

On the Conformation of  $\beta$ -Substituted Ethyl Radicals<sup>1</sup>D. Griller<sup>2</sup> and K. U. Ingold\*

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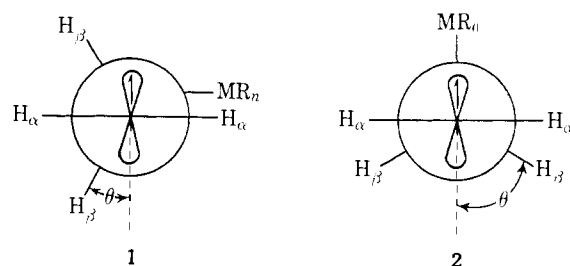
**Abstract:** A large number of 1,1-di-*tert*-butyl-2-substituted ethyl radicals,  $B_2\dot{C}CH_2MR_n$ , have been prepared, principally by radical addition to 1,1-di-*tert*-butylethylene. The epr spectral parameters for these sterically hindered radicals are compared with those of the analogous, but unhindered, 2-substituted ethyl radicals,  $\dot{C}H_2CH_2MR_n$ . In  $B_2\dot{C}CH_2MR_n$  all  $MR_n$  groups eclipse the orbital occupied by the unpaired electron (*i.e.*, the  $C_\alpha$   $p_z$  orbital). This same conformation (2) is adopted by  $\dot{C}H_2CH_2MR_n$  radicals when M is from rows 2, 3, or 4 of the periodic table, but when M is from row 1 the preferred conformation (1) is that with the  $MR_n$  group lying in the nodal plane of the  $C_\alpha$   $p_z$  orbital. Since the calculated extents of hyperconjugative delocalization of unpaired spin density into the  $C_\beta$ -M bond are about the same in  $B_2\dot{C}CH_2MR_n$  whether M is carbon or silicon, it is concluded that the difference in conformation produced by these two elements in  $\dot{C}H_2CH_2MR_n$  radicals cannot be due to hyperconjugation. Some other interaction, such as  $p\pi$ - $d\pi$  bonding, must be invoked to account for the preference for conformation 2 with row 2 elements. Although  $\beta$ -hydrogen splittings serve to distinguish between conformation 1 and 2, it is suggested that they may not be a reliable guide to possible small distortions of the  $\beta$  carbon from its normal tetrahedral geometry. Other conclusions are that  $B_2\dot{C}CH_2C_6H_5$  and analogous radicals have the phenyl ring arranged with one edge towards the unpaired electron and that all  $B_2\dot{C}CH_2MR_n$  radicals have planar ligand geometry at the  $\alpha$  carbon.

The conformations adopted by  $\beta$ -substituted ethyl radicals,  $R_nMCH_2\dot{C}H_2$ , are determined by measurement of the isotropic epr hyperfine splittings due to the  $\beta$  hydrogens,  $a^{H\beta}$ . These splittings depend on the angle  $\theta$  between the principal axis of the p orbital containing the unpaired electron and the C-H bond on the  $\beta$ -carbon atom and can be represented by the empirical relationship<sup>3</sup>

$$a^{H\beta} = B_0 + B \cos^2 \theta \quad (1)$$

where  $B_0$  and  $B$  are constants ( $B_0 \simeq 3 \pm 2$  G,  $B \simeq 48 \pm 5$  G).<sup>3</sup> Under conditions where rotation about the  $C_\alpha$ - $C_\beta$  bond is rapid the average value of  $\cos^2 \theta$  is 0.5 and  $a^{H\beta} \simeq 27$  G. For many alkyl radicals the most stable conformation (*i.e.*, that approached at low temperatures) is 1, with  $\theta$  tending toward  $30^\circ$  and  $a^{H\beta}$  toward 39 G as the temperature is lowered. For example, for the propyl radical ( $MR_n = CH_3$ )  $a^{H\beta} \simeq 29$  G at  $-20^\circ$  and shows a steady increase with decreasing temperature with a value of  $\simeq 33$  G at  $-140^\circ$ .<sup>4</sup> However, when M is from rows 2, 3, or 4 of the periodic table conformation 2 is favored<sup>5-18</sup> with  $\theta \sim 60^\circ$  and

$a^{H\beta} \simeq 15$  G. For example, with  $MR_n = SiH_3$ ,  $a^{H\beta} = 17.68$  G at  $-70^\circ$ .<sup>5</sup>



The relationship between  $a^{H\beta}$  and  $\cos^2 \theta$  has generally been interpreted in terms of hyperconjugative interactions involving the unpaired electron. However, there has been considerable debate about the importance of hyperconjugation as a factor determining conformations 1 and 2. Thus, Kochi and Krusic<sup>5</sup> originally proposed that 2 was favored when M was a second row element because its vacant d orbitals could be used in 1-3 bonding with the p orbital containing the unpaired electron (p-d homoconjugation). The subsequent observation<sup>6,7,10</sup> of large hyperfine coupling to M was taken as evidence that hyperconjugative delocalization, between the  $C_\alpha$   $2p_z$  orbital and the  $C_\beta$ -M  $\sigma$  bond, was in part responsible for the observed conformational preference since it would be maximized in 2. Lyons and Symons<sup>6,7</sup> favor hyperconjugation alone as being responsible for conformation 2. They rationalized the difference in behavior between row 1 and row 2 M on the basis that hyperconjugation will be favored when  $R_nM$  is a pyramidal radical since contributions from structures of the type  $\dot{C}-C-MR_n \leftrightarrow C=C \cdot MR_n$  would require smaller changes in geometry than when  $R_nM \cdot$  is a planar radical.

In this paper we report the epr spectral parameters

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- (1) Issued as NRCC No. 14257.  
 (2) NRCC Postdoctoral Fellow, 1973-1975.  
 (3) (a) P. B. Ayscough, "Electron Spin Resonance in Chemistry," Methuen, London, 1967; (b) H. Fischer in "Free Radicals," Vol. II, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, Chapter 19.  
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 (12) D. J. Edge and J. K. Kochi, *Tetrahedron Lett.*, 2427 (1972).  
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 (14) A. J. Bowles, A. Hudson, and R. A. Jackson, *Chem. Phys. Lett.*, 5, 552 (1970).  
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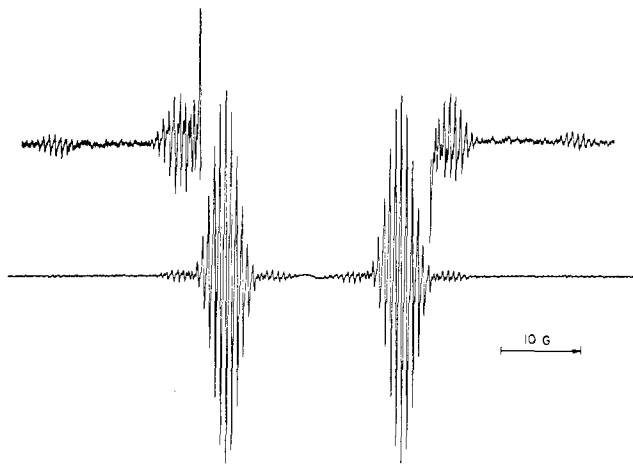


Figure 1. Epr spectrum of  $B_2\dot{C}H$ .

