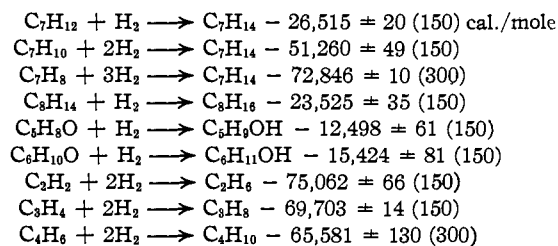We have restricted our discussion to the simplest organic compounds because only for them reliable thermochemical and structural data exist, but one could readily extend it *ad infinitum* by borrowing from the more qualitative organic evidence. Concluding, we wish to stress that steric hindrance in the sense discussed above is generally responsible for the effects of substituents upon the "standard" properties of functional groups in polyatomic molecules and that therefore it is rightly placed next to resonance in importance as the source of variety among organic compounds.

Summary

The following heats of hydrogenation have been determined. All data refer to 355°K. in the gaseous phase.

$C_7H_{12} + H_2 \longrightarrow C_7H_{14} - 26,515 \pm 20 \,(150)$ cal./mole
$C_7H_{10} + 2H_2 \longrightarrow C_7H_{14} - 51,260 \pm 49 \,(150)$
$C_7H_8 + 3H_2 \longrightarrow C_7H_{14} - 72,846 \pm 10 \,(300)$
$C_8H_{14} + H_2 \longrightarrow C_8H_{16} - 23,525 \pm 35 \,(150)$
$C_5H_8O + H_2 \longrightarrow C_5H_9OH - 12,498 \pm 61 \,(150)$
$C_6H_{10}O + H_2 \longrightarrow C_6H_{11}OH - 15,424 \pm 81 \,(150)$
$C_2H_2 + 2H_2 \longrightarrow C_2H_6 - 75,062 \pm 66 \,(150)$
$C_3H_4 + 2H_2 \longrightarrow C_3H_8 - 69,703 \pm 14 \,(150)$
$C_4H_6 + 2H_2 \longrightarrow C_4H_{10} - 65,581 \pm 130 \,(300)$

A consideration of the entire work on the heats of addition reactions and of other experimental data found in the literature reveals the large magnitude of steric hindrances exercised by non-bonded atoms in simple organic molecules. These repulsive interactions are stronger than supposed hitherto and contribute largely to the variation in the properties of the functional groups.

Internal Rotation and Resonance in Hydrocarbons

BY EVERETT GORIN, JOHN WALTER AND HENRY EYRING

Introduction

Recent experimental evidence indicates the existence of a potential barrier of the order of 3000 cal. restricting the rotation of the methyl groups about the C–C bond in ethane. The data on the specific heat of ethane gas at low temperatures[1] and the entropy of ethane as determined both from the third law and from the hydrogenation of ethylene are in accord with this assumption.[2] The structure of the rotation bands in the ethane spectrum has also been interpreted as indicating a barrier of at least 2000 cal.[3]

On the other hand the repulsion due to the hydrogen atoms calculated according to standard quantum mechanical procedure for the usual valence bond structure yields a potential barrier of 300 cal. with a minimum corresponding to the staggered position of symmetry D_{3d}. In this calculation the van der Waals attractive potential between hydrogens was taken as $101/R^6$.[4]

It was pointed out by Penney[5] that with the Slater–Pauling model for the carbon bond in ethane the repulsions taken account of in the above calculation are the only ones present if we use the single valence structure.

Barrier Height if Protons Replace Hydrogen Atoms.—If we suppose the hydrogen atoms be replaced by protons, the structure otherwise remaining unchanged, the potential barrier from the coulomb repulsions is 5200 cal. with a minimum in the staggered position. This is of course an upper limit and a more exact calculation than

(1) Kistiakowsky and Nazmi, *J. Chem. Phys.*, **6**, 18 (1938); Hunsman, *Z. physik. Chem.*, **B39**, 23 (1938); Wilson, *J. Chem. Phys.*, **6**, 740 (1938); see, however, Eucken and Weigert, *Z. physik. Chem.*, **B23**, 265 (1933).

(2) Smith and Vaughan, *J. Chem. Phys.*, **3**, 341 (1935); Teller and Topley, *J. Chem. Soc.*, 876 (1935); Kemp and Pitzer, THIS JOURNAL, **59**, 276 (1937).

(3) Howard, *J. Chem. Phys.*, **5**, 451 (1937).

(4) H. Eyring, THIS JOURNAL, **54**, 319 (1932).

(5) W. G. Penney, *Proc. Roy. Soc.* (London), **A144**, 166 (1934).

the one which yielded 300 cal. could not give a much larger value since it can only be a small fraction of the 5200 cal.

Lack of Cylindricity of the C–C Bond.—The carbon–carbon bonding orbitals are distorted by the presence of the three hydrogen atoms on each methyl radical so that they are no longer cylindrically symmetric about the C–C bond. If this distortion were large, conceivably a large barrier might arise simply from the lack of cylindrical ·symmetry of the interaction between the carbon–carbon bonding orbitals. The orbital of lowest energy which can be added is limited by symmetry considerations to the $4f$ orbital, $\psi_{4f} = f(r) \sin^3 \theta \cos 3\varphi$, that is, the C–C bonding eigenfunction can be written as

$$\psi = c_1 \psi_{2t\sigma} + c_2 \psi_{4f}$$

where $\psi_{2t\sigma}$ is the tetrahedral function whose axis lies along the bond direction.

This $4f$ orbital overlaps the hydrogen nuclei only very slightly so that the perturbations of the hydrogen atoms can at most give rise to a very small value for c_2. If we consider that the interaction of the hydrogen atoms can be represented by their coulombic attraction for the C–C bonding orbitals, we can estimate roughly an upper limit for the barrier resulting from this cause. That this neglect of the exchange integrals will not change the order of magnitude of the coefficient c_2^2 is indicated by the calculations of Wood on methane,[6] where he finds the exchange and coulombic interactions are approximately equal in magnitude. The position of maximum binding is given by the position of maximum overlap of the two bond distributions if the exchange term in the (ff) interaction predominates, or by the position of minimum overlap if the coulombic term predominates. The potential barrier is of the form $V_0/2 \cos 3\chi$ where χ is the angle of rotation with respect to the opposed position as zero. V_0 is given by $c_2^2 (ff)$, where (ff) is the interaction between the f orbitals on the two carbon atoms. A variational calculation indicates that c_2 is of the order of magnitude of 0.015. Since the energy of an f orbital is near the ionization limit, we expect the (ff) binding to be considerably less than the binding due to the tetrahedral carbon orbitals. As the barrier is proportional to c_2^2, which as we see is small, we conclude that the contribution to the barrier from the dis-

tortion in the cylindrical symmetry of the carbon–carbon bonding orbitals is negligibly small.

