p-p Homoconjugation in the β-Chloroethyl Radical

Sir:

The intense interest in the mechanism of β-fluorine and β-chlorine hyperfine interactions in organic radicals is related to the unusual stereochemical and kinetic effects exerted by β-halogen substituents (particularly bromine) in a variety of homolytic reactions. A recent esr study[1a] has indeed shown that simple haloalkyl radicals, particularly those with halogen substituents in the β and γ positions, exist in unique conformations. The structures of the β-fluoro and β-chloroethyl[1b] radicals, especially the latter, are of interest because they are the closest relatives to the (as yet) elusive β-bromoethyl radical, which is itself the subject of considerable interest.

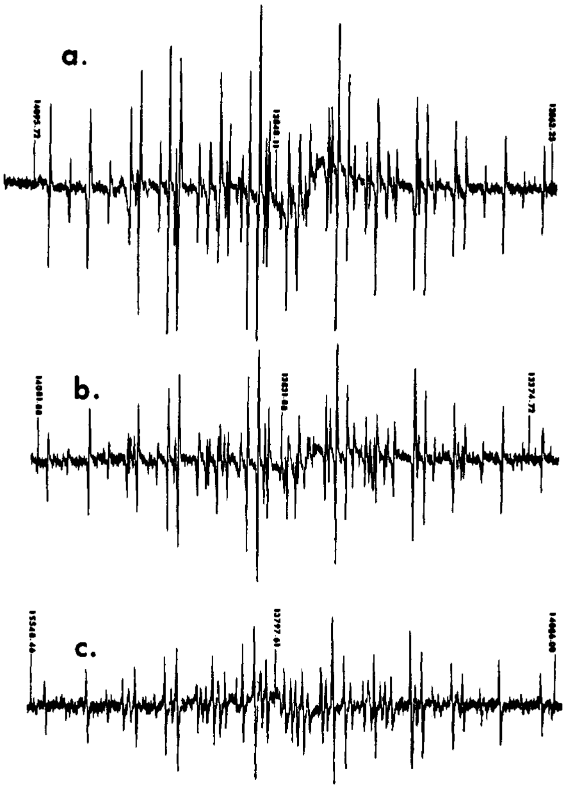


Figure 1. Electron spin resonance spectrum of β-chloroethyl radicals showing the temperature dependence of the hyperfine splitting by β protons, ^{35}Cl and ^{37}Cl at (a) −144°, (b) −125°, and (c) −117°, in cyclopropane solutions.

The well-resolved esr spectrum of the β-chloroethyl radical illustrated in Figure 1 showed no change in the α-proton hyperfine splitting (hfs) value between −60 and −130°. Significantly, the temperature-dependent hfs of the β protons showed a diametrically opposed trend from that of the β chlorine. Furthermore, the slopes and curvatures of the β proton and chlorine hfs plotted in Figure 2 indicate that they are close to limiting values at the lowest temperatures attained (−130°), in contrast to the β-hfs for *n*-propyl and *n*-butyl radicals also shown for comparison. These results and the absence of any selective line broadening in this temperature range are only consistent with the symmetrical conformation I.

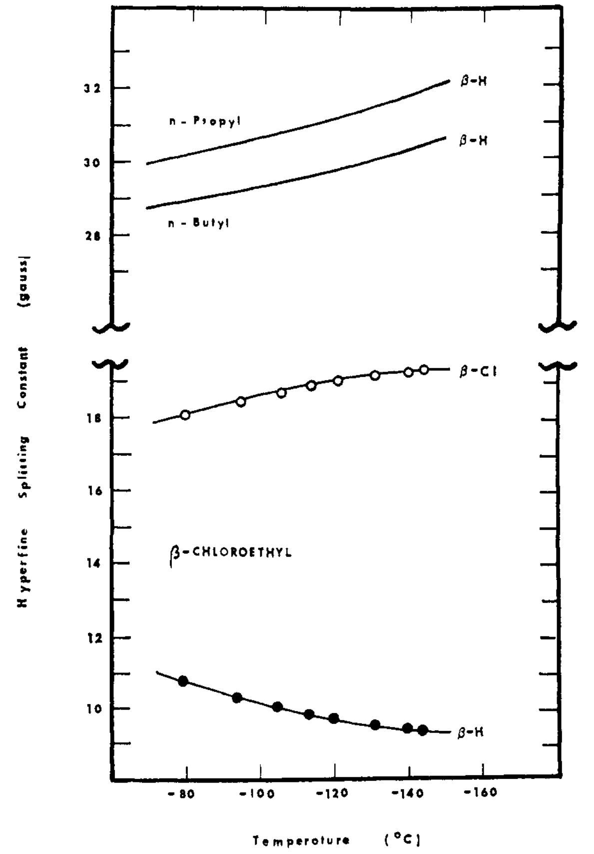
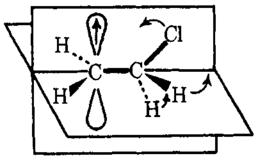


