained with UHF calculations on β-substituted ethyl radicals.[26-30] By contrast it was suggested on the basis of MRD–CI calculations on β-haloethyl radicals[11] that correlation effects should favor a planar radical site. However, the eclipsed conformation was found slightly pyramidal also at the MRD–CI level of theory in a more complete study on the β-fluoroethyl radical.[31] The SOMO is located in a syn position with respect to the substituent in the gauche conformation and in an anti position in the eclipsed conformation. Thus, it is extremely important to get knowledge of the changes in structural parameters as a function of the rotation angle ω. Geometries have been optimized at 15° intervals, and structural

(24) Pople, J. A.; Beveridge, D. L. *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970.
(25) Benson, G.; Hudson, A. *Theor. Chim. Acta* **1971**, *23*, 259.

(26) Schlegel, H. B. *J. Phys. Chem.* **1982**, *86*, 4878.
(27) Sosa, C.; Schlegel, H. B. *J. Am. Chem. Soc.* **1987**, *109*, 4193.
(28) Gonzalez, C.; Sosa, C.; Schlegel, H. B. *J. Phys. Chem.* **1989**, *93*, 2435.
(29) Schlegel, H. B.; Sosa, C. *J. Phys. Chem.* **1984**, *88*, 1141.
(30) Hopkinson, A. C.; Lien, M. H.; Csizmadia, I. G. *Chem. Phys. Lett.* **1980**, *71*, 557.
(31) Engels, B.; Peyerimhoff, S. D. *J. Phys. Chem.* **1989**, *93*, 4462.

Table IV. Total Energies (au) for the Ground State of β-Substituted Ethyl Radicals ($H_nM-CH_2-CH_2{}^{\bullet}$) at the UMP2/DZP+BF Level along with Relative Energies (kcal mol^{-1}) for Selected Structures

H_nM	ground state	eclipsed	gauche	staggered	bridged	dissociation
H	-78.865 69	0.0	0.0	0.15		
H_3C	-118.011 36	0.26	0.0	0.14	a	30.7[b]
H_2N	-134.035 73	0.05	0.0	0.25	53.0[c]	27.8[d]
						61.1[c]
HO	-153.887 25	0.76	0.0	0.83	61.6[c]	35.4[d,e]
						134.4[c]
F	-177.888 52	0.19	0.0	0.18	36.0[c]	51.4[c~e]
H_3Si	-369.006 46	0.0	1.80	2.53	22.9[b]	23.1[b]
H_2P	-420.246 40	0.0	1.68	2.32	8.4[d]	8.6[d]
					53.0[c]	63.9[c]
HS	-476.478 63	0.0	1.66	1.75	12.0[d,e]	12.6[d,e]
						109.4[c]
Cl	-537.878 39	0.0	1.44	2.01	13.3[c]	20.6[c~e]
					20.3[d,e]	

[a] Minimum not found. [b] $^2A'$ state. [c] $^2A_1$ state. [d] $^2B_2$ state. [e] $^2B_1$ state.

Scheme I
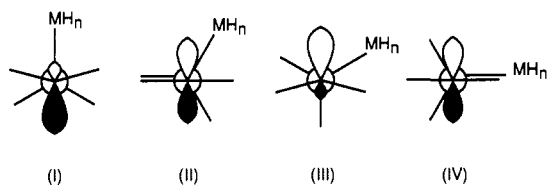
parameters have been interpolated at 5° intervals. The resulting rotation-energy curves are displayed in Figure 2. The structural parameters of the eclipsed and staggered ($\omega = 90°$) rotamers are listed in Tables II and III, respectively, as representative examples. The relative energies of the eclipsed, gauche, and staggered rotamers are reported in Table IV.

The most significant change in structural parameters in proceeding from the eclipsed to staggered conformation is found to be the large variation in the value of the angle γ. The radical site becomes nearly planar in the staggered rotamer, and an inversion about the radical center occurs during the rotation about the $C_\alpha-C_\beta$ bond as depicted in Scheme I.

The arrangement of atoms around the radical center changes during the internal rotation so as to minimize the bonding electron-pair repulsion. As a consequence, the anti I and gauche III rotamers are candidates for local energy minima on the rotation-energy surface, whereas the staggered rotamer IV is expected to be a transition state. This behavior has been found in radicals bearing second-row substituents. In fact, a local energy minimum exists near the eclipsed conformation also for M from the second row, except for M = O. The local minima occur at ω = 0.0, 0.5, and 1.0°, and the gauche/eclipsed energy differences are 0.26, 0.05, and 0.19 kcal mol^{-1} for M = C, N, and F, respectively. The rotation about the $C_\alpha-C_\beta$ bond is nearly free since the energy barrier which separates the gauche III and anti I rotamers is less than 0.4 kcal mol^{-1}. The present results are in accord with the conformational preferences found for the β-fluoroethyl,[26] β-hydroxyethyl,[27] and propyl[28] radicals at the UHF/3-21G level, but the relative gauche/eclipsed energy stability is reversed in propyl, the eclipsed rotamer I being predicted to be more stable than the gauche rotamer III by 0.05 kcal mol^{-1} at the UHF/3-21G level. This reverse trend in energy stability affects both the magnitude and the temperature dependence of the rotationally averaged β-splitting (vide infra). For radicals containing third-row heteroatoms, the rotation barrier arises up to about 2 kcal mol^{-1}. The staggered rotamer IV is found to be the transition state for the interconversion between the anti rotamers I, except in the β-thiylethyl radical. In this case a shallow energy minimum occurs in the staggered conformation. In contrast with UHF/4-31G[30] but in concordance with UHF/6-31G*[29] calculations on the β-chloroethyl radical, no energy minimum exists near the gauche conformation for M from the third row. The unexpected shape of the rotation-energy curves displayed from radicals containing third-row elements can be explained with the largely stabilizing interaction occurring between the SOMO and σ^*(C-M) MO. In
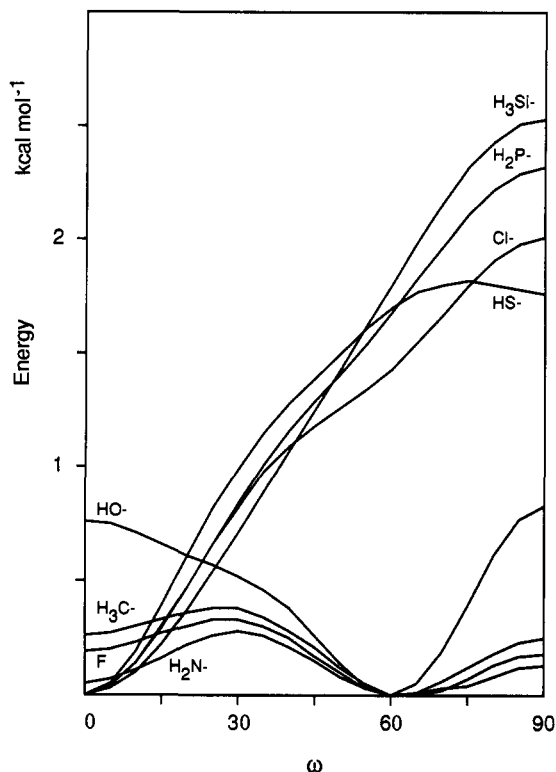