Barrier Due to Hybridization between Tetrahedral and 3d Orbitals.—It is also possible to modify the C–H bonding functions in such a way that the sum of their charge distributions is not cylindrically symmetric about the C–C bond. To do this it is necessary to take such a linear combination of the $2s$, $2p$, and $3d$ orbitals as to give three equivalent bonds. For simplicity, we have taken the combination which gives four equivalent tetrahedral bonds.[7]

$$\psi_{111} = c_1 s + \frac{c_2}{(3)^{1/2}} (p_x + p_y + p_z) +$$
$$\frac{c_3}{(3)^{1/2}} (d_{x+y} + d_{x+z} + d_{y+z})$$
$$\psi_{1\bar{1}\bar{1}} = c_1 s + \frac{c_2}{(3)^{1/2}} (p_x - p_y - p_z) +$$
$$\frac{c_3}{(3)^{1/2}} (-d_{x+y} - d_{x-z} + d_{y+z})$$
$$\psi_{\bar{1}1\bar{1}} = c_1 s + \frac{c_2}{(3)^{1/2}} (-p_x + p_y - p_z) +$$
$$\frac{c_3}{(3)^{1/2}} (-d_{x+y} + d_{x+z} - d_{y+z})$$
$$\psi_{\bar{1}\bar{1}1} = c_1 s + \frac{c_2}{(3)^{1/2}} (-p_x - p_y + p_z) +$$
$$\frac{c_3}{(3)^{1/2}} (+d_{x+y} - d_{x+z} - d_{y+z})$$
$$(2)$$

The coördinate system used here is so defined that the carbon atom is located at the origin. The x, y and z axes are perpendicular to the faces of the cube about the carbon atom as center. The four orbitals point out toward the 111, $1\bar{1}\bar{1}$, $\bar{1}1\bar{1}$ and $\bar{1}\bar{1}1$ corners of the cube.

Slater's wave functions were used for the s and p orbitals with effective nuclear charge equal to 3.25. This same effective nuclear charge was also used in the d orbitals. No doubt a better value for the energy could have been obtained by introducing the effective nuclear charge as a variable parameter in the d functions. This, however, has not been done as we were only interested in a rough estimate of the energy. The coefficients are chosen so that the functions are normalized and orthogonal. We have considered that as a good approximation the amount of d-ness in the C–H bonds of ethane is the same as in methane. The third relationship necessary to fix the values of the coefficients is given by the condition that the total energy of methane must be a minimum. The energy of the methane molecule upon the assumption of electron pairing can be expressed approximately as

$$E = Q_1 + 4\alpha - 3(\beta + \gamma + 2\delta). \tag{3}$$

(6) Wood, *Trans. Faraday Soc.*, **28**, 877 (1932).

(7) L. Pauling, THIS JOURNAL, **53**, 1367 (1931).

Q_1 = orbital energy + coulombic interaction between all orbitals.

α = exchange energy of C–H bond.

δ = exchange energy of C with H orbitals not bound together.

β = exchange energy between two H atoms.

γ = exchange energy of carbon orbitals.

The coefficient c_3 in equation (2) can be determined by minimizing the energy as expressed in (3). The exchange integral α gives a contribution of the same sign and the same order of magnitude as the coulombic integrals, while the integrals β and δ are small. Neglecting the integrals α, β, δ, since the effect of including α, β, δ would be to increase c_3, we calculate a minimum value for $c_3 = 0.086$. If we assume, as is reasonable from Wood's calculation on methane, that the exchange and coulombic integrals are equal, we get a value twice as large. The sums of the squares of the eigenfunctions give for the non-cylindrically symmetric part of the charge distribution the expression

$$\frac{2}{3\pi}\left(\frac{15}{2}\right)^{1/2} c_2 c_3 \, f(r) \sin^3 \theta \cos 3\varphi \qquad (4)$$

where $f(r)$ is the product of the normalized radial part of the $2p$ and $3d$ eigenfunctions. The electrostatic interaction of the two charge distributions also gives a barrier of the form

$$(V_0/2) \cos 3\chi$$

Rigorously, we would have to subtract from V_0 an amount corresponding to one-half the exchange interactions between those parts of the orbitals not bound together which depend upon the angle χ. This can at most be equal to $1/2 V_0$, and probably would be considerably less. Since for the electrostatic repulsion between the electrons the coulombic integral is always greater than the neglected exchange integral, V_0 is equal to the coulombic interaction between the two charge distributions, one on each carbon atom, given by (4).

In kcal., the calculated value of V_0 is $23.2 c_3^2$. Including the exchange integrals would approximately double the calculated value $c_3 = 0.086$ so that we take as a reasonable value $c_3 = 0.15$; we have a maximum for the barrier due to this interaction between the hybridized C orbitals of 500 cal. favoring the staggered configuration.

There is still one other contribution to the barrier arising from this hybridization, *i. e.*, that due to interaction between the H atoms on one carbon with the carbon orbital on the other. Again we will consider only the coulombic inter-

action since including the exchange integrals would at most reduce the barrier arising in this way by a factor of two. The coulombic potential of an electron in the field of a hydrogen atom is given by $-\dfrac{e^2}{a_0}\left(1 - \dfrac{a_0}{r}\right)e^{-2\,r/a_0}$. The coulombic integral between the non-symmetrical part of the charge distribution about the carbon atom is therefore given by

$$-\frac{e^2}{a_0}\left(\frac{3.25}{a_0}\right)^6 \frac{6^{1/2}\, c_2 c_3}{729\pi} \int r_a{}^3 \exp.(-{}^5/_6 \cdot 3.25 r_a/a_0)(x_a{}^3 -$$
$$3 x_a y_a{}^2)\left(1 + \frac{a_0}{r_b}\right)\exp.(-2 r_b/a_0)\mathrm{d}\tau \quad (5)$$

Here r_a, x_a, y_a, z_a refer to a coördinate system about the carbon atom as center and the z-axis lies along the C–C bond direction. r_b refers to the hydrogen atom as center of coördinates. Upon evaluating this integral and introducing the value 0.15 for c_3 we obtain for a hydrogen atom in the opposed position 120 cal. Due to the three-fold symmetry of the charge distribution all hydrogen atoms are equivalent. In the staggered position the integral is just the negative of this, *i. e.*, -120 cal. The barrier is thus equal to 12×120 cal. or 1440 cal. This is larger than the effect calculated previously and of opposite direction. If we included exchange interactions this would be reduced at most to 700 cal. Summarizing the results, then, we get the following contributions to the barrier, 300 cal. staggered from the hydrogen repulsions, 250 minimum to 500 cal. maximum from the interaction between the hybridized carbon orbitals with the staggered configuration favored and 700 minimum to 1400 maximum cal. from the interactions between the hydrogen atoms and the hybridized carbon orbitals with the opposed configuration stable. We thus see that the sum of these effects gives a small barrier of up to 600 cal. with the opposed configuration the stable one. It is a rather surprising result that there should be enough resonance between the tetrahedral sp^3 configuration of carbon and the higher configurations containing $3d$ orbitals to actually change the stable form from the staggered to the opposed configuration. However, there are still other resonance effects to consider which we will now discuss.