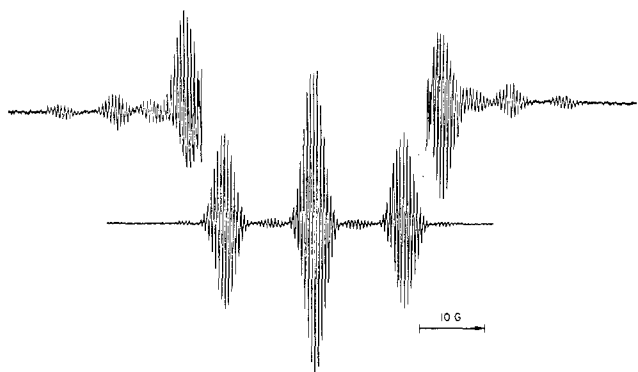
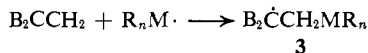


Figure 2. Epr spectrum of  $B_2\dot{C}CH_2CF_3$ .

for a large number of  $\beta$ -substituted  $\alpha,\alpha$ -di-*tert*-butylethyl radicals, **3**, that have been prepared by radical



addition to  $B_2CCH_2$  (throughout this paper B designates the  $(CH_3)_3C$  group). These radicals undergo first- and/or second-order decay processes with rate constants several orders of magnitude less than those observed for less hindered alkyl radicals,<sup>19</sup> presumably because of the steric influence of the two *tert*-butyl groups.<sup>20</sup> As a result, radical concentrations of *ca.*  $10^{-4}$  to  $10^{-5}$  M are readily attainable and  $^{13}C$  hyperfine splittings could be measured from the  $^{13}C$  present in natural abundance. The two  $\alpha$ -*tert*-butyl groups confer conformation **2** on all radicals of type **3** we have observed. This allows us to prove that the conformation of  $\dot{C}H_2-CH_2MR_n$  radicals containing a row 2 element M cannot be determined by hyperconjugative forces alone.<sup>21</sup> Additional conclusions are drawn regarding the interpretation of  $^{13}C_\alpha$  hyperfine splittings and their relation to radical planarity.

## Experimental Section

**Materials.** Unless otherwise noted all reagents were commercial materials that were carefully purified before use. 1,1-Di-*tert*-

(19) G. D. Mendenhall, D. Griller, D. Lindsay, T. T. Tidwell, and K. U. Ingold, *J. Amer. Chem. Soc.*, **96**, 2441 (1974).

(20) G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 3422 (1973).

(21) A preliminary account of some of this work has appeared. D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6459 (1973).

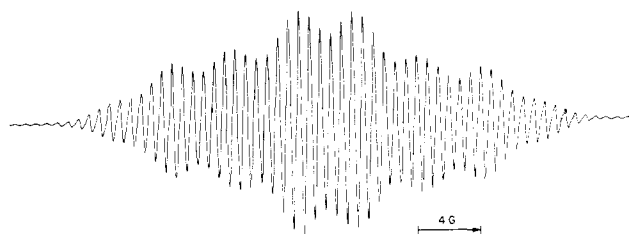


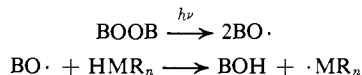
Figure 3. Epr spectrum of  $B_2\dot{C}CH_2OCF_3$ .

butylethylene and tri-*tert*-butylethylene were generously supplied by Professor T. T. Tidwell (University of Toronto). 3-Bromo-1,1,1-trifluoropropane<sup>22</sup> and 3-iodo-1,1,1-trifluoropropane<sup>23</sup> were prepared by standard literature methods and were purified by preparative vpc. 1,4,6,9-Tetraoxa-5-phosphaspiro[4,4]nonane was prepared by the method of Houalla, *et al.*<sup>24</sup> Trimethylborane was generated in a high vacuum system by reaction of the trimethylborane-pyridine complex with concentrated sulfuric acid.

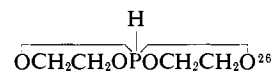
**Radical Generation.** Solutions prepared for epr work generally contained the reagents in concentrations of *ca.* 10–15% v/v in inert hydrocarbons such as cyclopropane. In experiments where di-*tert*-butyl peroxide, BOOB, was a reagent it was sometimes used as the solvent. Benzene and toluene were also used as solvents occasionally.

The  $R_nM\cdot$  radicals were generated photochemically by the methods outlined below. At 25° in the presence of 1,1-di-*tert*-butylethylene, adduct radicals **3** were generally observed at concentrations of  $10^{-4}$  to  $10^{-5}$  M using 10% of the output of a 250-W medium pressure mercury lamp. Increasing the light intensity did not improve the spectra significantly, presumably because **3** begins to compete with the  $B_2CCH_2$  for the  $R_nM\cdot$  radicals. Epr spectra were recorded both on an E-4 and on an E-12 Varian epr spectrometer. The spectra of  $B_2\dot{C}H$  and of two typical adduct radicals are shown in Figures 1, 2, and 3.

### Method A. Photolysis of BOOB in the Presence of $HMR_n$ .

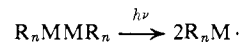


This method was used for  $\cdot MR_n = \cdot Cl$ ,<sup>13,18</sup>  $\cdot CCl_3$ ,<sup>25</sup>  $\cdot SiMe_3$ ,<sup>5</sup> and



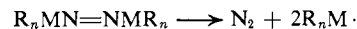
all of which formed type **3** radicals.

### Method B. Photolysis of $R_nMMR_n$ .



Type **3** radicals were found for  $R_nM\cdot = CF_3O\cdot$  and  $CF_3S\cdot$ . No radicals were detected at 25° or at very low temperatures in cyclopropane for  $R_nM\cdot = BO\cdot$ ,  $F_2N\cdot$ ,  $Me_3Sn\cdot$ ,  $MeS\cdot$ , and  $MeSe\cdot$ . The mixture of  $N_2F_4$ ,  $B_2CCH_2$ , and cyclopropane exploded violently shortly after the epr experiments were completed.

### Method C. Photolysis of $R_nMN=NMR_n$ .



This method was applied with  $R_nM\cdot = \cdot B$  and  $\cdot CF_3$ , only the latter yielded a type **3** radical. There was no evidence for the potential intermediate diazenyl radical,  $R_nMN=N\cdot$ , or for its addition to  $B_2CCH_2$ .