Figure 2. Potential energy as a function of the torsion angle ω for β-substituted ethyl radicals at the UMP2/DZP+BF level.

fact, σ^*(C-M) MOs lie low in energy only for M from third and higher rows as observed experimentally by means of the electron transmission spectroscopy (ETS).[32] MXSα calculations on *tert*-butyl halides $(CH_3)_3CM$,[33] which reproduce very well the features appearing in the ET spectra, confirm the large increase in the electron affinity of the MO mainly localized at the carbon–halogen bond on going from second- to higher-row atoms, the computed electron affinities being -7.30, -1.50, -0.95, and 0.05 eV for M = F, Cl, Br, and I, respectively. The SOMO–σ^*(C-M) interaction stabilizes the eclipsed conformation, and its strength decreases following approximately a $\cos^2 \omega$ law. This explains the lack of an energy minimum near the gauche conformation. The changes in structural parameters are also consistent with the nature of this interaction. Tables I–III show that the C–M bond lengths increase, owing to the antibonding contribution, much more for M from the third (by about 0.03 Å) than from the second row (by about 0.01 Å) in proceeding from the

(32) Modelli, A.; Distefano, G.; Guerra, M.; Jones, D.; Rossini, S. *Chem. Phys.* **1988**, *125*, 389.

(33) Modelli, A.; Scagnolari, F.; Distefano, G.; Guerra, M.; Jones, D. *Chem. Phys.* **1990**, *145*, 89.

Table V. Best-Fit Coefficients of the Expansion of the Rotation Potentials $V(\omega)$ and of the β-Splittings $a_\beta(\omega)$ Computed at the UMP2/DZP+BF and UHF/DZP+BF Level, Respectively

H_nM	V_0	V_2	V_4	V_6	V_8	a_0	a_2^c	a_2^s	a_4^c	a_4^s	a_6^c
H	0.150	−0.150	0.0	0.0	0.0	24.44	−11.02	−0.31	−0.14	19.04	−0.57
H_3C	0.120	0.339	−0.008	−0.205	0.018	23.05	−10.76	−0.24	−0.18	16.84	−0.49
H_2N	0.238	0.102	−0.029	−0.255	0.011	21.49	−12.59	−0.21	−0.22	14.29	−0.83
HO	0.114	0.305	0.534	−0.371	0.180	21.05	−13.42	−0.26	−0.20	13.36	−0.66
F	0.149	0.229	0.015	−0.222	0.021	20.49	−14.67	−0.18	−0.06	11.96	−0.81
H_3Si	2.522	−2.418	0.019	−0.116	−0.008	25.37	−8.77	−0.29	−0.13	20.64	−0.32
H_2P	2.455	−2.104	−0.127	−0.214	−0.007	23.43	−9.68	−0.38	−0.24	17.77	−0.62
HS	2.393	−1.647	−0.505	−0.128	−0.112	22.41	−11.25	0.24	0.08	14.85	−1.01
Cl	2.175	−1.741	−0.175	−0.265	0.011	21.90	−12.64	−0.21	−0.19	13.78	−0.67

staggered rotamer IV, where the $2p_z$–σ^* interaction is absent, to the eclipsed rotamer I, where this interaction reaches its maximum. At the same time, the $C_\alpha C_\beta M$ bond angles and the C_α–C_β bond lengths decrease by about 2° and 0.01 Å, respectively, for M from the third row, whereas they do not appreciably change for M from the second row. This behavior confirms that the stabilizing one-electron interaction is mainly operative in radicals containing third-row heteroatoms.

The present theoretical calculations predict β-substituents containing third-row heteroatoms to be constrained to the eclipsed conformation by a sizable barrier, in full agreement with the conformational preference determined from experimental β-splittings.[5] On the other hand, the shape of the computed rotation–energy curves for radicals bearing second-row substituents is partially consistent with experimental evidence. In fact, the calculations indicate that the rotation about the C_α–C_β bond is quasi-free as observed experimentally, while the staggered conformation IV is found not to be an energy minimum on the rotation–energy surface as established experimentally but rather the transition state between two equivalent energy-minimum gauche conformations. The present results also indicate that the low β-splittings observed in radicals constrained to the eclipsed conformation cannot be interpreted as due to a tilt of the substituent toward the radical center. In order to elucidate these points, β-splittings have been evaluated theoretically.