Resonance Involving Double Bond Structures.—In discussing the resonance between the single and double bond structures it is convenient to adopt the nomenclature for the electronic orbitals indicated by the letters in Fig. 1. Reso-

nance between the following bond structures was considered in the usual quantum mechanical scheme to find the lowest energy. The eigenfunctions are indicated by writing together the

$$\begin{vmatrix} 3\alpha - \dfrac{W}{3} & \dfrac{3}{4}(\xi + \mu - 2\zeta) \\[2mm] \dfrac{3}{4}(\xi + \mu - 2\zeta) & \dfrac{15}{4}\alpha + \dfrac{3}{4}(\xi + \mu + 2\zeta) - \dfrac{3}{4}W \\[2mm] \dfrac{3}{2}(\epsilon + \varphi - 2\eta) & -\dfrac{3}{2}(\gamma + \beta) \end{vmatrix}$$

two letters which form a bond.

$$\begin{aligned}
\psi_1 &= ae \ cg \ bf \ dh \ kn \ il \ jm \\
\psi_2 &= ae \ fl \ bi \ dh \ cg \ kn \ jm \\
\psi_3 &= em \ aj \ dh \ bf \ cg \ il \ kn \\
\psi_4 &= gn \ ck \ dh \ ae \ bf \ il \ jm \\
\psi_5 &= bk \ fn \ dh \ ae \ cg \ jm \ il \\
\psi_6 &= fm \ bj \ ae \ cg \ dh \ kn \ il \\
\psi_7 &= el \ ai \ dh \ bf \ cg \ kn \ jm \\
\psi_8 &= en \ ak \ dh \ cg \ bf \ jm \ il \\
\psi_9 &= ci \ gl \ ae \ bf \ jm \ kn \ dh \\
\psi_{10} &= cj \ gm \ ae \ bf \ dh \ kn \ il
\end{aligned} \tag{6}$$

From symmetry considerations we know that the proper linear combination of eigenfunctions must have the form

$$\varphi = a\psi_1 + b\sum_{i=2}^{4}\psi_i + c\sum_{j=5}^{10}\psi_j \tag{7}$$

This leads to the following secular equation

$$\begin{aligned}
&a(H_{11} - S_{11}E) + 3b(H_{12} - S_{12}E) + 6c(H_{1,10} - S_{1,10}E) = 0. \\
&3a(H_{12} - S_{12}E) + b[3H_{22} + 6H_{23} - (3S_{22} + 6S_{23})E] \\
&\quad + 6c[H_{10,2} + H_{10,3} + H_{10,4} - (S_{10,2} + S_{10,3} + S_{10,4})E] = 0 \\
&(6a[H_{1,10} - S_{1,10}E) + 6b[H_{10,2} + H_{10,3} + H_{10,4} \\
&\quad - (S_{10,2} + S_{10,3} + S_{10,4})E] + 6c[H_{55} + 2H_{56} + 3H_{57} \\
&\quad - (S_{55} + 2S_{56} + 3S_{57})E] = 0
\end{aligned} \tag{8}$$

The exchange integrals between the following pairs of orbitals are indicated by the Greek letters.

$$\begin{aligned}
\alpha &= ae &= bf &= cg &= kn &= jm &= il \\
\theta &= dh \\
\xi &= bi &= aj &= ck \\
\mu &= fl &= em &= gn \\
\zeta &= am &= cn &= bl &= if &= je &= kg \\
\epsilon &= cj &= ci &= ak &= ai &= bk &= bj \\
\varphi &= gm &= gl &= em &= el &= fn &= fm \\
\eta &= cm &= cl &= al &= an &= bn &= bm &= ie \\
&= ig &= jf &= jg &= kf &= ke \\
\delta &= ec &= eb &= fa &= fc &= ga &= gb &= il \\
&= in &= jl &= jn &= km &= kl &= df &= de \\
&= dg &= lh &= hm &= hn \\
\beta &= eg &= ef &= fg &= lm &= mn &= nl \\
\gamma &= ac &= ab &= bc &= ij &= jk &= ik &= db \\
&= ad &= cd &= jh &= ih &= kh \\
\sigma &= dm &= dl &= dn &= hf &= he &= hg \\
\lambda &= di &= dj &= dk &= ah &= eh &= ch
\end{aligned} \tag{9}$$

The matrix components were calculated in the way described by Eyring and Kimball.[8] Deter-

(8) H. Eyring and G. E. Kimball, J. Chem. Phys., 1, 239 (1933); see, also, Pauling, ibid., 1, 280 (1933).

minant (8) after the slight rearrangement corresponding to orthogonalizing the three eigenfunctions which are the coefficients of a, b and c in equation (7) takes the simplified form

$$\begin{vmatrix} \dfrac{3}{2}(\epsilon + \varphi - 2\eta) \\[2mm] -\dfrac{3}{2}(\gamma + \beta) \\[2mm] \dfrac{15}{2}\alpha + \dfrac{3}{2}(\epsilon + \varphi + 2\eta) + 3\delta - \dfrac{3}{2}(\gamma + \beta) - \dfrac{3}{2}W \end{vmatrix} = 0 \tag{10}$$

W of equation 10 is related to E by

$$W = E - Q + 1/2\Sigma - 3/2\,\theta,$$

where E is the actual total bonding energy for ethane formed from two quadrivalent carbon atoms. Q is the coulombic energy and Σ is the sum of the 91 exchange integrals listed in (9).
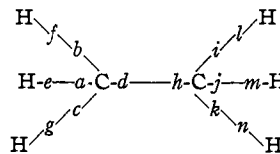

Fig. 1.

In the following numerical calculations for the difference in energy between staggered and opposed forms due to the double bonds we assume the usual tetrahedral carbon bonds. In Table I we list the values for the exchange integrals occurring in (10) for the various calculations of interest. All values in Table I are in kcal.

