On the Magnetic Susceptibility of Pyridine

By

Juro Maruha and Matsuo Terakura

(Received February 6, 1958)

Many workers have made physico-chemical studies of pyridine, not only experimentally, but theoretically, as it has especially similar structure to benzene. Consequently, theoretical explanations were introduced successfully about experimental results of ultraviolet spectra, dipole moments, bond distances, etc., of pyridine.

On molecules containing hetero-atoms in the conjugated system, it is important what values we adopt of the Coulomb integral (α) of nitrogen atom and the exchange integral (β) of carbon—nitrogen, when they are calculated by means of the LCAO–MO method. The calculation had been done frequently using the corrected value, $\alpha_N = \alpha_C + 2\beta$, but recent work suggests that $\alpha_C + 0.5\beta$ is a rather more likely value.[1] And the results do not so differ from those by the simple MO method using $\alpha + 0.5\beta$, even if the calculations would be made to self consistent by a process of successive approximation. While, Orgel et al.[2] adopted following parameters, when they computed dipole moments of a series of conjugated heterocyclic compounds, $\alpha_{(C)} = \alpha$, $\alpha_{(-N=)} = \alpha + \beta$, $\alpha_{(C(-N))} = \alpha + 0.1\beta$, $\beta_{(C-C)} = \beta$, and $\beta_{(C-N)} = 1.2\beta$. It gave very good results about such compounds. The introduction of a hetero-atom, of course, must bring about changes to the Coulomb integral and the exchange integral, and the above choice of parameters is more adequate in comparison with the calculation adding the correction to nitrogen atom only.

On the other hand, F. London gave a theory[3] of magnetic susceptibilities due to π–electrons in aromatic compounds, that is to say, magnetic susceptibilities due to molecular orbitals of π–electrons, when a magnetic field applies perpendicularly to the molecular plane, and later, H. Brooks[4] considered a influence of the overlap integral between adjacent atoms, and as the consequence they obtained very suitable results about hydrocarbons.

We have performed measurements of magnetic susceptibilities about two component systems of organic substances such as pyridine-water, pyridine-acetic acid, etc., and studied the interaction between the two ones. As we needed to carry out the calculation of magnetic susceptibility due to π–electron, we, in accordance with the method of London, calculated using parameters selected by Orgel and obtained reasonable values.

If a magnetic field (H) is applied perpendicularly to the molecular plane, London's secular equation is given by a following equation, the exchange integral β being unity,

$$|\eta_{kl}\exp(2\pi i f_{kl})-X\delta_{kl}|=0, \tag{1}$$

where $X=(E-\alpha)/\beta$ and $f_{kl}=\dfrac{e}{hc}\cdot\dfrac{1}{2}H(x_ky_l-x_ly_k)$; f_{kl} is a magnetic flux passing through the triangle formed by the neighbouring atoms k, l and the origin arbitrarily chosen in the plane of the molecule. δ_{kl} is Kronecker's delta and η_{kl} equals to unity, when l neighbours with k, otherwise zero.

In this work, however, we adopt the parameters of Orgel in the equation (1), then we can write explicitly the following form

$$\begin{vmatrix} -X+1 & 1.2\varepsilon_1 & & & & 1.2\varepsilon_6{}^* \\ 1.2\varepsilon_1{}^* & -X+0.1 & \varepsilon_2 & & & \\ & \varepsilon_2{}^* & -X & \varepsilon_3 & & \\ & & \varepsilon_3{}^* & -X & \varepsilon_4 & \\ & & & \varepsilon_4{}^* & -X & \varepsilon_5 \\ 1.2\varepsilon_6 & & & & \varepsilon_5{}^* & -X+0.1 \end{vmatrix}=0 \tag{2}$$

where $\varepsilon_n=\exp(2\pi i f_{n,n+1})$ and $\varepsilon_n{}^*=\exp(-2\pi i f_{n,n+1})$. Expanding (2) and after some approximations, we obtain

$$F(X)+1.44(2\pi f)^2=0. \tag{3}$$

$F(X)$ equals to a equation introduced by simple LCAO–MO, in other words, it corresponds to the equation putting $\varepsilon=\varepsilon^*=1$. Therefore, considering the symmetry group of the pyridine molecule (C_{2v}), we can solve in the following factors,

$$X^2-0.1X-1=0 \tag{4}$$
$$X^4-1.1X^3-5.78X^2+3.2X+5.56=0 \tag{4'}$$

Each root X' for the occupied levels is shown in Table I.