Figure 2. Temperature dependence of the β-proton (●) and the β-^{35}Cl (○) hyperfine splittings in the β-chloroethyl radical.

The unusually small value of the β-proton hfs in the chloroethyl radical cannot be quantitatively accounted for by effecting any conformational change in the radical by rotation about bonds. For example, the low-temperature limit for the β splittings by two equivalent β protons in a "frozen" β-chloroethyl radical (*i.e.*, a conformation I in which the β-chlorine eclipses the p orbital at the radical center) is 13.5 G.[2] The anomaly can be resolved if the radical is distorted at the β carbon so that the two equivalent β protons are displaced toward the nodal plane.[3] Such a distortion could result from the interaction between the orbitals on chlorine and the radical center.



I

In this report we wish to probe the mechanism of this interaction by comparing the esr parameters (especially

---

(1) (a) D. J. Edge and J. K. Kochi, to be published; (b) A. J. Bowles, A. Hudson, and R. A. Jackson, *Chem. Phys. Lett.*, **5**, 552 (1970).

(2) (a) P. J. Krusic and J. K. Kochi, *ibid.*, **93**, 846 (1971); (b) P. J. Krusic, P. Meakin, and J. P. Jesson, *J. Phys. Chem.*, **75**, 3438 (1971).

(3) The temperature dependence of the β-proton hfs indicates that the low-temperature limit is only 8–9 G for the β-chloroethyl radical.[1] To achieve this value, a distortion at the β carbon of 25–30° is obtained from INDO molecular orbital calculations using a simple model based on the frozen conformation of the ethyl radical.[2a] However, the magnitude of this distortion is no doubt exaggerated due to the assumptions made in the calculations.

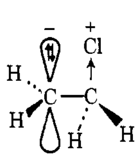
Table I. Esr Parameters of Alkyl and β-Haloalkyl Radicals

Radical $\cdot CH_2CH_2X$	T, °C	$\langle g \rangle$[a]	$\langle A_{H\alpha} \rangle$, G	$\langle A_{H\beta} \rangle$, G	X	$\langle A_X \rangle$, G
$\cdot CH_2CH_3$	−180	2.00260[b]	22.38	26.87		
$\cdot CH_2CH_2CH_3$	−130	2.00265	22.10	31.12	CH_3	0.27[c]
$\cdot CH_2CH_2F$	−122	2.00249	22.15	27.92	^{19}F	45.44
$\cdot CH_2CH_2Cl$	−120	2.00214	21.75	10.20	^{35}Cl	18.78
					^{37}Cl	15.65

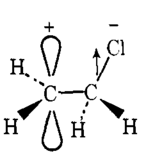
[a] Corrected to second order with respect to hyperfine interactions. [b] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963). [c] Proton.

the g factors) obtained for the series of related radicals listed in Table I.

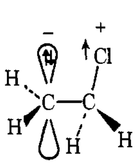
The β-chloroethyl radical is uniquely characterized by an isotropic *g factor which is far smaller than those of alkyl radicals* and is even less than the g factor of a free spin, *viz.*, 2.00232. The large negative shift ($\Delta g = -0.00046$) indicates that the odd electron is delocalized onto orbital(s) around the chlorine nucleus, and possibly includes the C–Cl σ-bonding orbital II, the C–Cl σ-antibonding orbital III, and the p and d orbitals of chlorine, IV and V, respectively, pictorially represented below.