In all the calculations of Table I where the value of an integral for a staggered configuration is not explicitly given it was taken equal to the corresponding value in calculation 1. The same is true for opposed configurations. In calculating the integrals α and δ the values given by Van Vleck[9] for the elementary $N_{\sigma\sigma} = 2.3$, $N_{ss} = +2.0$, $N_{\pi\pi} = -0.6$ and $N_{\sigma s} = +1.0$ in volts were used in his formulas

$$-4\alpha = N_{ss} + 3N_{\sigma\sigma} + 2(3)^{1/2}N_{\sigma s}$$
$$-12\delta = 3N_{ss} + N_{\sigma\sigma} + 8N_{\pi\pi} - 2(3)^{1/2}N_{\sigma s}$$

to give his values $\alpha = 72$ cal., $\delta \approx 0$. Van Vleck's formula

$$16\gamma = F_0(2s;\ 2s) - 2F_0(2s;\ 2p) + F_0(2p;$$
$$2p) + 28\,F_2 + 4\,G_1$$

with the value given by Voge[10] for the F's and G's was used to calculate γ. β was taken from the H–H Morse curve with the constants $D = 102.4$, $r_0 = 0.74$, $\omega_0 = 4375$ which gives a value for Morse's a of 1.94. The exchange binding was

(9) J. H. Van Vleck, J. Chem. Phys., 2, 20 (1933).
(10) H. H. Voge, ibid., 4, 581 (1936).

TABLE I

	α	β	γ	δ	ϵ	φ	η	μ	ξ	ζ	W	ΔW	ΔE
Calcd. 1 staggered	72	19.4	−20.7	0	17.2	1.9	0	0.4	28.7	3.7	658.0		
opposed	72	19.4	−20.7	0	17.2	0.5	1.1	3.8	28.7	1.5	659.4	1.4	0.7
Calcd. 2 staggered						5.4		1.6			660.9		
opposed						2.4		8.6			663.1	2.2	1.3
Calcd. 3 staggered					18.2				26.7		658.0		
opposed					16.2				30.7		660.0	2.0	1.3
Calcd. 4 staggered					18.2	5.4		1.6	26.7		660.9		
opposed					16.2	2.4		8.6	30.7		663.7	2.8	1.9
Calcd. 5 staggered					12.3	5.4		1.6	38.7		662.6		
opposed					22.3	2.4		8.6	18.7		661.3	−1.3	−2.2

taken as 0.8 of the total. ζ and η are special cases of the more general integral

$$I = 3/4 \left\{ C_1^2 N_{\sigma\sigma} + \frac{2}{\sqrt{3}} C_1 N_{\sigma s} + 1/3 N_{ss} + (C_2^2 + C_3^2) N_{\pi\pi} \right\}$$

where

$C_1 = 2/3 \sqrt{2}\, a \cos \varphi + b/3$
$C_2 = (1 - a^2 \sin {}^2\varphi)^{-1/2}(-2/3\, 2^{1/2}\, b - 1/3\, a \cos \varphi)$
$C_3 = (1 - a^2 \sin {}^2\varphi)^{-1/2}(2/3\, 2^{1/2}\, a^2 \sin \varphi \cos \varphi - 1/3\, ab \sin \varphi)$.

in which $a = 0.486$, $b = -0.874$. φ is the angle of rotation of the hydrogen atom about the C–C axis. $\varphi = 0$ where the hydrogen atom and the interacting carbon orbital lie in a plane which includes the C–C bond direction. ζ is obtained from these formulas by inserting $\varphi = 0$ for the opposed form and $\varphi = 180°$ for the staggered configuration. For η, one should use $\varphi = 120°$ for the opposed form and $\varphi = 60°$ for the staggered. The integrals $N_{\sigma\sigma}$, $N_{\sigma s}$, etc., were assumed to vary with the distance in the way given by a C–H Morse curve.

The exchange interaction between carbon orbitals other than those forming the carbon-carbon bond and on opposite carbons can be expressed in terms of the more fundamental integrals by the formula

$$I_{\text{carbon–carbon}} = C_2^4 (N_{yy,yy} - N_{xy,xy}) \cos^2 \omega + \{ C_1^2 C_2^2 (2N_{ssyy} + 2N_{syys}) + C_1 C_2^2 C_3 (4N_{syyz} + 2N_{yysz}) + C_2^2 C_3^2 (2N_{yyzz} + 2N_{yzzy}) \} \cos \omega + C_1^4 N_{ssss} + C_2^4 N_{zyzy} + C_3^4 N_{zzzz} + 2C_1^2 C_2^2 N_{ysys} + C_1^2 C_3^2 \{2N_{ssss} + 4N_{szsz}\} + 2C_2^2 C_3^2 N_{yzyz} + 4C_1 C_3^3 N_{zzzs} + 4C_1^3 C_3 + C_1 C_2^2 C_3 \{4N_{ysyz} + 2N_{yyss}\}$$ where $c_1 = 1/2$ $c_2 = (2/3)^{1/2}$ $c_3 = (2(3)^{1/2})^{-1}$

where the integrals $N_{mn,op}$ are defined by the expression

$$N_{mn,op} = \int \int \psi_{am}(1)\, \psi_{bn}(1)\, H'\, \psi_{ao}(2)\, \psi_{bp}(2)\, dv_1\, dv_2$$

where a refers to the function ψ_a about carbon atom a as center and b to function ψ_b about the carbon atom b.

$$H' = e^2 \left(1/r_{12} + \frac{z^2}{R} - \frac{z}{r_{a1}} - \frac{z}{r_{b2}} \right)$$

z is the effective nuclear charge of the carbon atom. The coefficient $(N_{yy,yy} - N_{xy,xy})$ of $\cos^2 \omega$ is $(C_{\pi\pi\pi\pi} - C_{\pi\pi'\pi'\pi})$ in Penney's notation.[11] We have used the value of 1.5 e. v. given for this quantity by Pauling and Wheland.[12] The estimates given by Penney[13] were used as a basis for evaluating the part of the integral that is independent of ω. The estimates are listed below:

$N_{ssss} = C_{ssss} = 1.0$ $N_{szsz} = C_{\sigma\sigma s} \cong 1.75$
$N_{xyxy} = C_{\pi\pi'\pi'\pi} \cong 0$ $N_{zzzs} = C_{\sigma z\sigma\sigma} \cong 2.29$
$N_{zzzz} = C_{\sigma\sigma\sigma\sigma} = 3.0$ $N_{ssss} = \cong 1.32$
$N_{sszz} = C_{ss\sigma\sigma} \cong 1.75$ $N_{yzyz} = -0.5$
     $N_{ysys} = -0.4$

No integrals similar to $N_{yz,yz}$ were estimated by Penney. They must be negative, however, since due to orthogonality only the electrostatic repulsion term e^2/r_{12} need be considered. From similar integrals evaluated by Bartlett[14] we can expect them to be relatively small. We arbitrarily take for the integrals $N_{yz,yz}$ and $N_{ys,ys}$ the values -0.5 and -0.4 volt, respectively. None of the integrals involved in the coefficient of $\cos \omega$ have been evaluated. However, we would expect this coefficient to be small since the integrals involved are alternately $+$ and $-$, i. e., the integrals $N_{ss,yy}$, $N_{yy,sz}$ and $N_{yy,zz}$ are positive in the sense here used, i. e., positive energy corresponds to attraction, while $N_{sy,ys}$, $N_{sy,yz}$ and $N_{yz,zy}$ are negative. The coefficient should be positive since the maximum binding should be obtained when the orbitals are cis where their overlap is greatest. Also similar integrals evaluated by Bartlett indicate that the positive integrals are considerably greater in

(11) W. G. Penney and G. B. B. M. Sutherland, J. Chem. Phys., **2**, 492 (1934).