### Method D. Photolysis of BOOB in the Presence of Organometallic Compounds.



where X = main group element. A type **3** radical was obtained with  $R_nM\cdot = \cdot C_6H_5$  from triphenylarsenic<sup>27</sup> and triphenylborane.

(22) H. Bodor, A. Leroy, and L. Pujol, *Bull. Soc. Chim. Fr.*, 251 (1968).

(23) R. N. Haszeldine, *J. Chem. Soc.*, 2856 (1949).

(24) D. Houalla, M. Sanchez, L. Bestier, and R. Wolf, *Org. Magn. Resonance*, **3**, 45 (1971).

(25) A. Hudson and H. A. Hussain, *Mol. Phys.*, **16**, 199 (1969).

(26) D. Griller and B. P. Roberts, *J. Chem. Soc. Perkin 2*, 1416 (1973).

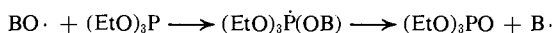
(27) E. Furimsky, J. A. Howard, and J. R. Morton, *J. Amer. Chem. Soc.*, **94**, 5932 (1972).

**Table I.** Epr Parameters for 1,1-Di-*tert*-butyl 2-Substituted Ethyl and Related Alkyl Radicals at 25° (Hyperfine Splitting Constants Are Given in Gauss)

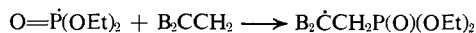
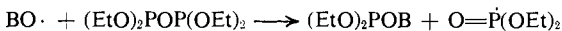
Radical	<i>g</i>	Solvent	$a^H$		$a^{13C}$		$a^{other}$	$\rho_\sigma^a$
			$\beta$	$\gamma$	$\alpha$	$\gamma(B)$		
$B_2\dot{C}CH_2CF_3$	2.0026	$\Delta^b$	12.16	0.45 <sup>c</sup>	45.45	11.53	$^{13}C_\gamma(CF_3) = 30.08$ ; $^{19}F(3F) = 0.90^c$	0.108
$B_2\dot{C}CH_2CCl_3$	2.0034	BOOB	10.68	0.42 <sup>c</sup>	45.57	10.44	$^{13}C_\gamma(CCl_3) = 34.00$ ; $^{35}Cl(3Cl) \approx 2.10^c$	0.122
$B_2\dot{C}CH_2SiMe_3$	2.0024	BOOB	15.76	0.36	46.35	10.23	$^{29}Si = 35.02$	0.116
$B_2\dot{C}CH_2Si(t-Bu)_3$	2.0024	$\Delta^b$	15.78	<i>d</i>	47.38	10.10	$^{29}Si = 30.87$	0.102
$B_2\dot{C}CH_2SiCl_3$	2.0030	BOOB	14.58	0.43 <sup>c</sup>	<i>d</i>	<i>d</i>	$^{29}Si = 77.24$ ; $^{35}Cl(3Cl) \approx 2.2^c$	0.255
$B_2\dot{C}CH_2OCF_3$	2.0023	$\Delta^b$	7.22 <sup>c</sup>	0.61 <sup>c</sup>	$\sim 45.5$	<i>d</i>	$^{19}F(3F) = 3.02^c$	
$B_2\dot{C}CH_2SCF_3$	2.0028	CF <sub>3</sub> SSCF <sub>3</sub>	10.42	0.46	<i>e</i>	<i>e</i>	$^{19}F(3F) = 4.99$	
$B_2\dot{C}CH_2(C_6H_5)$	2.0024	C <sub>6</sub> H <sub>6</sub>	12.95	0.44	47.2	10.88	<i>f</i>	
$B_2\dot{C}CH_2(C_6F_5)$	2.0025	Hexane	14.72	0.40	49.0	10.28	$^{19}F(1F) = 17.59$	
$B_2\dot{C}CH_2(4-C_6H_4F)$	2.0024	Hexane	13.06	0.45	46.5	10.56	<i>f</i>	
$B_2\dot{C}CH_2(2,4-C_6H_3F_2)$	2.0024	Hexane	12.90	0.44	47.2	10.70	<i>f</i>	
$B_2\dot{C}CH_2P(O)(OEt)_2$	2.0028 <sup>g</sup>	BOOB	14.00	0.42	<i>e</i>	10.38	$^{31}P = 109.4^g$	0.101
$B_2\dot{C}CH_2P\left(\begin{array}{c} O \\ / \quad \backslash \\ O \quad O \end{array} (CH_2)_2\right)_2$	2.0032 <sup>g</sup>	BOOB	13.13	<i>d</i>	$\sim 44.5$	10.51	$^{31}P = 128.9^g$	0.119
$B_2\dot{C}CH_2Cl$	2.0029	$\Delta^b$	6.88	0.4	<i>e</i>	<i>e</i>	$^{35}Cl = 22.45^h$	<i>i</i>
$B_2\dot{C}H^m$	2.0026	BOOB		0.68 <sup>j</sup>	42.98 <sup>j</sup>	12.25 <sup>j</sup>	$H_\alpha = 21.73$ ; <sup>j</sup> $^{13}C_\beta = 10.87$ ; <sup>j</sup>	0.084 <sup>k</sup>
$B_3\dot{C}^m$	2.0025	BOOB		0.51	51.10 <sup>j</sup>	10.99	$^{13}C_\beta = 10.71$ ; <sup>j</sup>	0.079 <sup>k</sup>
$(Me_3Si)_2\dot{C}H^m$	2.0027 <sup>l</sup>	BOOB		<i>d</i>	<i>e</i>	<i>e</i>	$H_\alpha = 15.2$	
$(Me_3Si)_3\dot{C}^n$	2.0027	BOOB		0.38	$\sim 26$	5.2	$^{29}Si = 13.5$	
$B_2\dot{C}Cl$	2.0058	BOOB		<i>d</i>	<i>e</i>	<i>e</i>	$^{35}Cl = 2.26$	
$CF_3CH_2\dot{C}H_2$	2.0028	BOOB	25.60		<i>e</i>	<i>e</i>	$^{19}F(3F) = 0.33$ ; $H_\alpha(2H) = 22.88$	