β-Proton Hyperfine Coupling Constants. The theoretical hyperfine coupling constant should be computed by employing a wave function of high quality close to the nucleus, depending only on the spin density at that point, and its value should be averaged over the vibrational modes. Averaging over all of the normal modes is very expensive in terms of computer time by using the present basis set. Moreover, only a semiaccurate estimate of a_β was obtained for the ethyl radical by including in the basis set many more functions than those used in the present calculations.[34] Thus, only qualitative information has been obtained by averaging $a_\beta(\omega)$ over the rotational motion. This approximation is justifiable either when the frequency of the rotational motion is much lower than those relative to other internal motions, or if the value of a_β varies linearly along low-frequency local modes which can couple with the rotational mode. Lacking experimental information on the vibrational frequencies of β-substituted ethyl radicals, preliminary calculations have been carried out to verify the second condition. The calculations show that this condition is not satisfied only in the case of rotation about the C–M bond. However, the variation of a_β with rotation about the C_α–C_β bond is much larger than that produced by rotation about the C–M bond; thus the approximation employed here is expected not to affect the qualitative conclusions. The expansion coefficients of the potentials $V(\omega)$ and of the β-splittings $a_\beta(\omega)$ employed in the calculations are collected in Table V. The theoretical values of $\langle a_\beta \rangle$ computed at lowest measured temperature along with the temperature coefficients da_β/dT are reported in Table VI. For the ethyl radical, the computed $\langle a_\beta \rangle$ value is independent of temperature and can be considered as the free-rotation limit ($a_\beta = A + B/2$). As can be seen from Table VI, the theoretical values

Table VI. Rotationally Averaged β-Splittings, $\langle a_\beta \rangle$, and Temperature Coefficients, $d\langle a_\beta \rangle/dT^a$ (Experimental Values Are Reported in Parentheses[b])

H_nM	$\langle a_\beta \rangle$ (G)		$d\langle a_\beta \rangle/dT$ (mG/K)		T (K)	$I \times 10^{40}$ (g cm^2)
H	24.43	(26.87)	0	(0)	153	1.882
	15.18[c]					
H_3C	25.58	(30.33)	−13	(−28)	163	2.809
	22.24[d]		5			
	25.34[e]		−12			
H_2N	21.75	(25.6)[f]			298	2.815
HO	22.90	(27.8)	−6	(−5)	280	2.839
F	23.06	(27.92)	−15	(−30)	151	2.815
H_3Si	17.60	(17.1)[g]	8	(13)[g]	128	2.893
H_2P	15.83	(16.1)[g]	13	(22)[g]	207	2.932
HS	12.88	(13.5)[g]	14	(25)[g]	149	2.934
Cl	11.13	(10.20)	17	(20)	148	2.931

[a] Computed by using the expansion coefficients of $V(\omega)$ and of $a_\beta(\omega)$ collected in Table V. [b] Taken from ref 1. [c] Using $V_0 = -V_2 = 2.5$ kcal mol^{-1}; $V_4 = V_6 = V_8 = 0$. [d] Putting V_0 and V_2 equal to 0.29 and −0.10 kcal mol^{-1}, respectively. [e] Using $V_2 = 0.3$ kcal mol^{-1}; $V_0 = V_4 = V_6 = V_8 = 0$. [f] Taken from ref 35. [g] Experimental value for the radical with the methylated heteroatom.

agree fairly well with the experimental trends. In particular, for M from the second row the temperature coefficients are negative and the $\langle a_\beta \rangle$ values are close to the free-rotation limit in agreement with experiment, being independent of the electronic structure of the heteroatom. However, the $\langle a_\beta \rangle$ values are systematically too low by about 2 G. This suggests that the gauche/eclipsed energy differences should be slightly underestimated at the UMP2/DZP+BF level of theory. Explorative calculations have shown that the $\langle a_\beta \rangle$ values increase and closely reproduce the experimental trends when the gauche/eclipsed energy difference is increased by only 0.3 kcal mol^{-1} by adding a 2-fold V_2 contribution to the potential, the energy curves maintaining the shape displayed in Figure 2. In the case of the propyl radical, the use of a modified potential that simulates the reverse trend in the gauche/eclipsed stability found at the UHF/3-21G level of theory results in a sizable lowering of $\langle a_\beta \rangle$, breaking thus the correlation between theory and experiment. More interestingly, the temperature coefficient changes its sign, becoming positive in contrast with experiment. Thus, UHF/3-21G calculations wrongly predict the eclipsed conformation to be the most stable in propyl. On the other hand, the use of a potential having a minimum in the staggered conformation, as suggested experimentally, does not appreciably change the value of $\langle a_\beta \rangle$ computed with the UMP2/DZ+BF rotation potential. Thus, the theoretical results indicate that the trends in the experimental β-splittings of radicals bearing second-row substituents are equally consistent with an absolute energy minimum in the gauche conformation III. For M from the third row, the computed $\langle a_\beta \rangle$ values are low and vary with the electronegativity of the heteroatom M. Increasing the eclipsed/staggered energy difference by 0.3 kcal mol^{-1} has remarkably little effect on the $\langle a_\beta \rangle$ values. This different behavior is due to a higher barrier to rotation and to the large influence exerted on the β-splitting by the heteroatom in the eclipsed conformation.[17] Indeed, Figure 3 shows that the mean values of the β-splittings ($\bar{a}_\beta = (a_{2\beta} + a_{3\beta})/2$) differ sizably in the eclipsed conformation. The differences decrease as the value of the dihedral

(34) Feller, D.; Davidson, E. R. *Theor. Chim. Acta* **1985**, *68*, 57.
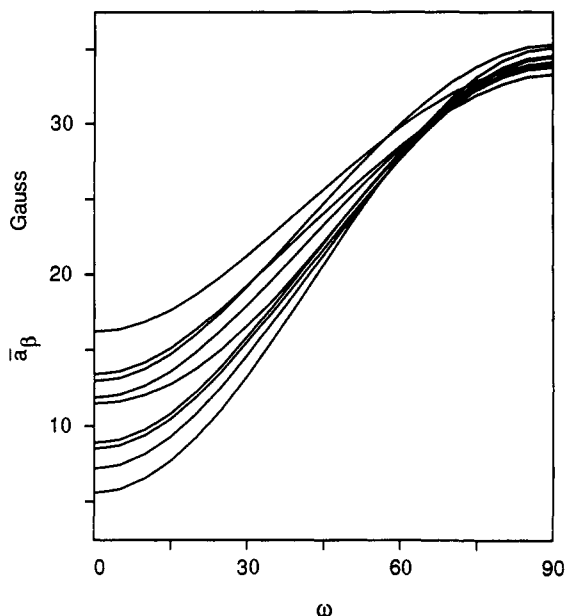(35) Dewing, J.; Longster, G. F.; Myatt, J.; Todd, P. F. *Chem. Commun.* **1965**, 391.