(12) L. Pauling and G. W. Wheland, ibid., **1**, 362 (1933).

(13) W. G. Penney, Proc. Roy. Soc. (London), **A146**, 223 (1934).

(14) J. H. Bartlett, Phys. Rev., **37**, 507 (1931); Furry and Bartlett, ibid., **38**, 1615 (1931); **39**, 210 (1932).

magnitude than the negative ones. In calculations 1 and 2 the coefficient of cos ω was chosen to be zero while in 3 and 4 it was taken to be 2 kcal. The value of I_{C-C} in kcal. is then

$$I_{C-C} = 15.3 \cos^2 \omega + 13.4 \text{ in calculations 1 and 2}$$
(11)
$$I_{C-C} = 15.3 \cos^2 \omega + 2.0 \cos \omega + 13.4 \text{ in calculations}$$
3 and 4

ξ in the opposed form is obtained by inserting ω = 0 in (11), while in the staggered configuration ω = 180°. η is obtained from (11) by using the values ω = 60 and 180° for the staggered and opposed configurations, respectively. In calculations 1 and 3 the Heitler–London values were used for the hydrogen–hydrogen interactions, μ and φ, while in calculations 2 and 4 80% of the Morse curve values were taken.

Calculation 5 was undertaken to show that by a proper choice of the unknown coefficient of cos ω in the exchange integral I_{C-C} the staggered form could be made stable with respect to the opposed. The coefficient was taken to be −10 kcal. This seems to us to be unreasonable since it makes this interaction stronger in the *trans* position than in the *cis* position while one would expect that since the overlap is strongest in the *cis* position that it would be more stable. The last column gives the difference ΔE in the energies of the staggered and opposed configuration when the van der Waals forces are neglected. If the van der Waals forces are included about 400 cal. should be added to this figure. The effect of the *d*-ness would also be approximately additive since the presence of a small amount of *d*-ness in our wave functions should not appreciably affect the resonance energy. If this effect is included, then an additional 300 to 900 cal. should be added to ΔE.

Possible Effect of Resonance on Melting Points.—There is a well-known rule that the more symmetrical a molecule, other things being equal, the higher its melting point. In certain cases at least this is associated with the fact that the more symmetrical compounds are able to make their rotational transitions at low temperatures, *i. e.*, in the solid state and therefore there is not the incentive to melt that there otherwise would be. We see this most readily from the equation connecting the heat and entropy of melting $\Delta F = 0 = \Delta H - T\Delta S$ or $T = \Delta H / \Delta S$. Thus effects which increase ΔS or decrease ΔH lower the melting point. In Fig. 2 are plotted the heats, temperatures and entropies of melting for the

paraffins. The values for methane are taken from Bichowsky and Rossini.[15] Those for ethane are from Witt and Kemp,[16] while those for propane are from Kemp and Egan.[17] Parks, Shomate, Kennedy and Crawford[18] provide the values for butane while the other values are from the treatise, "The Science of Petroleum."[19]
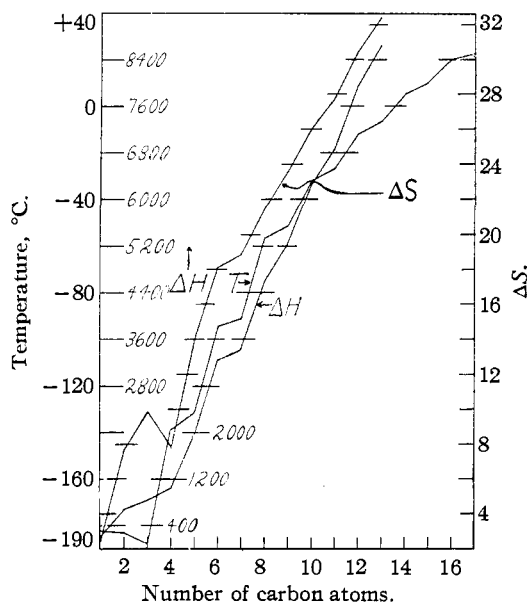

Fig. 2.—Heat, entropy and temperature of melting of paraffins.

The initial drop in the melting points from methane to propane is associated with an increase in the entropy of fusion which more than offsets the increase in the heat of fusion. This may be understood in the following way. In the liquid state these molecules presumably rotate very nearly freely about all axes as is shown by their normal entropy of vaporization at their boiling points. The entropies of vaporization from methane to butane are 19.37, 19.09, 19.42, 19.50. The value for methane is from the "International Critical Tables." The other values come from the sources quoted above. The almost spherical structure of methane permits it to rotate in the solid so that we expect a value only slightly larger than the two units of communal entropy.[20] The

(15) Bichowsky and Rossini, "Thermochemistry," Reinhold Publ. Corp., New York, N. Y., 1936.
(16) Witt and Kemp, THIS JOURNAL, **59**, 273 (1937).
(17) Kemp and Egan, *ibid.*, **60**, 1521 (1938).
(18) Parks, Shomate, Kennedy and Crawford, *J. Chem. Phys.*, **5**, 359 (1937)
(19) "The Science of Petroleum," Oxford University Press, New York, N. Y., 1938.
(20) J. Hirschfelder, D. Stevenson and H. Eyring, *J. Chem. Phys.*, **5**, 896 (1936).

observed value is 2.48 e. u. On the other hand ethane being able to rotate only about the C–C axis in the solid would be expected to get an increase in entropy due to changing from oscillation to free rotation about the other two axes. The observed value is 7.60 e. u. If the end of the vector which coincides with the C–C axis is free to describe ten times as large a solid angle in the liquid as in the solid it would explain the increase of entropy from 2.48 to 7.60. The greater value of 9.86 e. u. for propane arises in all probability from restricted rotation about all three axes in the solid state. Butane has a lower entropy change of 7.79 e. u. For longer hydrocarbons than butane there is little even–odd alternation except near hexane. The older entropy quoted by Landolt–Börnstein for hexane would fall more nearly on the straight line through the higher values. We must conclude that the considerable alternation above butane in the melting points arises principally from ΔH rather than ΔS. Going with large ΔH values of fusion we will necessarily have large changes in the density. The problem is thus reduced to a determination of the cause of the relatively better packing in the solid for the even members of the series. Müller,[21] for example, concludes, from his X-ray studies, that the relatively higher melting points of the even dicarboxylic acids is associated with closer packing and with different symmetry properties associated with a modified crystal form. Malkin[22] has criticized the theories advanced by Nekrassow,[23] Müller,[21] and Pauly[24] to explain alternating properties which are based on the fact that in the even series the terminal groups are *trans* while in the odd compounds they are *cis* with respect to one another. He shows that in the case of vertical chains there is no difference in the spacing of the planes containing the terminal groups and therefore there should be no difference in melting point for even and odd compounds. Malkin then divides long chain compounds into two series: those that show alternation and those that do not. The monobasic acids, dibasic acids, and their methyl esters, for example, belong to the alternating series. In all these substances there is a transition in the solid just below the melting point from the vertical chain structure to one where they are tilted with respect to the long

axis of the crystal. Malkin finds that for the tilted chains there is a large difference in the spacing of the terminal planes for the even and odd compounds, i. e., the density is greater for the even compounds than for the odd ones. He gives a geometrical explanation for the observed difference in spacing. By this he explains the fact that the even compounds melt higher and also why the transition to the tilted structure takes place with greater ease in the even series.