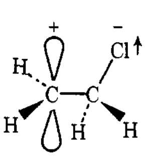
II



III



IV



V

The delocalization of the odd electron onto d orbitals of heavy atoms located in the β position has indeed been shown to produce a negative Δg.[4] However, for a β-chlorine substituent the magnitude of this interaction, V, is insufficient to account for the observed Δg, since the latter is given by $4\xi_d\rho_d/(\epsilon_p - \epsilon_d)$,[4] where ξ_d and ρ_d are the spin–orbit coupling constant and the odd electron density of the chlorine d orbitals, respectively, and $\epsilon_p - \epsilon_d$ represents the difference in energies of the odd electron and d orbitals. Employing values of $\xi_d = 8$ cm^{-1},[5] $\epsilon_p = -(9.8\text{–}6.9)$ eV,[6] $\epsilon_d = -2.2$ eV,[7] and an upper limit to ρ_d of 0.2, we can estimate Δg according to this mechanism as only $-(0.00010\text{–}0.00016)$.

In order to assess the relative importance of the other interactions, we employ the theory of the g factor,[8] using a model of localized two-center σ molecular orbitals and one-center lone-pair orbitals. Thus, hyperconjugative delocalization onto the C–Cl σ orbitals (*i.e.*, admixing II or III with I) produces a positive Δg because of the high-lying lone-pair orbitals of chlorine which are perpendicular to the σ orbitals. On the other hand, the odd electron delocalization onto the lone-pair orbital (n_{Cl}) directed toward the radical center gives a negative Δg component due to the low-lying[9] C–Cl σ-antibonding orbital (σ_{CCl^*}), as well as a positive Δg component arising from the chlorine lone-pair orbital (n_{Cl}') which is perpendicular to n_{Cl}. In order to estimate the g factor by the above mechanism, the following molecular orbitals were employed: $\varphi(\sigma_{CCl^*}) = 0.932\chi_{Cl} - 0.954\chi_C$,[10] [$\epsilon_{\sigma^*} = -5.20$ eV];[12] $\varphi(n_{Cl})$; $\varphi(n_{Cl}') = $ 3p AO's $\perp$ C–Cl, [$\epsilon_n = \epsilon_{n'} = -11.42$ eV];[13] $\varphi(\sigma_{CCl}) = 0.608\chi_{Cl} + 0.571\chi_C$.[10] The odd electron orbital φ_p which represents the mixing of II, III, and IV with I has the form

$$\varphi_p = \chi_\pi + C_\sigma\varphi(\sigma_{CCl}) + C_\sigma{}^*\varphi(\sigma_{CCl^*}) + C_n\varphi(n_{Cl}) + \ldots \quad (1)$$

in which χ_π designates the $2p_\pi$ orbital on the radical center. The isotropic g factor of the β-chloroethyl radical is then derived as[8, 15]

$$g = g_e + \Delta g_C + 0.0092C_\sigma{}^2 + 0.0210C_{\sigma^*}{}^2 - 0.0059C_n{}^2 \quad (2)$$

where g_e and Δg_C are the g factor of the free spin and the contribution from the odd electron density in the alkyl moiety, respectively, and both are approximated by the g factor of ethyl radical. In order to account for the negative Δg observed, $C_n{}^2$ in eq 2 must be dominant over $C_\sigma{}^2$ and $C_{\sigma^*}{}^2$. The latter are negligible in the simplest formulation,[16] which would indicate a 7% spin delocalization to the 3p orbital of chlorine from the radical center. Such a homoconjugative interaction, together with the inequivalence of the hfs of the α and β protons, lends support for an asymmetric bridging of the chlorine atom to the radical center. Furthermore, the p–p homoconjugation should be larger in the corresponding β-chloroethyl *cation* due to the empty π orbital on carbon, and the latter is supported by nmr studies which indicate a trend toward symmetrical bridging.[17]

(4) T. Kawamura and J. Kochi, *J. Amer. Chem. Soc.*, **94**, 648 (1972).

(5) C. E. Moore, *Nat. Bur. Stand.* (*U.S.*) *Circ.*, No. 467, 195 (1949).

(6) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).

(7) K. A. Levison and P. G. Perkins, *Theor. Chim. Acta*, **14**, 206 (1969).

(8) A. J. Stone, *Proc. Roy. Soc., Ser. A*, **271**, 424 (1963); *Mol. Phys.*, **6**, 509 (1963).

(9) T. Yonezawa, H. Kato, H. Saito, and K. Fukui, *Bull. Chem. Soc. Jap.*, **35**, 1814 (1962); K. Fukui, K. Morokuma, H. Kato, and T. Yonezawa, *ibid.*, **36**, 217 (1963).