Figure 3. Dependence of the mean values of the β-splittings ($\bar{a}_\beta$) on the rotation angle ω in β-substituted ethyl radicals at the UHF/DZP+BF level; the ordering of ($\bar{a}_\beta$) at $\omega = 0°$ is that displayed in Figure 4a.
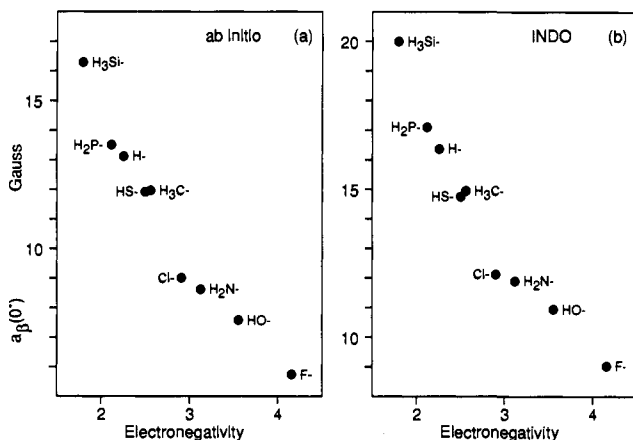

Figure 4. Plot of a_β in the eclipsed conformation versus the Allred–Rochow electronegativity computed (a) at the UHF/DZP+BF level and (b) with the INDO method.

angle ω increases and become negligible in the staggered conformation. Figure 4a shows also that the a_β value in the eclipsed conformation strictly depends on the electronegativity[36] of the heteroatom.

As regards the temperature coefficients, they are positive as observed experimentally, the agreement with experiment being fairly good considering the approximations employed in the calculation. More interestingly, Table VI shows that the computed $\langle a_\beta \rangle$ value for M = Si (17.60 G) is higher than that computed for the ethyl radical (15.18 G) when constrained to the eclipsed conformation by a rotation barrier of the same magnitude. This finding agrees with the experimental results[37] which show that the β-splittings of β-silylethyl radicals are higher than the value expected according to eq 1. By contrast, this apparently anomalous result was again interpreted by Ingold and co-workers[37] as due to geometric rather than to electronic factors, by admitting a tilt of the substituent in the opposite side away from the radical center. It should be remarked that the same group[12] hypothesized an asymmetric bridged assistance from silicon to explain the preferential formation of β-silylalkyl radicals in hydrogen-abstraction reactions. Other contradictory interpretations were provided by

Kochi and co-workers[38] to support the asymmetric bridged hypothesis. They invoked an asymmetric bridged structure to explain the low values of the β-splitting observed in β-oxygen alkyl radicals when the β-substituent is constrained to the eclipsed conformation because of steric hindrance as in $CH_3O–CH_2–C(CH_3)_2$·. This is in contrast with the hypothesis proposed by the same group[39] that the strong interaction occurring between the SOMO ($2p_z$) and the vacant d and/or σ^* orbitals is the driving force to bridging. In fact, this stabilizing one-electron interaction was supposed to be very weak in radicals bearing second-row substituents for explaining their preference for the staggered conformation. On the contrary, low β-splittings in hindered β-oxygen alkyl radicals are mainly a result of electronic effects being related to the high electronegativity of the oxygen atom as clearly shown in Figure 4a.

Theoretical $\bar{a}_\beta$ values have been also computed by means of the INDO method, since this method was employed in previous studies on β-substituted ethyl radicals and is still widely used for assigning hyperfine coupling constants with considerable success, being a quick, efficient, and inexpensive method. As Figure 4 shows, the values of $\bar{a}_\beta(0°)$ computed with the INDO and ab initio methods follow the same trends against the electronegativity of the heteroatom, the values computed with the INDO method being systematically higher by about 3 G. Thus, both methods are expected to provide the same qualitative information on these radicals. By contrast, previous INDO calculations performed on ethyl[7] and β-chloroethyl[8] predicted a tilt of substituents containing third-row elements of about 30° toward the radical center in the eclipsed conformation. This discrepancy does not depend on the reliability of the INDO method but arises because of an incorrect approach to the problem under investigation. In fact, information about the structure of β-substituted ethyl radicals was obtained either by computing a_β for the classical and distorted ethyl radical or by optimizing the CCCl bond angle. In the former case, incorrect information has been obtained since the electronic influence of the substituent on the value of a_β was not taken into account. In fact, the substituent was replaced with an hydrogen atom lacking at that time INDO parameters for third-row elements. The present calculations indicate that model systems employing second-row heteroatoms would have provided more correct information showing also the trends in the value of a_β with the electronic structure of the substituent. In the latter case, the optimum CCCl bond angle was determined by utilizing a semiempirical method which was parametrized so as to provide reasonable hyperfine coupling constants rather than to predict structural parameters.[24]

Both ab initio and INDO calculations performed on β-chloroethyl in the eclipsed conformation assuming a planar radical site show how the lowering of the a_β value upon pyramidalization (9.5% and 12.5%, respectively) is much less than that necessary (about 50%)[13] to reproduce the experimental β-splitting. Hence, the dependence of the transmission of spin density to the β-protons on the electronegativity of the heteroatom M is the dominant factor in determining the trends in the a_β values. The lack of correlation between the β-splittings and the group electronegativity of substituents containing second-row heteroatoms in substituted 1,1-diphenylethyl radicals[16] can be attributed to an incorrect use of the experimental data. The ESR spectra were recorded at room temperature, and the temperature dependence of the β-splittings was not examined at all; as a consequence, there was no experimental evidence that the substituents were locked in the eclipsed conformation. In particular, the β-splittings of radicals bearing second-row substituents could be higher than expected because they are affected to a larger extent by librational or rotational modes since the unhindered radicals adopt the gauche conformation. The temperature dependence shown by hindered β-halo *tert*-butyl radicals[13] could supports this hypothesis. At 214 K the β-splitting in β-fluoro-*tert*-butyl (10.4 G) is much higher than that in β-chloro-*tert*-butyl (6.3 G). However, the β-splitting is nearly

(36) Allred, A. L.; Rochow, E. G. *J. Inorg. Nucl. Chem.* **1958**, *5*, 264.
(37) Scaiano, J. C.; Ingold, K. U. *J. Phys. Chem.* **1975**, *80*, 275.