<sup>a</sup> See text for method of calculation. <sup>b</sup>  $\Delta$  = cyclopropane. <sup>c</sup> Estimated by computer simulation. <sup>d</sup> Not resolved. <sup>e</sup> Not detected. <sup>f</sup> The observed hyperfine splitting pattern suggests that  $a^{ortho-H}$  (presumably only one ortho hydrogen involved) is approximately equal to  $a^{H\gamma}$  for the *tert*-butyl hydrogens. The relatively large line widths preclude meaningful computer simulation. *N.B.* If  $a^{ortho-H}(B_2\dot{C}CH_2-C_6H_5):a^{ortho-F}(B_2\dot{C}CH_2C_6F_5)$  is approximately equal to  $a_0^H:a_0^F$ , then the calculated value for  $a^{ortho-H}$  is  $\sim 0.5$  G. <sup>g</sup> Corrected using the Breit-Rabi equation. <sup>h</sup> Signal too weak to measure  $a^{37Cl}$ . <sup>i</sup> A value of  $\rho_\sigma = 0.054$  can be calculated from  $a^{35Cl}$  but is very uncertain since the *s* character of the C-Cl  $\sigma$  and  $\sigma^*$  orbitals is unknown; see footnote 23, ref 13. <sup>j</sup> Measured for this work. <sup>k</sup> Values for  $B_2\dot{C}CH_2CH_3$ . The calculation of  $\rho_\sigma$  is based on the assumption that  $a^{13C\gamma}$  for  $B_2\dot{C}H$  and  $B_3\dot{C}$  would be only half as large as  $a^M$  for  $B_2\dot{C}CH_2CH_3$  in conformation 2, since the B groups in  $B_2\dot{C}H$  and in  $B_3\dot{C}$  are rotating freely. <sup>l</sup> Measured at  $-40^\circ$ . <sup>m</sup> Reference 20. <sup>n</sup> Reference 59.

Trimethylborane<sup>28</sup> and tris(dimethylamino)phosphine<sup>29a</sup> gave only methyl<sup>29b</sup> and dimethylamino, respectively, in the presence of the olefin. Triethylphosphite gave the *tert*-butoxytriethoxyphosphoranyl radical<sup>30</sup> and B radicals formed by its  $\beta$  scission. Neither of the radicals formed a type 3 adduct.

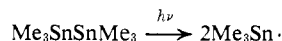


Tetramethyl pyrophosphite,  $(EtO)_2POP(OEt)_2$ , gave the diethoxyphosphonyl radical<sup>31</sup> adduct with the olefin. In no case was

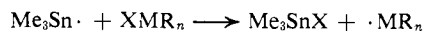
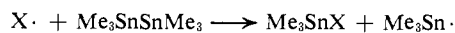
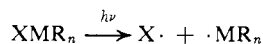


evidence found for the addition of the intermediate radical  $BO\dot{X}$  ( $MR_n$ )<sub>2</sub> to the olefin.

**Method E. Photolysis of Hexamethylditin and Organic Bromides or Iodides.**



and/or



(28) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 3942 (1969).

(29) (a) R. W. Dennis and B. P. Roberts, *J. Organometal. Chem.*, **43**, C2 (1972). (b) Since submission of this manuscript,  $B_2\dot{C}CH_2CH_3$  ( $a^{H\beta} = 11.1$ ,  $a^{HCH_3} = 0.10$ , and  $a^{H\gamma} = 0.48$  G) and  $B_2\dot{C}CH(CH_3)_2$  ( $a^{H\beta} = 2.7$ ,  $a^{H\gamma} = 0.54$  G) have been reported: K. Schreiner and A. Berndt, *Tetrahedron Lett.*, 3411 (1973).

(30) A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem., Int. Ed. Engl.*, **10**, 738 (1971).

(31) A. G. Davies, D. Griller, and B. P. Roberts, *J. Amer. Chem. Soc.*, **94**, 1782 (1972).

Type 3 radicals were obtained by this method from  $CF_3I$ ,  $C_6BrF_6$ , 2-bromo-1,4-difluorobenzene, and 4-bromofluorobenzene.

The 3,3,3-trifluoropropyl radical,  $CF_3CH_2\dot{C}H_2$ , was generated by a variety of methods since its unequivocal identification and the value of  $a^{H\beta}$  becomes an important part of our arguments. An excellent spectrum was obtained using  $Me_3Si\cdot$  (from  $Me_3SiH$  and BOOB)<sup>32</sup> to abstract bromine from  $CF_3CH_2CH_2Br$ . A less intense, but otherwise similar spectrum was obtained by the same method with  $CF_3CH_2CH_2I$ , by method E with the bromide, and by photolysis of  $CF_3I$  in ethylene. However, photolysis of  $CF_3I$ , ethylene, and hexamethylditin did not give a sufficiently intense signal for useful epr measurements to be made.

## Results

Epr parameters measured at 20° for the radicals observed in this work are recorded in Table I. This table also includes calculated values for the unpaired spin density in the  $C_\beta$ -M  $\sigma$  bond,  $\rho_\sigma$  (see Discussion).

**Temperature Dependence of  $a^{H\beta}$ .** The  $\beta$ -hydrogen hyperfine splittings for  $B_2\dot{C}CH_2MR_n$  radicals were virtually temperature independent. Thus, for  $MR_n = CF_3$ ,  $SiMe_3$ ,  $SiBu_3^n$ ,  $SiCl_3$ ,  $C_6H_5$ ,  $4-C_6H_4F$ , and  $2,4-C_6H_3F_2$  the  $a^{H\beta}$  values decreased by 1% or less on decreasing the temperature from +20 to  $-100^\circ$ . In contrast,  $a^{H\beta}$  for  $CF_3CH_2\dot{C}H_2$  increased from 25.60 G at  $-40^\circ$ , to 26.04 G at  $-80^\circ$ , and to 26.30 G at  $-120^\circ$ .

The  $B_2\dot{C}CH_2SCF_3$  radical showed a broadening of the lines corresponding to  $M_I = \pm 0.5$  of the quartet splitting due to the three equivalent fluorine atoms as the temperature was decreased. This is indicative of restricted rotation of the  $CF_3$  group.<sup>5</sup>

(32) A. Hudson and R. A. Jackson, *Chem. Commun.*, 1323 (1969).

## Discussion

$a^M$  Values and the Role of Hyperconjugation in  $\beta$ -Substituted Ethyl Radicals. A resumé of the debate concerning the importance of hyperconjugation as a factor controlling conformation has been given in the introductory statements.

The freely rotating  $\beta$ -methyl group in  $B_2\dot{C}CH_3$  has  $a^{H\beta} = 22.35$  G.<sup>33</sup> According, therefore, to eq 1, a  $B_2\dot{C}CH_2MR_n$  radical which is in conformation 2 and has a tetrahedral (undistorted)  $\beta$  carbon would have  $a^{H\beta} \approx 0.5(22.35 - 3.0) + 3.0 \approx 13$  G. Since all the  $B_2\dot{C}CH_2MR_n$  radicals studied have  $a^{H\beta} < 16$  G, and essentially independent of temperature, it would appear that all of these radicals adopt conformation 2 and that there is little or no rotational motion about the  $C_\alpha-C_\beta$  bond at ambient temperatures even when M is an element from row 1 of the periodic table. This behavior contrasts with that of  $\dot{C}H_2CH_2MR_n$  radicals having M from row 1 since these radicals have 1 as their preferred conformation (see introductory statements). The preference of  $B_2\dot{C}CH_2MR_n$  radicals for conformation 2 must be due to the steric requirements of the *tert*-butyl groups.