Those compounds which, according to Malkin, do not show alternation such as the paraffins, ethyl esters, and alcohols possess vertical chains and do not show a transition to the tilted form.

Beach[25] has explained alternating properties on the basis of alternating strong and weak bonds while Cuy[26] and Pauly[24] attribute the phenomena to alternately positive and negative carbon atoms. Malkin criticizes these theories since one would expect alternation in other physical properties as well as melting points which are not in general observed.[27]

The paraffins and ethyl esters which are cited by Malkin as examples of non-alternating series of compounds really do show alternation as is illustrated for the paraffins in the figure. Since these cases are not explained on a purely geometrical basis, some other explanation must be sought. We propose a theory which has some points of similarity to Beach's theory of alternating strong and weak bonds. Our calculations on ethane have shown that resonance with double bond structures lowered the total energy by about 12 kcal. in the opposed form and 10 kcal. in the staggered form. Now if we consider propane we see that it is possible to have a double bond between any two of the neighboring carbon atoms but not between both simultaneously as the structure corresponding to drawing two double bonds on the same carbon lies so high in energy above the normal state as not to contribute appreciably to the stability of the molecule. In the case of butane, however, it is possible to have structures containing two double bonds simultaneously which contribute to the total energy in the same way as in ethane. Thus we see in general that in the odd series both end carbons cannot be simultaneously double bonded while in the even compounds the end carbons can both be double bonded simul-

(21) Müller, *Proc. Roy. Soc.* (London), **A124**, 317 (1929).

(22) Malkin, *J. Chem. Soc.*, 2796 (1931).

(23) Nekrassow, *Z. physik. Chem.*, **128**, 208 (1927).

(24) Pauly, *Z. anorg. Chem.*, **119**, 271 (1922).

(25) Beach, *Z. physik. Chem.*, **50**, 43 (1905).

(26) Cuy, *Z. anorg. Chem.*, **115**, 273 (1921).

(27) Verkade, Coops and Hartman, *Rec. trav. chim.*, **45**, 373, 503 (1926).

taneously. The hydrogen atoms attached to the end carbons in the even series will thus be more free on the average to form bonds of a coördination type with other molecules than in the odd series. This is because there is a somewhat unoccupied 1s level on a hydrogen attached to a carbon that has become double bonded, which is available for coördination bonding with similar atoms on neighboring molecules. We call such binding intermolecular coördination to distinguish it from the intramolecular coördination binding between the hydrogen atoms in a single ethane molecule. Thus the intermolecular forces will be stronger in the even than in the odd compounds and they will consequently melt higher. Most of these coördination bonds would be broken in the liquid state due to the expansion which usually takes place upon melting. One would expect as is observed, therefore, that alternation in physical properties should be much less marked in the liquid state. This relative lack of alternating properties in the liquids is due to the lack of alternation in the molar refraction of even and odd compounds, and indicates that the binding forces in the liquid are largely of the polarization type. The importance of coördination type of binding in determining the stability of crystals and its relative unimportance for the stability of normal liquids is illustrated in the case of ethylene. Thus ethylene melts 13° higher than ethane but boils 17° lower. This can be explained by the tendency of the electrons forming the double bond to couple on to the double bond of another ethylene molecule. The coördination binding between the double bonds would not be nearly as strong in the liquid because of rotation and therefore liquid ethylene would be expected to boil lower than ethane due to its fewer number of hydrogen atoms. Because ethylene rotates in the liquid it is less dense than liquid ethane.

In the ordinary hydrogen bonding as in water there is in addition to the electrostatic binding between the hydrogen and oxygen atoms of neighboring molecules a large amount of this coördination type of binding. Due to the large electrostatic contribution we would expect the hydrogen bonding in water to be much stronger than the intermolecular binding discussed above. This coordination binding may also explain why one gets tilting of the chains in the cases discussed by Malkin and thus enhancement of the alternating phenomena. For example, according to Malkin,

the methyl esters form double molecules in the crystal and tilted chains while the ethyl esters form only single molecules in the crystals and vertical chains. This property of forming tilted chains is evidently connected with how well the ends of the molecules form bonds with their neighbors. Thus, in the methyl esters, part of the double bond in the carbonyl group will tend to go over toward the methyl group, thus releasing the methyl hydrogens to form coördination bonds with the atoms at the end of the chain of the neighboring molecules. When the methyl group is replaced by an ethyl group, the same tendency to loosen the hydrogen atoms at the end of the molecule will no longer be present since the end methyl group is now farther removed from the carbonyl group and also because of the alternation in double bond effect. The methyl esters would thus be expected to form double molecules and tilted chains much more readily than the ethyl esters.

This phenomenon of the tendency of a double bond to be partially shared by its neighboring single bonds is illustrated by the general reactivity of the α-carbon atom in the carboxylic acids and especially by the marked reactivity of the hydrogens attached to the α-carbon in malonic acid. This type of effect is also illustrated by the definite shortening of the C–C single bond in methylacetylene as compared with its value in saturated hydrocarbons.[28a] The shortening of a single bond which is next to a double or triple bond has been discussed by Pauling, Brockway and Beach.[28b]

An interesting example of what we have called intermolecular coördination is exhibited by the solid hydroboranes. Bauer and Pauling[29] have pointed out that the twenty-one structures for diborane each having two one-electron bonds resonate to form the stable molecule. One of the structures is the following $H : \overset{\text{H}}{\underset{\text{H}}{\overset{..}{B}}} : \overset{\text{H}}{\underset{\text{H}}{\overset{..}{B}}} : H$. As a result all the hydrogens will on the average be sharing less than the usual two electrons and so will tend to form coördination compounds with neighboring molecules. Since such bonds are short range they will decrease rapidly with the expansion accompanying either a rise of temperature or the melting process. This will give

(28) (a) G. Herzberg, F. Patat and H. Verleger, J. Phys. Chem., **41,** 121 (1937); (b) Pauling, Brockway and Beach, THIS JOURNAL, **57,** 2705 (1935).