(38) Cheng, K. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 1383.
(39) Kawamura, T.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 648.

Properties of β-Substituted Ethyl Radicals

J. Am. Chem. Soc., Vol. 114, No. 6, 1992 2083

independent of temperature in β-chloro-*tert*-butyl, whereas it decreases to 5.5 G at 77 K in β-fluoro-*tert*-butyl. Alternatively, substituents containing second-row elements could deviate from the eclipsed conformation. Significant differences in the value of the dihedral angle ω at the absolute energy minimum could cause a breakdown in the correlation between the β-splittings and the group electronegativity of β-substituents. It should be remarked that a departure of about 5° from the eclipsed conformation was roughly estimated from the observed selective line broadening by the same authors.[16] The trends in the β-splittings of partially hindered β-oxygen and β-sulfur *tert*-butyl radicals $CY_3M-CH_2-C(CH_3)_2$· (M = O, S; Y = H, F) could support this second hypothesis.[38] In fact, the β-splittings of β-sulfur alkyl radicals indicate that the β-substituent is constrained, as expected, in the eclipsed conformation, the β-splitting being 11.20 G at 189 K and 11.12 G at 177 K for Y = H, and F, respectively. By contrast, the β-splittings of β-oxygen alkyl radicals show that the substituent departs from the eclipsed conformation by replacing the bulky CF_3 group with the smaller CH_3 group. At 172 K, the β-splitting for Y = F is 10.02 G as expected for a radical constrained to the eclipsed conformation, whereas for Y = H the β-splitting is much higher being 18.4 G. This value lies intermediate between that expected for a radical locked in the eclipsed conformation ($\approx$10 G) and for an unhindered radical having an energy minimum in the gauche conformation (>27 G). In order to obtain qualitative information on these hypotheses, theoretical β-splittings have been evaluated as a function of the rotation-barrier height ΔV by using selected shapes of the rotation-potential well. In the calculations the expansion coefficients of $a_\beta(\omega)$ for β-hydroxy- and β-thiylethyl radicals have been utilized since the β-splittings in β-oxygen 1,1-diphenylethyl radicals are surprisingly higher than in corresponding β-sulfur radicals. For example, the β-splitting was found to be 9.58 G in $CH_3-CH_2O-CH_2-CPh_2$· and 7.57 G in $CH_3-CH_2S-CH_2-CPh_2$·. Furthermore, this trend is in evident contrast with that observed in hindered β-substituted 1,1-di-*tert*-butylethyl radicals.[5] In this case the β-splitting in the oxygen derivative (7.2 G) is independent of temperature, suggesting that the substituent is firmly locked in the eclipsed conformation, and is lower than in the sulfur derivative (10.4 G) in full accord with the electronegativity trend. In order to discriminate between these hypotheses, two model potentials have been investigated as a function of the rotation-barrier height ΔV: (i) a potential well having a single minimum in the eclipsed conformation obtained by truncating the potential expansion at the 2-fold V_2 term (model I); (ii) potential wells having a double minimum about the eclipsed conformation obtained by adding V_2 and V_4 contributions to the potential computed for β-hydroxyethyl at the UMP2/DZP+BF level. The V_2 contribution determines the barrier height, whereas the V_4 contribution causes a shift of the energy minimum away from the eclipsed conformation (model II). It is evident from Table VII that the $\langle a_\beta \rangle$ values strongly depend both on the rotation-barrier height ΔV and on the shape of the rotation-potential well. In particular, different populations of torsional levels in the eclipsed conformation cannot cause breaking in the correlation between the β-splittings and the group electronegativity of β-substituents since changes in the barrier height ΔV of the single minimum potential (model I) produce too small variations in the β-splitting to reverse the expected trends as observed experimentally in 1,1-diphenylethyl radicals. However, the moderate dependence of the $\langle a_\beta \rangle$ values on the rotation-barrier height accounts for the fairly good correlation found between the β-splittings of radicals bearing third- and higher-row substituents and the group electronegativity of β-substituents. On the other hand, the comparison of the theoretical $\langle a_\beta \rangle$ values of β-thiylethyl (model I) with those of β-hydroxyethyl computed with a potential well having the absolute minimum at ω equal to about 15° (model IIB) and 25° (model IIC) indicates that the high values of the β-splitting observed in radicals bearing second-row substituents as well as the lack of correlation between the β-splittings and the group electronegativity of β-substituents are due to a different departure of β-substituents from the eclipsed geometry. Table VII shows also how information

Table VII. Room-Temperature Rotationally Averaged β-Splittings, $\langle a_\beta(298\ K) \rangle$, of the β-Hydroxy- and β-Thiylethyl Radicals Computed at the UHF/DZP+BF Level as a Function of the Rotation-Barrier Height ΔV (kcal mol^{-1}) for Selected Shapes of the Rotation-Potential Well

| | model I[a] | | model II[b] | | |
| | | | | HO– | |
ΔV	HS–	HO–	A	B	C
2.0	15.45	12.61	14.39	16.37	17.02
3.0	14.04	10.83	12.21	14.24	15.07
4.0	13.22	9.90	10.73	12.96	13.93
5.0	12.93	9.37	9.88	12.13	13.17

[a] $V_2 = -V_0$, $V_4 = V_8 = 0$; minimum at $\omega = 0°$, $V(0°) = 0.0$ kcal mol^{-1}. [b] Potentials obtained by adding V_2 and V_4 contributions with a fixed ratio to the coefficients reported in Table V for β-hydroxyethyl. The V_0 term has been changed appropriately: (A) $V_4 = 0$, minimum at $\omega = 0°$; (B) $V_4 = -V_2/4$, minimum at $\omega \approx 15°$, $V(0°) = 0.1$ kcal mol^{-1}; (C) $V_4 = -V_2/3$, minimum at $\omega \approx 25°$, $V(0°) = 0.25$ kcal mol^{-1}.

on the structure of β-substituted ethyl radicals might be obtained from experimental a_β values by examining conformationally rigid radicals in which the β-substituent is firmly locked in the eclipsed conformation. Thus, the temperature dependence of β-splittings should be accurately studied to avoid misleading comparisons of β-splittings between different radicals.