In those  $\cdot CH_2CH_2MR_n$  radicals which adopt conformation 2 (*i.e.*, those with M from rows 2, 3, and 4 of the periodic table) the observation of a large hyperfine splitting due to M has been taken as evidence that hyperconjugation was responsible for part, or all, of the bonding required to produce this conformation. The extent of delocalization of unpaired spin density into the  $C_\beta-M$  bond,  $\rho_\sigma$ , may be calculated from the relation<sup>7, 10</sup>

$$\rho_\sigma = 4a^M/a_0^M$$

where  $a^M$  is the observed coupling and  $a_0^M$  is the coupling constant for M with unit unpaired electron density in its valence shell s atomic orbital.<sup>34, 35</sup>

With  $B_2\dot{C}CH_2CF_3$ ,  $B_2\dot{C}CH_2CCl_3$ , and  $B_2\dot{C}CH_2SiMe_3$  (all of which adopt conformation 2) we calculate that  $\rho_\sigma = 0.108$ , 0.122, and 0.106, respectively. Thus, in conformation 2 the extents of hyperconjugative delocalization towards  $CF_3$ ,  $CCl_3$ , and  $SiMe_3$  are very similar.<sup>36</sup> However, when the steric constraint of the

(33) K. S. Chen and J. K. Kochi, private communication.

(34) Although approximate  $sp^3$  hybridization at M is assumed in this equation, fairly large changes in the s:p ratio would not substantially alter our conclusions.

(35) Values of  $a_0^M$  (ignoring differences in  $g$  factor) were taken from J. E. Wertz and J. R. Bolton, "Electron Spin Resonance," McGraw-Hill, New York, N. Y., 1972.

(36) Unfortunately, the most obvious comparison between carbon and silicon was not obtained since the  $B_2\dot{C}CH_2B$  radical was not formed when B $\cdot$  was generated in the presence of  $B_2C=CH_2$  (presumably either for steric reasons or because B $\cdot$  is insufficiently electrophilic). However, we feel that the  $SiMe_3$  adduct should, in any case, be compared with the  $CF_3$  or  $CCl_3$  adducts since at least some of the factors that are believed to promote hyperconjugation to an  $SiMe_3$  group should also enhance hyperconjugation to  $CF_3$  or  $CCl_3$  relative to  $CMe_3$ . That is, when R is more electronegative than M, the M-R bonds will adopt more  $\pi$  character and the  $C_\beta-M$  bond more  $\sigma$  character. As a consequence, the  $C_\beta-H$  bonds have increased  $\pi$  character and the hyperconjugative canonical structure  $B_2C=CH_2\cdot MR_n$  becomes more favored.<sup>37</sup> This suggests that comparisons between different M should involve groups where the electronegativity difference between M and R ( $x_M - x_R$ ) is similar. Values of  $(x_M - x_R)$ <sup>38</sup> are:  $SiMe_3 = -0.7$ ,  $CMe_3 = 0$ ,  $CCl_3 = -0.55$ , and  $CF_3 = -1.3$ . That is, in our opinion,<sup>39</sup> the  $\rho_\sigma$  value found for  $B_2\dot{C}CH_2SiMe_3$  should indeed be compared with the values found for  $B_2\dot{C}CH_2CF_3$  and  $B_2\dot{C}CH_2CCl_3$ . However, the fact that electronegativity differences do not wholly determine  $\rho_\sigma$  is indicated by  $B_2\dot{C}CH_2SiCl_3$  for which  $\rho_\sigma = 0.255$  and  $(x_M - x_R) = -1.25$ .

(37) As a corollary, hyperconjugation in  $B_2\dot{C}CH_2MR_n$  and  $\dot{C}H_2CH_2MR_n$  will be favored for nonplanar  $\cdot MR_n$  radicals (see introductory

*tert*-butyl groups is removed, the  $a^{H\beta}$  splittings indicate that for  $\dot{C}H_2CH_2CF_3$  free rotation occurs about the  $C_\alpha-C_\beta$  bond at ambient temperatures and the slight increase in the splitting with decreasing temperature (see Results) indicates that conformation 1 is preferred. This conformation (or one close to it)<sup>41</sup> is also preferred by  $\cdot CH_2CH_2CCl_3$  ( $a^{H\beta} = 22.3$  G from  $-20$  to  $-160^\circ$ ).<sup>13</sup> In contrast,  $\cdot CH_2CH_2SiMe_3$ <sup>10</sup> and  $\cdot CH_2CH_2SiEt_3$ <sup>5</sup> adopt conformation 2. Hence, hyperconjugation cannot be responsible for the different conformational preferences when M = carbon or silicon<sup>42</sup> in unhindered  $\beta$ -substituted ethyl radicals<sup>44, 45</sup> and some other interaction (possibly  $p\pi-d\pi$  bonding)<sup>5, 46</sup> must be invoked to explain the preference for conformation 2 when M is from row 2, 3, or 4 of the periodic table. In radicals such as  $\cdot CH_2CH_2Cl$  and  $\cdot CH_2CH_2PR_2$  (in which M has lone pairs of electrons)  $p\pi-p\pi$  homoconjugative bonding seems to be fairly well accepted,<sup>13-18, 47</sup> (see, however, following section).

$a^{H\beta}$  Values and Conformational Assignments. The common interpretation of  $a^{H\beta}$  simply in terms of the angle  $\theta$  between the p orbital containing the unpaired electron and the  $C_\beta-H$  bonds is extremely valuable in distinguishing between conformations 1 and 2. However, it is possible that more subtle conformational effects are not so easily identified.

If the ligands on the  $\beta$  carbon of a  $\beta$ -substituted ethyl radical are arranged tetrahedrally, then the minimum value of  $a^{H\beta}$  expected on the basis of eq 1 is *ca.* 15 G (see introductory statements).<sup>48</sup> Although a slightly smaller minimum value may obtain for  $B_2\dot{C}CH_2MR_n$ ,<sup>33</sup> the actual values of  $a^{H\beta}$  for many of these radicals are considerably less than 15 G. Unexpectedly low values of  $a^{H\beta}$  have normally been interpreted in terms of a bridging structure<sup>5, 13-18, 47</sup> involving movement of M towards the  $2p_z$  orbital of the  $\alpha$  carbon. As a consequence, the  $\beta$  hydrogens are displaced away from their tetrahedral position towards the nodal plane of the unpaired electron orbital so that their interaction with this electron decreases.

statements) and  $\cdot MR_n$  are nonplanar when R is more electronegative than M.<sup>40</sup> That is, hyperconjugation will be favored for  $MR_n = CF_3$ ,  $CCl_3$ , and  $SiMe_3$  (relative to  $CMe_3$ ) and the hybridization of M in the adduct radicals<sup>34</sup> should be similar for these three groups.

(38) M. L. Huggins, *J. Amer. Chem. Soc.*, **75**, 4123 (1953).

(39) A different interpretation of our results has been offered by Professor M. C. R. Symons (private communication).