(29) Bauer and Pauling, ibid., **58,** 2403 (1936); Bauer, ibid., **59,** 1096 (1937).

a relatively higher ΔH for melting without a corresponding increase in ΔS so that from the formula $\Delta H/\Delta S = T$ we expect higher melting points for the boranes than for the corresponding hydrocarbons in spite of the fact that the former contain two less electrons. That this is true is shown by the following comparisons

	B$_2$H$_6$	C$_2$H$_6$	B$_4$H$_{10}$	C$_4$H$_{10}$	BCl$_3$	CHCl$_3$
M. p., °C.	−165.5	−183.2	−120	−139	−107	−70
B. p., °C.	−92.5	−89	18	−0.6	18.2	61.2

When this coördination cannot take place as in BCl$_3$, we have a melting point considerably lower, rather than higher, than CHCl$_3$ the most nearly analogous carbon compound containing two more electrons.

X-Ray and Other Evidence Concerning Relative Stabilities of Staggered and Opposed Configurations.—The X-ray evidence on solid hydrocarbons[30] indicates that they are in the form of a zigzag chain with all the carbon atoms in a plane. This structure corresponds to the staggered configuration about all of the carbon–carbon linkages. This seems to us to be a serious objection against any theory which postulates the opposed as the stable structure as does the theory of intramolecular coördination proposed above. This objection possibly can be met in the following way. The same carbon atom cannot support two double bonds simultaneously, so that we would expect that the carbon–carbon bonds would be alternately double and single. Thus in butane we would have two double bonds at the end carbons with a single bond in the middle. If we assume that the single bond can assume the staggered configuration this would lead to a plane structure for butane. However, when a fifth carbon atom is added it would no longer tend to be in the plane of the other four. Thus, in order to get a plane zigzag structure it is necessary to assume that every fifth carbon atom is forced into the plane by the crystal forces, which expenditure of energy is compensated for by the resultant better packing. Since the crystal energy that is available is of the order 4000 kcal. per C–C bond, as is shown by the heat of sublimation of the hydrocarbons, this is by no means impossible. Electron diffraction and Raman investigations on dichloroethane[31] indicate that the chlorine atoms are in the *trans* position, *i. e.*, that the configuration is the staggered one about the C–C axis. The electronega-

tivity of the chlorines, however, withdraws electrons away from the carbons so that a double bond cannot be formed easily between the carbon atoms. We would thus expect that the C–C bond would remain single and that the repulsions of the chlorines would determine the stability of the *trans* position. The importance of the electron affinity of the halogen in chemical reactions is shown by the results of Conn, Kistiakowsky and Smith[32] on the heats of halogenation of substituted ethylenes. The greater the number of substituted alkyl radicals the higher is the heat of halogenation. This is explained easily by the fact that in the substituted compounds there is a greater reservoir of electrons for the chlorines to draw upon. This effect more than compensates for the increased steric repulsions in the substituted compounds.

Attempts have been made to interpret the infrared and Raman spectra of liquid ethane as indicating the stability of either the opposed or the staggered structure. Thus Bartholemé, Karweil and Schafer[33,34] conclude on the basis of Raman spectra that the molecular symmetry is D$_{3h}$, *i. e.*, opposed since the observed frequency at 2260 cm.$^{-1}$ cannot be fitted to D$_{3d}$, the staggered form. Crawford, Avery and Linnett[35] have attempted to effect a complete analysis of the vibrational spectrum of ethane and conclude that at the present time the evidence is insufficient to exclude the D$_{3d}$ configuration. Prof. E. B. Wilson[36] informs us that the most recent considerations do not allow them to reach any conclusion concerning the relative stabilities of the staggered and opposed forms.

It is interesting to compare the relative stabilities of cyclopentane and cyclohexane. In cyclopentane the configuration about all the carbon–carbon bonds is the opposed form. In cyclohexane, however, in the chair form all the bonds are staggered, we might expect, therefore, that if the staggered structure is the stable one, then cyclohexane would be more stable by 3 kcal. per methylene group. Heat of combustion data[37] show, however, that cyclohexane is only slightly more stable than cyclopentane, the heat of com-

(30) See "Structurbericht," 1913–1928.

(31) J. Y. Beach and K. J. Palmer, *J. Chem. Phys.*, **6**, 639 (1938); B. Trumpy, *Z. Physik*, **90**, 133 (1934); **98**, 624 (1935).

(32) J. B. Conn, G. B. Kistiakowsky and E. A. Smith, THIS JOURNAL, **60**, 2764 (1938).

(33) E. Bartholemé and J. Karweil, *Z. physik. Chem.*, **39B**, 1 (1938).

(34) J. Karweil and K. Schafer, *ibid.*, **B40**, 382 (1938).

(35) B. L. Crawford, Jr., W. H. Avery and J. W. Linnett, *J. Chem. Phys.*, **6**, 682 (1938).

(36) E. B. Wilson, private communication.

(37) Kharasch, *J. Research Bur. Standards*, **2**, 359 (1929).

bustion per methylene group being 157.5 kcal. as compared with 157.9 kcal. for cyclopentane. In the boat form of cyclohexane, however, two of the bonds can be opposed, while the greater possibility of resonance with double bonded structures in cyclohexane would tend to stabilize it with respect to cyclopentane. Cyclopentane would also be expected to have some strain, so that the above evidence can be reconciled with the opposed structure. If cyclohexane were flat, for example, all the bonds would be opposed. The fact that among the cyclic hydrocarbons the even members melt higher is exactly as would be expected on the coördination theory but cannot be understood on the theory of Malkin for straight chain compounds. This alternation is illustrated in Fig. 3. With the information available we are unable to rule out the possibility that alternations in entropy are more important in the cyclic than in the straight chain paraffins. We see no reason for expecting this, however.

Eyring[38] has derived a formula for the mean length of a hydrocarbon chain which as was stated is valid under conditions of free rotation. This formula in simplified form is

$$C_\text{n} = C_1 \left\{ \frac{n - x(2 + nx - 2x^n)}{(1 - x)^2} \right\}^{1/2}$$

where C_a is the length of the molecule, C_1 is the distance between neighboring carbon atoms, x is the cosine of the valence angle. Several investigators have concluded that the agreement between experimentally determined lengths and the result given by this formula is evidence of free rotation in these long chain compounds. We would like to point out, however, that even with high barriers one obtains the same result if the molecule vibrates about two equivalent minima 180° apart, three equivalent minima 120° apart, or any higher number of symmetrically placed equivalent minima.