Bridged Structure. Calculations have also been performed on the symmetric bridged structure **1b** for estimating the lower energy limit for the shuttle motion of the substituent between the C_α and C_β atoms. In fact, an energy mapping for this process is very expensive in terms of computer time. The $^2A_1$ ($^2A'$ for H_3M bridged groups) and $^2B_2$ states have been optimized since these states can be involved as intermediates or transition states along the shuttling coordinate. The shuttle motion is possible if the dissociation path which leads from the bridged structure to ethylene plus H_nM·

$$\begin{array}{c} MH_n \\ /\overset{\bullet}{}\backslash \\ CH_2-CH_2 \end{array} \longrightarrow C_2H_4 + H_nM^\bullet \qquad (15)$$
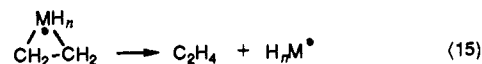
is energetically disfavored because either the bridged structure is much more stable than the separate monomers or a high barrier prevents dissociation. Hence, energy has also been computed as a function of the internal Q coordinate which describes the dissociation path (see Figure 1b). The resulting energy profiles are shown in Figure 5. The zero of energy is taken as the energy of the asymmetric ground state. The $^2A_1$ energy curve for M = S is not fully reported in Figure 5, since at intermediate Q distances the SH bond dissociates leading to thiirane plus hydrogen.

A pronounced potential minimum exists at intermediate Q distances only for the $^2A_1$ state, whereas the $^2B_2$ and $^2A'$ energy curves present a very flat minimum relative to dissociation at large Q distances only for M from the third row. Formation of a loose complex is probably due to the high polarizability of third-row atoms. The well depth is on the order of 0.3 kcal mol^{-1}, and the structural parameters in the complex are essentially unchanged with respect to the corresponding ones in the separate monomers. It is should be remarked that no minimum has been found for the $^2A_1$ state in preliminary calculations carried out at the self-consistent-field (SCF) level of theory (UHF/DZP+BF). This indicates that the usual procedure consisting of geometry optimization of ground and transition states at the SCF level followed by single-point calculations, including some form of electron correlation,[40] can provide incorrect results. Optimized structural parameters of the bridged structure are listed in Table VIII for the $^2A_1$ ($^2A'$ for H_3M bridged groups) state. Bridged-structure energies are reported in Table IV along with dissociation energies. As can be seen from Table VIII, the optimized $C_\alpha-C_\beta$ bond lengths are much closer to a double rather than to a single carbon–carbon bond length, and the optimized C–M bond lengths are much longer than the normal single bond lengths. The bridged structure in

(40) Hehre, W.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.
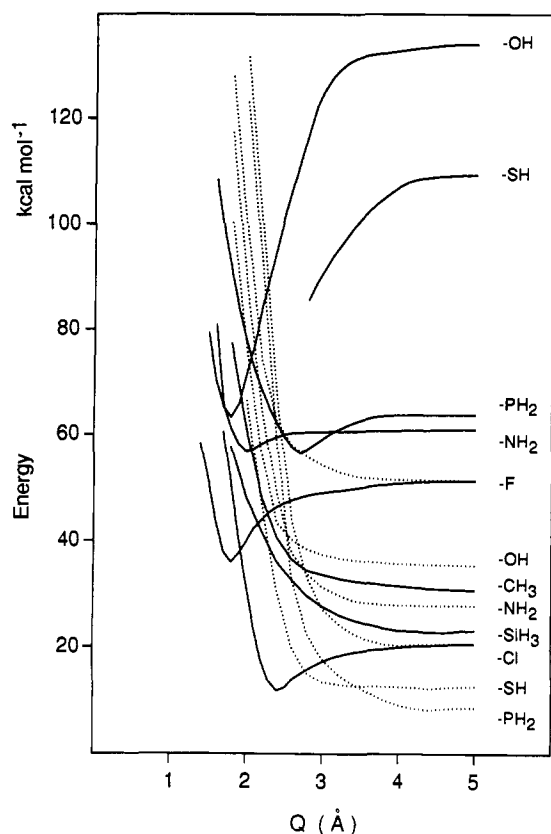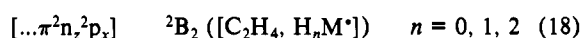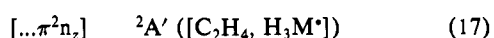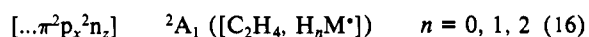
Figure 5. Energy profiles along the dissociation path leading to ethylene plus $H_nM^\bullet$ at the UMP2/DZP+BF level: $^2B_2$ states (dashed lines), $^2A_1$ and $^2A'$ states (solid lines).

Table VIII. Optimized Structural Parameters[a] of β-Substituted Ethyl Radicals (H_nM–CH_2–$CH_2^\bullet$) in the $^2A_1$ State of the Bridged Structure at the UMP2/DZP+BF Level
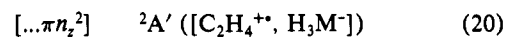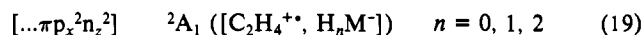
H_nM	r(C–C)	r(C–M)	∠HCH	r(C–H)	γ	Q
$H_3C^{b,c}$						
H_2N^d	1.401	2.000	117.5	1.088	171.1	1.874
HO[e]	1.421	1.859	118.2	1.087	169.2	1.718
F	1.394	1.926	118.4	1.086	176.2	1.796
$H_3Si^{c,f}$	1.348	4.775	117.2	1.089	180.0	4.727
H_2P^g	1.408	2.36	117.2	1.089	168.9	2.25
HS^h						
Cl	1.367	2.584	117.8	1.088	177.6	2.492