(40) For leading references see ref 3b; and also, J. Cooper, A. Hudson, and R. A. Jackson, *Mol. Phys.*, **23**, 209 (1972); R. V. Lloyd and M. T. Rogers, *J. Amer. Chem. Soc.*, **95**, 1512, 2459 (1973); L. Kaplan in "Free Radicals," Vol. II, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, Chapter 18.

(41)  $(a^{H\beta})_{\dot{C}H_2CH_2CF_3}/(a^{H\beta})_{B_2\dot{C}CH_2CF_3} \approx (a^{H\beta})_{\dot{C}H_2CH_2CCl_3}/(a^{H\beta})_{B_2\dot{C}CH_2CCl_3}$ .

(42) The barrier to internal rotation in  $\dot{C}H_2CH_2SiEt_3$  has been calculated to be 1.2 kcal/mol.<sup>5, 44</sup> There is no such barrier in  $\dot{C}H_2CH_2CF_3$  though this radical can (to judge from the di-*tert*-butyl case) obtain the same degree of hyperconjugative delocalization.

(43) The accuracy of this value has been questioned.<sup>7</sup>

(44) For theoretical calculations on hyperconjugative effects on the conformations of  $\beta$ -substituted ethyl radicals, see R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Amer. Chem. Soc.*, **94**, 6221 (1972).

(45) For possible consequences of  $\alpha$  substitution on the conformations of  $\alpha, \beta$ -disubstituted ethyl radicals, see A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Magn. Resonance*, **11**, 100 (1973).

(46) The very small anisotropy of  $a^M$  does, however, argue against this particular type of bonding.<sup>7</sup>

(47) I. Biddles and A. Hudson, *Chem. Phys. Lett.*, **18**, 45 (1973).

(48) This conclusion is unaffected whether the splitting occurs entirely by hyperconjugation or whether, as seems more probable,<sup>49</sup> hyperconjugation and spin polarization are of about equal importance.

(49) Y. Ellinger, A. Rassat, R. Subra, G. Berthier, and P. Millie, *Chem. Phys. Lett.*, **11**, 362 (1971).

It has been shown<sup>45</sup> that substituted ethyl radicals with electron-withdrawing groups on the  $\beta$  carbon can adopt conformation **2** when electron-donating groups are attached to the  $\alpha$  carbon. A clear-cut example of this phenomenon is provided by the  $\text{CF}_3\text{O}$  group which prefers conformation **1** in  $\dot{\text{C}}\text{H}_2\text{CH}_2\text{OCF}_3$  ( $a^{\text{H}\beta} = 28.7$  G at  $-74^\circ$ ,<sup>5</sup> and 29.4 G at  $-100^\circ$ <sup>50</sup>) but increasingly favors conformation **2** upon the introduction of  $\alpha$ -alkyl substituents (at  $-100^\circ$ ,  $a^{\text{H}\beta} = 16.6$  G for  $\text{Me}\dot{\text{C}}\text{HCH}_2\text{OCF}_3$ ,<sup>50</sup> 10.0 G for  $\text{Me}_2\dot{\text{C}}\text{CH}_2\text{OCF}_3$ ,<sup>50</sup> and 7.2 G for  $\text{B}_2\dot{\text{C}}\text{H}_2\text{OCF}_3$ ). The monotonic decrease in  $a^{\text{H}\beta}$  along this series can be rationalized as being due to an increasing contribution from the canonical structure  $\text{R}_2\text{C}^{\pm}\text{CH}_2\text{OCF}_3$  which, since the  $\text{R}_2\text{CCH}_2\cdot^+$  fragment would be planar, will cause the  $\beta$  hydrogens to move towards the nodal plane of the orbital containing the unpaired electron. A similar monotonic decrease in  $a^{\text{H}\beta}$  occurs along the same series with the  $\text{SCF}_3$  group ( $a^{\text{H}\beta} = 13.8$  G at  $-83^\circ$  for  $\dot{\text{C}}\text{H}_2\text{CH}_2\text{SCF}_3$ ,<sup>5</sup> 11.8 G for  $\text{Me}\dot{\text{C}}\text{HCH}_2\text{SCF}_3$  at  $-102^\circ$ ,<sup>50</sup> 11.12 G for  $\text{Me}_2\dot{\text{C}}\text{H}_2\text{SCF}_3$  at  $-96^\circ$ ,<sup>50</sup> and 10.4 G for  $\text{B}_2\dot{\text{C}}\text{H}_2\text{SCF}_3$ ). These results suggest that hyperconjugation can be important when strongly electron-withdrawing groups are placed on  $\text{C}_\beta$  and electron-donating groups on  $\text{C}_\alpha$ . However, this does not affect our conclusions regarding hyperconjugation in those cases where electron release and electron withdrawal are less important (e.g.,  $\dot{\text{C}}\text{H}_2\text{CH}_2\text{CF}_3$  and  $\dot{\text{C}}\text{H}_2\text{CH}_2\text{SiMe}_3$ ).

The preference of  $\beta$ -chloroalkyl radicals for conformation **2** has been interpreted in terms of  $\pi\text{p}-\pi\text{p}$  homoconjugation.<sup>13-18,47</sup> While the push-pull effect described above cannot account for the conformational preference since  $\dot{\text{C}}\text{H}_2\text{CH}_2\text{F}$  favors conformation **1** ( $a^{\text{H}\beta} = 27.9$  G at  $-122^\circ$ ),<sup>12,13</sup> it may explain the decrease in  $a^{\text{H}\beta}$  along the series  $\dot{\text{C}}\text{H}_2\text{CH}_2\text{Cl}$  (10.2 G),<sup>15</sup>  $\text{Me}\dot{\text{C}}\text{HCH}_2\text{Cl}$  (7.79 G),<sup>18</sup> and  $\text{Me}_2\dot{\text{C}}\text{H}_2\text{Cl}$  (6.18 G).<sup>18</sup> It would appear, therefore, that while the conformational preference of substituted ethyl radicals may be determined by an interaction "through space" of the unpaired spin with  $\text{MR}_n$ , the extent of distortion of  $\text{C}_\beta$  (i.e., "bridging") may be closely related to the nature of the  $\alpha$  substituents.

There are indications that  $a^{\text{H}\beta}$  values are not such accurate guides to the  $\text{C}_\beta$  geometry as has sometimes been assumed. For instance,  $a^{\text{H}\beta}$  for  $\text{Me}_2\dot{\text{C}}\text{H}_2\text{Cl}$  is less than for  $\text{B}_2\dot{\text{C}}\text{H}_2\text{Cl}$  (6.88 G). This trend is the opposite of that found for the  $\text{CF}_3\text{O}$  and  $\text{CF}_3\text{S}$  groups despite the fact that steric effects for Cl should be intermediate between these two groups. It could be argued that in the  $\cdot\text{Cl}$ -olefin adducts the  $\beta$  carbon is maximally distorted in  $\text{Me}_2\dot{\text{C}}\text{H}_2\text{Cl}$  and that replacement of the  $\alpha$ -methyl groups by *tert*-butyl groups introduces steric factors that force the chlorine back from its (otherwise) most favorable position. However, until independent evidence regarding the structure of these radicals is available we suggest that such "precise" interpretations of  $a^{\text{H}\beta}$  are unwarranted.