The fact that agreement of observed lengths with this formula implies a random distribution of the orientations about the single bonds would seem at first sight inconsistent with the long zigzag chain observed in the solid compounds. However, the measurements of lengths which fit this formula were made in solvents consisting of small molecules. When the long chain compounds are dissolved in a solvent of this kind there is no longer the advantages in lying flat that they would have if they were present in an environment of their

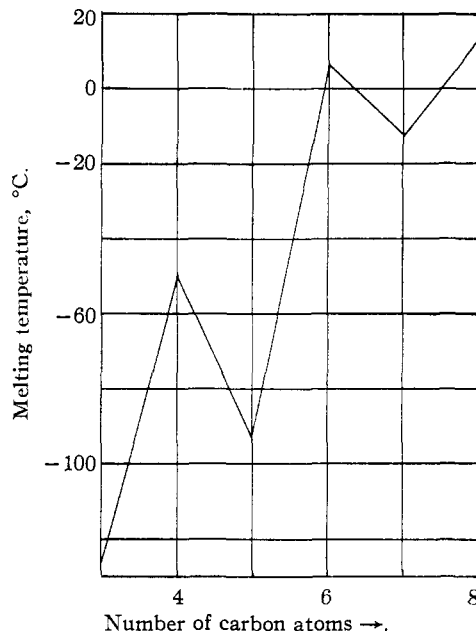(38) H. Eyring, *Phys. Rev.*, **38**, 746 (1932).

Fig. 3.—Melting temperatures of cycloparaffins.

own molecules and consequently they can curl up with little or no extra energy.

Addendum.—Since this paper was completed, an article by Eucken and Schäffer[39] has appeared in which the view is put forward that the potential barrier in ethane arises from the induction by the C–H dipoles on each methyl group of a lack of cylindrical symmetry in the carbon–carbon bonding orbitals. They write the perturbed orbital in the form $\psi_{2t\sigma}(1 + 0.1 \cos 3\varphi)$ where $\psi_{2t\sigma}$ is the unperturbed bonding orbital and the factor $(0.1 \cos 3\varphi)$ arises from perturbation of the carbon hydrogen orbitals. Since the orbitals in this form show 4% greater overlap in the opposed as compared with the staggered configuration, the opposed configuration should be more stable by about 4% of the binding energy, giving a potential barrier of the order of 3000 kcal.

We have discussed this effect in the first section of this paper using a somewhat different potential and have concluded that this effect gives a negligibly small contribution to the barrier. In view of the results of Eucken and Schäffer we have repeated this calculation using as they did a potential due to a charge of one-tenth the electronic charge at each of the hydrogen nuclei. The perturbed eigenfunction can be written as

$$\psi'_{2t} = \psi_{2^t\sigma} + \frac{0.3 \int \psi_{2t\sigma} \dfrac{e^2}{r_\text{b}} \psi_{4f} \, d\tau}{E_0 - E_{4f}} \psi_{4f}$$

(39) Eucken and Schäffer, *Naturwissenschaften*, **8**, 122 (1939).

where the factor 0.3 arises from the fact that there are three equivalent charges of 0.1 each on each methyl group. $E_0 - E_{4f}$ is the difference in energy of the $4f$ and normal states and is about equal to the ionization potential or 10–12 electron volts. The functions $\psi_{2i\sigma}$ and ψ_{4f} were chosen to be hydrogen-like and are given below. The effective nuclear charge equal to three

$$\psi_{2i\sigma} = Are^{-1/2\,r/a_0}\,(1 + \sqrt{3}\cos\Theta)$$
$$\psi_{4f} = Br^3 e^{-3/4\,r/a_0}\,\Theta_{33}\,\Phi_{3\cos\varphi}$$

is approximately that obtained by application of Slater's[40] rules for the screening constants of atomic orbitals. A and B are normalizing factors, and $AB = (2.45 \times 10^{-2})/\sqrt{\pi}$. The phase of $\Phi_{3\cos\varphi} = (1/\sqrt{\pi})\cos 3\varphi$ was so chosen that the hydrogen atoms lie in the planes $\varphi = 0$, $\pi/3$ and $2\pi/3$ corresponding to the maximum values of $\Phi_{3\cos\varphi}$. The term $1/r_b$ was expanded in terms of spherical harmonics about the center of the carbon atom. Due to orthogonality, all terms integrate out except those involving the harmonics $\Theta_{33}\phi_3\cos\varphi$ and $\Theta_{43}\phi_3\cos\varphi$. The result is that $0.3\int \psi_{2i\sigma}e^2/r_b\psi_{4f}d\tau = 1.56 \times 10^{-2}$ e. v. and the coefficient of the $4f$ function is correspondingly about 1.5×10^{-3}. This coefficient is, as we see, so small that no appreciable contribution to the barrier can come from this cause, in agreement with our earlier result and in disagreement with Eucken and Schäffer. The barrier therefore arises from other causes such as are considered in this paper.

(40) Slater, *Phys. Rev.*, **36**, 57 (1930).

We wish to express our appreciation to Drs. William Baker and John Beach for helpful discussions.

Summary

1. The problem of restricted rotation about the C–C bond in ethane is discussed. It is shown that the repulsions between the hydrogen atoms cannot account for a barrier of 3000 cal. The effect of the distortion of the spherical symmetry around the carbon atoms by the perturbations of the hydrogen atoms is considered. It is shown that this effect tends to make the opposed form more stable but also cannot account for a barrier of the required height. The effect of resonance with double bonded structures is then considered and it is shown that with reasonable assumptions concerning the angular dependence of the exchange integrals between carbon orbitals, the opposed structure is the stable one with a barrier height of 0.7 to 1.9 kcal. If we add to this the effect of the dissymmetry of the carbons a barrier of the right order of magnitude is obtained.

2. It is shown that this effect of resonance with double bonded structures can be used to explain the alternation in physical properties such as melting points of long chain compounds.

3. The experimental evidence in favor of the staggered or opposed structures for long chain and cyclic compounds is discussed.

Primary and Secondary Acids and Bases

BY GILBERT N. LEWIS AND GLENN T. SEABORG

The most general classification[1] of bases and acids does not extend the class of bases much beyond the group of substances now recognized under that name. On the other hand, if we define an acid as any substance one of whose atoms is capable of receiving into its valence or coördination or resonance shell the basic electron-pair of another atom, then we have a great group of generalized acids in which the hydrogen acids are not the strongest and not always the most typical members.

The self-consistency of this group of generalized

(1) Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, 1923, p. 142.

acids has been brought out in a recent paper[2] which emphasizes the extraordinary similarity in every type of behavior, extending even to the colors of their compounds with indicators, between hydrogen acids and all the other acids of the class. All the acids can be ranked roughly by their strengths. Thus, for example, sulfur dioxide is ordinarily weaker than hydrochloric acid, which in turn is much weaker than boron trifluoride or stannic chloride. Aside, however, from these considerations of relative strength, there was proposed in that paper an entirely independent classification into *primary* and *secondary*

(2) Lewis, "Acids and Bases." *J. Franklin Inst.*, **226**, 293 (1938).