

Electronic Shifts at Moderate Temperatures in Metals of Group VIII

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taken in directions of the maxima of f_3 and f_4 . With no loss in generality and a considerable gain in the simplicity of the equations, orbitals f_1 and f_2 can be chosen with their maxima in the xz plane, equally inclined to the z axis. By symmetry, f_3 and f_4 then lie in the yz plane, also equally inclined to the z axis.

Applying the usual normalization and orthogonality conditions we have:

$$f_1 = as + bp_z + (1/2)^{1/2} p_x, \quad (1)$$

$$f_2 = as + bp_z - (1/2)^{1/2} p_x, \quad (2)$$

$$f_3 = bs - ap_z + (1/2)^{1/2} p_y, \quad (3)$$

$$f_4 = bs - ap_z - (1/2)^{1/2} p_y, \quad (4)$$

$$b = +(\frac{1}{2} - a^2)^{1/2}. \quad (5)$$

We now determine the value of a (and b by Eq. (5)) so that f_1 will have the maximum value in a particular direction θ_0 in the xz plane by setting $df_1/da = 0$. This requires that

$$a = \left(\frac{1}{2 + 6 \cos^2 \theta_0} \right)^{1/2}, \quad (6)$$

$$b = \left(\frac{3 \cos^2 \theta}{2 + 6 \cos^2 \theta_0} \right)^{1/2}. \quad (7)$$

The angle θ_{34} between the bonds formed with the orbitals f_3 and f_4 is given by the expression:

$$\tan \theta_{34} = \frac{-2(1 + 3 \cos^2 \theta_0)^{1/2}}{3 \cos^2 \theta_0}. \quad (8)$$

We have calculated the H-C-H angle, θ_{34} , and bond strengths, f_{01} and f_{03} , for several values of $2\theta_0$, the C-C-C angle (Table I). Assuming bond energies proportional to

TABLE I.

$2\theta_0$ ($=\theta_{12}$)	Strength of bonds (1) and (2) f_{01}	θ_{34}	Strength of bonds (3) and (4) f_{03}
0°	1.414	126° 52'	1.982
60°	1.887	121° 58'	1.989
90°	1.984	115° 23'	1.995
108°	2.000	109° 58'	2.000
109° 28'	2.000	109° 28'	2.000
120°	1.996	105° 50'	1.998
180°	1.932	90°	1.732

square of bond strength and using¹ 59 and 87 kcal. for normal C-C and C-H bond energies, we obtain 10 and 2 kcal. as the strain energies per CH₂ group of cyclopropane and cyclobutane in fair agreement with experimental values of about 10 and 4⁵ (estimated from cyclobutane derivatives). Probably about 2 kcal. should be added to the calculated values for torsional strain.⁶ The energy calculation does not apply to ethylene because the bond is much shorter than it is in normal paraffins.

That the exterior angle in cyclopropane is not 180° as suggested by Duffey is shown conclusively by the large dipole moment of 1,1-dichlorocyclopropane.⁷ Also, the calculation Duffey quotes from Herzberg⁸ is incorrect. The correct C-C distance for 180° angle is 1.616 Å not 1.556 Å. The moment of inertia of cyclopropane is fitted, for example, by $r_{C-C} = 1.530$ Å (electron diffraction),

$r_{C-H} = 1.070$, $\angle H-C-H = 125^\circ$. No unique angle is obtained from one moment of inertia. Finally, Donohue *et al.*⁹ find $120^\circ \pm 8^\circ$ for $\angle HCH$ in spiropentane. The electron diffraction of 1,1-dichlorocyclopropane would determine this angle.

In conclusion, it should be pointed out that the ideas of s, p hybridization and proportionality of energy to f^2 are approximations, and the agreement of these calculations with experiment is to a great extent fortuitous. For this reason, we did not attempt any further refinements such as simultaneous maximization of C-C and C-H bond energies.

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² National Research Fellow in chemistry.

³ G. H. Duffey, J. Chem. Phys. **14**, 342 (1946).

⁴ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940).

⁵ G. E. K. Branch and M. Calvin, *Theory of Organic Chemistry* (Prentice-Hall, Inc., New York, 1941), p. 279.

⁶ K. S. Pitzer, Science **101**, 672 (1945).

⁷ M. T. Rogers and J. D. Roberts, J. Am. Chem. Soc. **68**, 843 (1946).

⁸ G. Herzberg, *Infra-Red and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand, New York), p. 440. The C-C distance given for 120° is also incorrect.

⁹ J. Donohue, G. L. Humphrey, and U. Schomaker, J. Am. Chem. Soc. **67**, 332 (1945).

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FURTHER evidence has been secured, supplementing that offered some years ago for pure iron,¹ of what are believed to be specific electronic shifts in iron within ordinary temperature ranges. Similar series have also been established for all the other Group VIII metals by measurements of either the electrical resistance of pure or alloyed metal wires or of the electrolytic conductivity of glasses containing these metals. For all the metals, the temperatures of the discontinuities follow, within experimental limits, the simple Ritz formula:

$$T_k = ct[(1/n_0^2) - (1/n^2)],$$

where ct is a constant which is different for each metal; n_0 has the value 3 for Fe, Co, Ni, 4 for Ru, Rh, Pd, and 5 for Os, Ir, Pt; and n , for each metal, has the successive values $n_0 + 1$, $n_0 + 2$, \dots ∞ .

No change was found in the critical temperatures either with concentration or with the form of chemical combination. Hence the effect is believed to be a purely atomic phenomenon.

The fact that the Curie magnetic transition temperatures of Fe, Co, and Ni, all occur exactly at some definite term in the appropriate series indicates that the data may be of great importance in clarifying the theory of ferromagnetism.

Further details will be published shortly.

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¹ C. B. Post and W. R. Ham, J. Chem. Phys. **5**, 913-919 (1937).
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