[a] Bond lengths are given in angstroms, dihedral and bond angles in degrees. [b] Minimum not found. [c] $^2A'$ state. The optimized parameters of the H_nM group are the following. [d] r(NH) = 1.023, ∠HNH = 122.1. [e] r(OH) = 0.997. [f] r(SiH) = 1.487, ∠HSiH = 108.0. [g] r(PH) = 1.429; ∠HPH = 128.6. [h] The bridged structure in the $^2A_1$ state decomposes in thiirane plus hydrogen.
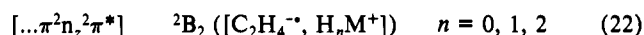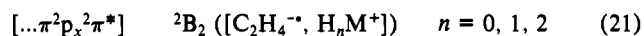
the $^2A_1$ state is thus well represented as formed by an ethylene molecule weakly interacting with the $H_nM^\bullet$ radical. In order to better understand the trends in the energy profiles, the electronic configurations are described in terms of the molecular orbitals localized at the ethylene (π,π^*) and $H_nM^\bullet$ (p, sp^n) monomers mainly interacting in the bridged structure

$$[...\pi^2p_x{}^2n_z] \qquad ^2A_1 \; ([C_2H_4, H_nM^\bullet]) \qquad n = 0, 1, 2 \quad (16)$$

$$[...\pi^2n_z] \qquad ^2A' \; ([C_2H_4, H_3M^\bullet]) \qquad\qquad\qquad (17)$$

$$[...\pi^2n_z{}^2p_x] \qquad ^2B_2 \; ([C_2H_4, H_nM^\bullet]) \qquad n = 0, 1, 2 \quad (18)$$

where n_z is a pure p atomic orbital in $M^\bullet$ and an sp^n-hybridized orbital in $H_nM^\bullet$. Since all states are dissociative at the SCF level, charge-transfer excited configurations are important in determining the shape of the computed energy curves. The lowest lying charge-transfer excited state results from the $\pi \rightarrow n_z$ (SOMO) excitation

$$[...\pi p_x{}^2n_z{}^2] \qquad ^2A_1 \; ([C_2H_4{}^{+\bullet}, H_nM^-]) \qquad n = 0, 1, 2 \quad (19)$$

$$[...\pi n_z{}^2] \qquad ^2A' \; ([C_2H_4{}^{+\bullet}, H_3M^-]) \qquad\qquad\qquad (20)$$

The lowest lying charge-transfer $^2B_2$ excited states are expected to occur at much higher energy resulting from the one-electron excitation to the empty π^* antibonding orbital of ethylene

$$[...\pi^2p_x\pi^*] \qquad ^2B_2 \; ([C_2H_4{}^{-\bullet}, H_nM^+]) \qquad n = 0, 1, 2 \quad (21)$$

$$[...\pi^2n_z{}^2\pi^*] \qquad ^2B_2 \; ([C_2H_4{}^{-\bullet}, H_nM^+]) \qquad n = 0, 1, 2 \quad (22)$$

As mentioned above, the $^2B_2$ state is dissociative, also including electron correlation. This means that the $^2B_2$ ground state should mix to a small extent with the charge-transfer excited $^2B_2$ states owing to the large energy gap. This hypothesis is confirmed by the small difference (<2 kcal mol^{-1}) occurring between the $^2B_1$ (not reported in Figure 5) and $^2B_2$ energy curves computed for β-haloethyl radicals. In fact, in both states the unpaired electron is localized in a pure p atomic orbital (p_x in $^2B_2$ and p_y in $^2B_1$), and excited $^2B_1$ states are expected not to lie at low energy. Indeed, the energy curve of the $^2B_2$ ground state shows the same behavior for all radicals, and the dissociation energy increases moderately with the electronegativity of the heteroatom following thus the energy trends of pure p atomic orbitals. Similarly, the absence of a minimum at intermediate Q distances in the $^2A'$ state indicates that the ground and charge-transfer states mix to a small extent. In this case the large energy gap is due to the very low electron affinity of $H_3M^\bullet$. On the other hand, the $^2A_1$ state is sizably affected by mixing with the low-lying charge-transfer excited state. The trends in the $^2A_1$ energy curves can be explained in the following way. The amount of mixing (M > HM > H_2M) at intermediate Q distances depends on the electron affinity of the $H_nM^\bullet$ radical in the $^2A_1$ state, which is proportional to the electronegativity of the heteroatom M. At large Q distances the $^2A_1$ total energy depends on the heteroatom hybridization. In fact, Table VII shows that the $^2A_1$ dissociation energy of β-haloethyl radicals is equal to that of the $^2B_2$ state, the SOMO being a pure p atomic orbital in both states. For the other substituents, the dissociation energy of the $^2A_1$ state is much higher than that of the $^2B_2$ state since the $^2A_1$ state of $H_nM^\bullet$ can be obtained by excitation of an electron from the hybridized n_z lone pair (A_1 symmetry) to the higher lying singly occupied p_x orbital (B_2 symmetry). The energy difference strongly increases following the energy lowering of the n_z orbital with increasing s–p hybridization ratio. In fact, the computed energy differences for [C_2H_4, HM$^\bullet$] (99 kcal mol^{-1} and 96.8 kcal mol^{-1} for M = O and S, respectively) are much larger than those evaluated for [C_2H_4, $H_2M^\bullet$] (33.3 kcal mol^{-1} and 55.3 kcal mol^{-1} for M = N and P, respectively).