(10) χ_{Cl} and χ_C represent the 3p atomic orbital of chlorine and the sp^3 hybrid orbital of carbon involved in the C–Cl σ bond. The coefficients are determined by solving the second-order secular equation, $|H_{ij} - S_{ij}\epsilon| = 0$. H_{ii} is approximated by the negative value of the valence state ionization potential[11] of the atomic orbital and H_{ij} is estimated by $1.75S_{ij}(H_{ii} + H_{jj})/2$.

(11) J. Hinze and H. H. Jaffe, *J. Amer. Chem. Soc.*, **84**, 540 (1962).

(12) Estimated from the first ionization potential[13] and n-σ^* transition[14] in the spectrum of chloromethane.

(13) D. C. Frost and C. A. McDowell, *Proc. Roy. Soc., Ser. A*, **241**, 194 (1957).

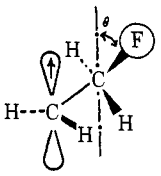
(14) G. Herzberg "Molecular Spectra and Molecular Structure," Vol. III, Van Nostrand Reinhold Co., New York, N. Y., 1966, Table 69; R. S. Mulliken, *J. Chem. Phys.*, **8**, 282 (1940).

(15) The value of −7.5 eV is adopted for the orbital energy of the odd electron which is lower than that for ethyl radical due to interaction with the β chlorine. The value of the 587 cm^{-1} is used for the spin–orbit coupling constant of the chlorine 3p orbital [E. U. Condon and G. H. Shortley, "Theory of Atomic Spectra," Cambridge University Press, New York, N. Y., 1953].

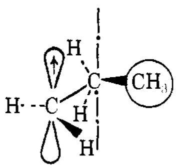
(16) The hyperconjugative interaction with the β chlorine cannot be simply computed from the value of the chlorine hfs and the contact term for chlorine, since the s characters of the C–Cl σ and σ^* orbitals are unknown.

(17) G. A. Olah, J. M. Bollinger, and J. Brinich, *J. Amer. Chem. Soc.*, **90**, 2587 (1968); G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969); G. A. Olah and J. M. Bollinger, *ibid.*, **89**, 4744 (1967).

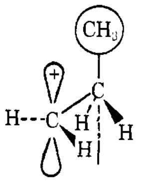
The shift in the g factor of the β-fluoroethyl radical is less than that of the β-chloroethyl radical (Table I). Thus, the magnitude of the p–p homoconjugation in this radical, previously proposed by Lossing[18] and by Iwasaki[19] on the basis of single-crystal studies, is smaller than the interaction in the β-chloroethyl radical. Interestingly, the conformation VI (θ = 50°) adopted by the β-fluoroethyl radical is also intermediate between that of the *n*-propyl radical, VII, and the β-chloroethyl radical (see ref 1). Recent calculations[20] show that the stable conformation of the *n*-propyl cation VIII (in contrast to the *n*-propyl radical) is one in which the methyl group eclipses the p orbital. The rotational barriers are also substantially higher (2.5 *vs.* 0.4 kcal/mol),[2b] which can be ascribed to stabilization of the cation by hyperconjugative effects. Since equilibrium conformations in an alkyl chain result from a delicate balance between steric repulsions and electron delocalization, the trend toward greater eclipsing of the halogen in proceeding from fluorine to chlorine is attributed to an increasing interaction between the odd electron orbital and the halogen,[16] and is consistent with the higher rotational barrier in the β-chloroethyl radical.



VI



VII



VIII

---

(18) R. J. Lossing, *J. Chem. Phys.*, 47, 3634 (1967).

(19) M. Iwasaki, *Mol Phys.*, 20, 503 (1970); *J. Amer. Chem. Soc.*, **92**, 6348 (1970).

(20) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *ibid.*, **92**, 6380, 6987 (1970).

T. Kawamura, D. J. Edge, J. K. Kochi*
Department of Chemistry, Indiana University
Bloomington, Indiana 47401

Received November 18, 1971

The Structure of Staphisine, a Novel Diterpene Alkaloid Dimer

Sir:

Staphisine, $C_{43}H_{60}N_2O_2$, mp 200–208°, $[\alpha]^{25}D$ −159° (benzene), was isolated by Jacobs and Craig in 1941 from the mother liquors accumulated during the isolation of delphinine from the seeds of *Delphinium staphisagria.*[1] Selenium dehydrogenation furnished a complex mixture from which products identified as pimanthrene and 1,3-dimethyl-7-isopropylphenanthrene were isolated.[2,3] Analytical and uv determinations showed the presence of an NCH_3 group and a conjugated double bond system in the molecule. Staphisine was reported to form several crystalline salts, including a mono- and a dimethiodide.[1] On the basis of these data, Craig and Jacobs postulated that staphisine is a diterpene alkaloid dimer with the molecular formula $C_{42}H_{60}N_2O$.[3]