As a second example, it might be tempting to interpret the relatively high  $a^{\text{H}\beta}$  values for  $\text{MR}_n = \text{SiMe}_3$  and  $\text{SiBu}_3$  in terms of a repulsion between these groups and the *tert*-butyl groups which causes the  $\beta$  hydrogens to move away from the nodal plane of the  $\text{C}_\alpha$   $p_z$  orbital. However, such a repulsion might be expected to reduce  $a^{\text{H}\beta}$  whereas, this splitting is actually larger for

(50) J. K. Kochi, private communication.

$\text{SiMe}_3$  than for the more bulky  $\text{SiBu}_3$  adduct.<sup>51</sup> Since the  $a^{\text{H}\beta}$  values are about the same for these two radicals (and are also about equal to the 15.35 G reported<sup>5</sup> for the less hindered  $\text{Me}_2\dot{\text{C}}\text{H}_2\text{SiEt}_3$  radical), it is far from clear whether the  $\text{C}_\beta$  geometry in these radicals is better reflected by their  $a^{\text{H}\beta}$  or  $a^{29\text{Si}}$  values.

In connection with the foregoing, it has been suggested that strongly electron-attracting  $\text{MR}_n$  groups will reduce  $a^{\text{H}\beta}$  simply by reducing the electron-releasing power of the  $\text{C}_\beta\text{-H}$  bonds.<sup>7,52</sup>

**$a^{13\text{C}\gamma}$ ,  $a^{\text{H}\gamma}$  and Splitting by Other Remote Atoms.** The splittings by the methyl carbons of the *tert*-butyl groups are all rather similar as are the splittings by the methyl hydrogens of these groups. What small differences there are show no very obvious correlation with radical structure. It could be argued that both  $a^{13\text{C}\gamma}$  and  $a^{\text{H}\gamma}$  should increase with decreasing steric crowding around the  $\alpha$  carbon since the B groups would not be forced so far from the radical center. The relatively large values found for both these splittings in the  $\text{B}_2\dot{\text{C}}\text{H}$  radical could be due partly to this factor.

The relatively large chlorine splittings in  $\text{B}_2\dot{\text{C}}\text{H}_2\text{CCl}_3$  and  $\text{B}_2\dot{\text{C}}\text{H}_2\text{SiCl}_3$  and the unusually high  $g$  factors for these radicals indicate a fairly strong interaction of the unpaired electron with the halogen.<sup>53</sup> This is probably due to the proximity of the bulky  $\text{MCl}_3$  groups to the  $\text{C}_\alpha$   $p_z$  orbital since the fluorine splitting in  $\text{B}_2\dot{\text{C}}\text{H}_2\text{CF}_3$  is only about half as great as the chlorine splitting in  $\text{B}_2\dot{\text{C}}\text{H}_2\text{CCl}_3$ , whereas fluorine splittings are normally very much greater than chlorine splittings. Moreover, with the more "remote" fluorines of the  $\text{OCF}_3$  and  $\text{SCF}_3$  adducts the value of  $a^{\text{F}}$  is increased, presumably because rotation of the  $\text{C}_\beta\text{-M}$  bonds can bring the  $\text{CF}_3$  groups closer to the  $\text{C}_\alpha$   $p$  orbital.<sup>54</sup> Rotation about the  $\text{S-CF}_3$  bond is restricted in  $\text{B}_2\dot{\text{C}}\text{H}_2\text{SCF}_3$  (see Results) as well as in  $\cdot\text{CH}_2\text{CH}_2\text{SCF}_3$ .<sup>5</sup>

Another interesting example of "through space" interaction is observed with  $\text{B}_2\dot{\text{C}}\text{H}_2\text{C}_6\text{F}_5$ . There is splitting by just one fluorine and since there is no fluorine splitting in the analogous 4-fluorophenyl radical, we conclude that the unique fluorine is probably in an ortho position. That is, the  $\text{C}_6\text{F}_5$  ring lies in the plane defined by  $\text{C}_\beta$ ,  $\text{C}_\alpha$ , and the  $\text{C}_\alpha$   $p_z$  orbital so that one ortho fluorine is brought fairly close to the orbital occupied by the unpaired electron. The absence of a fluorine splitting in the 2,4-difluorophenyl adduct radical we attribute to a conformation that prefers the ortho hydrogen rather than the ortho fluorine to be adjacent to the  $\text{C}_\alpha$   $p_z$  orbital. This radical and the 4- $\text{C}_6\text{H}_4\text{F}$  and  $\text{C}_6\text{H}_5$  adduct radicals probably have a fairly large splitting from the inward facing ortho hydrogen.

**$a^{13\text{C}\alpha}$  and Radical Planarity.** The  $^{13}\text{C}$  splitting due to the  $\alpha$  carbon in alkyl radicals gives information as to the planarity, or lack of it, of the radical.<sup>40</sup> Our data support Symon's view<sup>55</sup> that a value of  $a^{13\text{C}\alpha} \approx 46$  G for

(51) For the even less hindered  $\dot{\text{C}}\text{H}_2\text{CH}_2\text{SiEt}_3$ ,  $a^{29\text{Si}} = 37.4$  G.<sup>10</sup>

(52) For a discussion of this point, see J. A. Brivati, K. D. J. Root, M. C. R. Symons, and D. J. A. Tinling, *J. Chem. Soc. A*, 1942 (1969).

(53) For  $\dot{\text{C}}\text{H}_2\text{CH}_2\text{CCl}_3$ ,  $a^{35\text{Cl}}$  is not resolved,  $g = 2.00366$ , and for  $\dot{\text{C}}\text{H}_2\text{CH}_2\text{SiCl}_3$ ,  $a^{35\text{Cl}} = 1.0$  G and  $g \approx 2.00365$ .<sup>13</sup>

(54) For  $\cdot\text{CH}_2\text{CH}_2\text{OCF}_3$ , which prefers conformation **1**,  $a^{\text{F}} = 2.00$  G at  $-74^\circ$ , and for  $\cdot\text{CH}_2\text{CH}_2\text{SCF}_3$ , which adopts conformation **2**,  $a^{\text{F}} = 4.34$  G at  $-73^\circ$ .<sup>5</sup>

(55) M. C. R. Symons, *Mol. Phys.*, **24**, 461 (1972); *Tetrahedron Lett.*, 207 (1973).