From Figure 5 it is evident that a shuttle motion for the H_3M group cannot occur, since the $^2A'$ state is dissociative, as well as for the H_2P group, because the $^2A_1$ state lies high in energy above the dissociative $^2B_2$ state. For M = S, the probability of shuttling and/or formation of a stable bridged structure, invoked to explain the stereochemical control in β-mercaptoalkyl radicals,[6] should be ruled out since the bridged structure in the $^2A_1$ state decomposes into thiirane plus hydrogen. A shuttle motion for the H_2N, and HO groups is highly unlikely since the $^2A_1$ minimum lies high in energy above the $^2B_2$ dissociation limit, and the barrier to dissociation near the symmetric bridged structure, where the states correlating with the $^2A_1$ and $^2B_2$ state can mix producing thus an *avoided crossing*, is predicted to be very low. Shuttling could take place only in β-haloethyl radicals since the bridged structure lies low in energy relative to the dissociation limit. However, the frequency of shuttling should be very low in β-fluoroethyl because of the high barrier to shuttling (>35 kcal mol^{-1}) and of the low population of the eclipsed rotamer I due to a quasi-free rotation about the C_α–C_β bond. On the other hand, the shuttle motion is likely in β-chloroethyl owing to the high population of the eclipsed rotamer I and to the low barrier to shuttling. The same result was obtained with MRD–CI calculations on β-haloethyl radicals.[11] However, it was claimed that the β-chloroethyl radical possesses a "asymmetrically bridged structure". This conclusion

is somewhat misleading, being probably based upon the possibility of shuttling. Indeed, both the present and MRD–CI calculations indicate that β-chloroethyl is a classical radical. In fact, both calculations predict a tetrahedral arrangement of atoms around C_β at the absolute energy minimum, and that the rotational motion about the C_α–C_β bond is favored over the shuttle motion. The stereochemical control of small entity exercised by the chlorine atom[9] could be due to the high population of the eclipsed rotamer I in conjunction with the nonplanarity of the radical site[13] and/or steric hindrance of the β-substituent rather than due to shuttling since the present calculations show that this motion cannot occur for other β-substituted alkyl radicals (M = S, Si) where an analogous control was observed experimentally. In this connection, it is worthwhile to mention that MRD–CI calculations on β-bromoethyl[11] predicted that the shuttle motion is nearly free and favored over the rotational motion. This theoretical result is consistent with the complete stereochemical control exerted by the bromine atom. Indeed, the ESR spectra of β-bromoalkyl radicals[41] exhibit unusual features for β-substituted alkyl radicals. The spectral analysis of symmetric compounds as a function of temperature indicates that the bromine atom oscillates rapidly between two equivalent sites. However, it was suggested that the spectral features could also be interpreted as due to a rocking

motion. Investigation in this direction is now being made.

Conclusion

The structural parameters of β-substituted ethyl radicals containing second- and third-row elements are typical of a classical radical having a nonplanar radical center. Substituents containing second-row elements adopt a gauche conformation, but rotation about the C_α–C_β bond is nearly free. Substituents containing third-row elements are constrained to the eclipsed conformation by a sizable rotation barrier. The shuttle motion of the substituent between the C_α and C_β atoms is less favored with respect to the rotoinversion motion about the C_α–C_β bond. Shuttling is likely for the chlorine atom, highly unlikely for the H_2N, HO, and F groups, and impossible for the other substituents. These results are in contrast to the hypothesis that static or dynamic asymmetric bridging generally occurs in radicals bearing third-row substituents. By contrast, the experimental findings can be explained with the change in the rotoinversion energy surface on going from second- to third-row elements and with the remarkable dependence of the β-splitting on the electronegativity of the substituent in the eclipsed conformation.

(41) Maj, S. P.; Symons, M. R. C.; Trousson, P. M. R. *Chem. Commun.* **1984**, 561.

Stereomutation of Cyclopropane Revisited. An ab Initio Investigation of the Potential Surface and Calculation of Secondary Isotope Effects

Stephen J. Getty,[†] Ernest R. Davidson,[‡] and Weston Thatcher Borden*,[†]

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98195, and Department of Chemistry, Indiana University, Bloomington, Indiana 47405. Received July 25, 1991

Abstract: The transition states for single and double methylene group rotation on the singlet trimethylene potential surface have been located at the GVB/6-31G* level of theory, with one pair of electrons correlated. The preference for conrotatory double rotation over single rotation is found to be 0.97 kcal/mol at the GVB level, and is expected to increase slightly with inclusion of additional electron correlation, on the basis of SD-CI calculations on (0,0)- and (0,90)-trimethylene. At the SD-CI level, the transition state for disrotation is expected to be quite close in energy to that for single rotation, and passage over either of these transition states can lead to net one-center epimerization. The H/D kinetic isotope effects for passage over all three of these transition states have been calculated and found to be moderate and normal, with the β isotope effects much smaller than the α effects. On the basis of the isotope effects computed for conrotatory double methylene group rotation, the kinetic preference for cleavage of an isotopically less substituted bond in cyclopropane-*1,2-²H₂* (**1**) is calculated to be z_{12} = 1.13. This value is in good agreement with that assumed by Berson et al. in their analysis of the stereomutations of **1**. However, this value is very different from the value of z_{12} = 0.4 that is required in order to apply a common mechanistic interpretation to the experimental results obtained recently for cyclopropane-*1-¹³C-1,2,3-²H₃* (**2**) by Baldwin and co-workers, and to those obtained for **1** by both Berson et al. and Baldwin et al.

Introduction

Even after two decades of careful studies, the thermal stereomutations of cyclopropanes appear resolutely to resist all attempts at a unified mechanistic description.[1] Most experimental and theoretical effort has focused on distinguishing among three limiting stereomutation mechanisms. These three are (i) rotation of a single methylene group—the so-called Smith mechanism,[3] (ii) cleavage of a C–C bond to give a trimethylene diradical intermediate in which random loss of stereochemistry is at least competitive with ring closure—the Benson hypothesis,[4] and (iii)

coupled, simultaneous rotation of two methylene groups—the Hoffmann mechanism.[5]

(1) A number of reviews[2] chronicle the ample experimental literature on the subject, as well as the numerous theoretical studies of the trimethylene potential energy surface.

(2) (a) Borden, W. T. In *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; Wiley-Interscience: New York, 1985; Vol. 3, pp 151–188. (b) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981; pp 27–35. (c) Borden, W. T. In *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; Wiley-Interscience: New York, 1981; Vol. 2, pp 175–209. (d) Berson, J. A. In *Rearrangements in Ground And Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, pp 311–390.

(3) (a) Smith, F. T. *J. Chem. Phys.* **1958**, *29*, 235. (b) Kollmar, H. *J. Am. Chem. Soc.* **1973**, *95*, 966.

† University of Washington.
‡ Indiana University.