Although staphisine forms various salts, chemical degradation of the substance usually results in complex changes which give rise to numerous products. The alkaloid is also sensitive to heat and light. Staphisine does not react with hydroxylamine or acetic anhydride. Hydrogenation studies have shown absorption of approximately 2 mol of hydrogen/mol of staphisine, but the product is a mixture of isomers.[1] The mass spectrum of one of these isomers shows a molecular ion at *m/e* 640, indicating saturation of two double bonds. Microanalysis of staphisine shows 1.61% OCH_3, which, while low, is positive for the presence of a methoxyl group. The *N*-methyl analysis of 5.14% corresponds to between one and two *N*-methyl groups. The active hydrogen determination is negative.

The molecular ion at *m/e* 636.4648 in the mass spectrum of staphisine is in agreement with the molecular formula $C_{43}H_{60}N_2O_2$. The infrared spectrum of staphisine shows no absorption in the regions 4000–3100 and 2500–1750 cm^{-1}, and only very weak absorption at 1710 and 1630 in the region 1750–1500 cm^{-1}. This information, in view of the chemical data, suggests that the oxygen atoms are located in ether linkages [$\nu_{(CHCl_3)}$ 1101 (s), 1063 (s) cm^{-1} (COC)]. The ultraviolet spectrum shows absorption at λ_{max} (95% EtOH) 268 nm (ϵ 17,300), in agreement with a transoid heteroannular conjugated diene system adjacent to a cyclopropyl ring, as subsequently determined by the X-ray analysis (see below).

The nmr spectrum of staphisine is subject to a marked solvent dependence: (benzene-d_6) δ 0.18 (1 H, s, cyclopropyl), 0.72 (1 H, m, cyclopropyl), 0.85 (3 H, s, angular methyl), 0.95 (3 H, s, angular methyl), 2.03 (6 H, s, *N*-methyls), 2.22 (3 H, s, *O*-methyl), 3.18 (2 H, m, hydrogens adjacent to oxygen), 6.18 (1 H, d, vinyl proton) ppm. The nmr spectrum of a 2:1 molar mixture of $Eu(thd)_3$ to staphisine in CS_2 shows the 6 H singlet originally at δ 2.00 ppm shifted downfield and separated into two 3 H singlets at δ 2.99 and 3.28 ppm. The 3 H singlet at δ 2.20 ppm is not shifted and is assigned as the absorption of the methoxyl group.

Because of the small amount of staphisine available and the inconclusive nature of the chemical and spectral data we undertook a single-crystal X-ray structure determination of the monomethiodide of staphisine. This derivative [mp 285–290° dec] was prepared by treatment of an ethereal solution of staphisine with methyl iodide. Staphisine methiodide crystallized from 95% ethanol as thin plates in space group $P2_12_12_1$ with a = 47.95, b = 10.54, and c = 8.60 Å, $\alpha = \beta = \gamma$ = 90°, U = 4346 Å^3. The density calculated for $C_{43}H_{60}N_2O_2 \cdot CH_3I$ and Z = 4 is 1.19 g/cm^3, a value significantly lower than the observed density of 1.35 g/cm^3 (by flotation in pentane–carbon tetrachloride). Assuming one molecule of ethanol of crystallization per formula gives a calculated density of 1.26 g/cm^3. The elemental analysis of the salt is in agreement with one molecule of ethanol of crystallization per formula. *Anal.* Calcd for $C_{43}H_{60}N_2O_2 \cdot CH_3I \cdot C_2H_6O$: C, 66.97; H, 8.43; I, 15.38. Found: C, 67.16; H, 8.67; I, 17.07

Initially, data were collected by the Weissenberg equiinclination technique using multiple films and Cu Kα radiation. Data were estimated visually using a standard intensity strip prepared from the same crystal. The 1838 unique nonzero reflections were corrected for

---

(1) W. A. Jacobs and L. C. Craig, *J. Biol. Chem.*, **141**, 67 (1941).

(2) L. C. Craig and W. A. Jacobs, *ibid.*, **152**, 645 (1944).

(3) C. F. Huebner and W. A. Jacobs, *ibid.*, **169**, 211 (1947).