B· should not be cited as evidence for its nonplanarity.<sup>56</sup> Values of  $a^{13C\alpha}$  increase<sup>57</sup> along the series ·CH<sub>3</sub> (38.34 G),<sup>58</sup> CH<sub>3</sub>ĈH<sub>2</sub> (39.07 G),<sup>58</sup> cyclohexyl (41.3 G),<sup>58</sup> B<sub>2</sub>ĈH (42.98 G), B· and B<sub>2</sub>ĈCH<sub>2</sub>MR<sub>n</sub> (~46 G), and B<sub>3</sub>Ĉ (51.10 G). It seems unlikely that a radical with such bulky ligands as B<sub>3</sub>Ĉ could be anything but planar.

The low value of  $a^{13C\alpha}$  for the (Me<sub>3</sub>Si)<sub>3</sub>Ĉ radical (*ca.* 26 G)<sup>59</sup> has been interpreted in terms of a planar radical having significant delocalization of the unpaired electron (by analogy with (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Ĉ which has a similar  $a^{13C\alpha}$  value<sup>60</sup>). In this connection, it is worth noting that the s spin density on silicon is about 25% greater than that on the β carbons of B<sub>3</sub>Ĉ but that the s spin density on the carbon and hydrogen of the methyl groups is only about half as great in (Me<sub>3</sub>Si)<sub>3</sub>Ĉ as in B<sub>3</sub>Ĉ.

**$a^{13C\beta}$  and Related Splittings.** Hyperfine splittings by <sup>13</sup>C<sub>β</sub> atoms in natural abundance have not, apparently, been previously observed. The  $a^{13C\beta}$  values found for B<sub>2</sub>ĈH and B<sub>3</sub>Ĉ are a bit smaller than those reported for

(56) D. E. Wood, L. F. Williams, R. F. Sprecker, and W. A. Lathan, *J. Amer. Chem. Soc.*, **94**, 6241 (1972).

(57) An increase along the series CH<sub>3</sub>ĈH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>ĈH, B, is also predicted by theoretical calculations.<sup>3b</sup>

(58) R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967).

(59) A. R. Bassindale, A. J. Bowles, M. A. Cook, C. Eaborn, A. Hudson, R. A. Jackson, and A. E. Jukes, *Chem. Commun.*, 559 (1970).

(60) J. Sinclair and D. Kivelson, *J. Amer. Chem. Soc.*, **90**, 5074 (1968).

(<sup>13</sup>C enriched) simpler alkyl radicals, *viz.*, 13.57 G for ethyl,<sup>58</sup> 13.17 G for isopropyl,<sup>3b</sup> and 12.35 G for B.<sup>3b</sup> They are of similar magnitude to the  $a^{13C\gamma}$  values (as has been found in certain other radicals, *e.g.*, nitroxides<sup>61</sup> and semidionenes<sup>62</sup>).

The B<sub>2</sub>ĈCl radical shows no unexpected epr spectroscopic features. That is,  $a^{35Cl}$  is 2.6 G which is close to the values normally found for α-chloroalkyl radicals,<sup>14, 25, 40, 63</sup> and the g factor is significantly larger than the free spin value as a result of the relatively large spin-orbit coupling constant for chlorine. It was not possible to resolve the lines due to <sup>37</sup>Cl from those due to <sup>35</sup>Cl.

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(61) R. Briere, H. Lemaire, and A. Rassat, *J. Chem. Phys.*, **48**, 1429 (1968).

(62) G. A. Russell and G. R. Underwood, *J. Phys. Chem.*, **72**, 1074 (1968); G. A. Russell, D. F. Lawson, H. L. Malkus, and P. R. Whittle, *J. Chem. Phys.*, **54**, 2164 (1971).

(63) K. Möbius, K. Hoffmann, and M. Plato, *Z. Naturforsch. A*, **23**, 1209 (1968); R. P. Kohin, *J. Chem. Phys.*, **50**, 5356 (1969); A. Hudson, *Chem. Phys. Lett.*, **4**, 295 (1969); A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc. B*, 400 (1969); M. Ballester, J. Riera, J. Castaner, C. Badfa, and J. M. Monso, *J. Amer. Chem. Soc.*, **93**, 2215 (1971); J. P. Michaut and J. Roncin, *Chem. Phys. Lett.*, **12**, 95 (1971).

## Crystal Structure and Molecular Conformation of the Thyroid Hormone Distal 3,5,3'-Triiodo-L-thyronine<sup>1</sup>

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**Abstract:** The crystal structure of the thyroid hormone 3,5,3'-triiodo-L-thyronine (T<sub>3</sub>) has been determined and reveals the 3'-iodine in the distal position, *i.e.*, away from the alanine bearing ring. While this result had been anticipated from stereochemical and biological activity studies, previous crystallographic observations of structures in which the 3'-iodine was proximal had cast some doubt on the crystallographic stability of the 3'-distal conformation. The crystallographic observation of the two forms suggests that the relative energies of the two conformers are similar and that the barrier to internal rotation is not large. Recent molecular energy calculations on the barrier to rotation about the diphenyl ether linkage suggest that this is the case. The structure T<sub>3</sub> crystallizes in the monoclinic space group *P2*<sub>1</sub> with *a* = 13.891 (9), *b* = 5.999 (1), and *c* = 12.264 (3) Å and β = 116.81 (4)°. The final *R* index is 0.041. The planes of the two phenyl rings are skewed with respect to the ether C-O-C plane making angles of 115 and 21° with the inner and outer rings, respectively. The value of χ<sup>1</sup>, the torsional angle about the C<sup>α</sup>-C<sup>β</sup> bond, which describes the amino acid backbone conformation, is 195°.

The question of the conformational preference of the thyroid hormone, triiodothyronine (T<sub>3</sub>, Figure 1), has become increasingly important with the accumulation of recent evidence which suggests that this hormone plays a more significant role in biological activity than had been previously supposed. Recent studies have also established that thyroxine (T<sub>4</sub>) is converted to triiodothyronine in peripheral tissues.<sup>2-4</sup>

(1) Presented, in part, at the American Crystallographic Association Meeting in Storrs, Conn., June 1973.

(2) (a) M. I. Surks, A. R. Schadow, J. M. Stock, and J. H. Oppen-

The deiodination of T<sub>4</sub> yields two distinct conformers as illustrated in Figure 2, that is, a distal conformer in which the 3'-iodine is turned away from the inner ring and a proximal conformer with the 3'-iodine toward the inner ring. Because the 3' and 5' positions of the outer ring of T<sub>3</sub> are chemically equivalent but not conformationally equivalent, as shown by Jorgensen and

heimer, *J. Clin. Invest.*, **52**, 805 (1973); (b) J. H. Oppenheimer, H. L. Schwartz, and M. I. Surks, *ibid.*, **51**, 2493 (1972).

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(4) L. W. Braverman, S. H. Ingbar, and K. Sterling, *J. Clin. Invest.*, **49**, 855 (1970).