If f is smaller than 1, the root of the equation (3) is approximately

$$X=X'+X''(2\pi f)^2,$$

in which $X''=-1.44/F'(X')$. $F'(X)$ is the first derivative of $F(X)$. The value of X'' is also given in Table I.

Now, the diamagnetism due to electrons of the occupied levels was expressed by London as the following form,

Table I

Benzene*		Pyridine					
		Ⅰ		Ⅱ		Ⅲ	
X'	X''	X'	X''	X'	X''	X'	X''
2	—0.0278	2.84223	—0.00648	2.10745	—0.01892	2.50469	—0.01213
1	—0.0139	1.50694	+1.80456	1.16719	+0.47139	1.34547	+0.24821
1	—0.0139	1.00000	—0.12500	1.00000	—0.50000	1.05125	—0.28999
Sum : —0.0555		Sum : +1.67309		Sum : —0.04753		Sum : —0.05391	

*Values of Benzene cited from H. Brooks, J. Chem. Phys. 9, 463 (1941).

Ⅰ, calculated with $\alpha_N=\alpha_C+2\beta$.

Ⅱ, caluculated with $\alpha_N=\alpha_C+0.5\beta$.

Ⅲ, caluculated with Orgel's parameters.

$$2\sum\chi_{\text{occup}} = -4\sum(X'') \times |W_1|\left(\frac{2\pi eS}{hc}\right)^2,$$

where W_1 keeps almost a equal value for benzene and pyridine, and S indicates the area of the conjugated system. Therefore the summation of X'' would be compared with that of benzene. The values of it are shown in Table I, together with those of benzene. The values computed with the Coulomb integral of nitrogen atom using $\alpha+0.5\beta$, and $\alpha+2\beta$, are also given in Table I. The result using $\alpha+0.5\beta$ does not appreciably differ from that of Orgel's parameters, but the other one appears unacceptable. S is computed using carbon-carbon distance, 1.39 Å, and carbon-nitrogen distance, 1.37Å. Then $S_{\text{py}}/S_{\text{benz}} = 0.988$. The ratio of $\sum(X'')$ is 0.971. Consequently $\Delta K_{\text{py}}/\Delta K_{\text{benz}} = 0.948$, in which the ΔK is the magnetic contribution owing to the π-electron orbitals. If we adopt $\Delta K_{\text{benz}} = -54 \times 10^{-6}$ cgs.,[5] we obtain $\Delta K_{\text{py}} = -52.4 \times 10^{-6}$ cgs.

A measurement of magnetic anisotropy of pyridine is not yet made, but the magnetic susceptibility is measured repeatedly,[6] and our observed gram-susceptibility χ_g is -0.610×10^{-6}, so the molecular susceptibility $\chi_{\text{Mol}} = -48.3 \times 10^{-6}$ cgs., which agrees with M. French's.

On the other hand the molecular susceptibility including conjugated double bonds is calculated additively as follows,

$$\chi_{\text{Mol}} = \sum\chi_{\text{Atom}} + \Delta K/3,$$

in which χ_{Atom} is atomic increment. For pyridine,

$$\sum\chi_{\text{Atom}} = 5\chi_{(-C=)} + 5\chi_{(H-)} + \chi_{(-N=)}.$$

Here we adopt the following values,[7]

$$\chi_{(-C=)} = -3.36 \times 10^{-6}\text{cgs. and } \chi_{(H-)} = -2.93 \times 10^{-6}\text{cgs.}$$

Previous workers, however, did not determine the values of $\chi_{(-N=)}$, which we can now determined from the above mentioned values to be $\chi_{(-N=)} = 0$.

This is very interesting result, showing that if $-CH=$ group in hydrocarbon containing cojugated double bond is replaced by $-N=$ group, the molecular susceptibility only decreases by the value corresponding to $-CH=$, i.e., -6.29×10^{-6} cgs., under the condition of neglecting the change of the molecular orbital by π-electrons, as it has only little influence. We have a few case to examine the above fact, but the following compounds, whose values were determined in our laboratory and were given below, are good examples to confirm these circumstances.

$\chi_{\text{Mol}} \times 10^6$cgs.　　　-91.82　　　-85.4　　　-79.0[8]
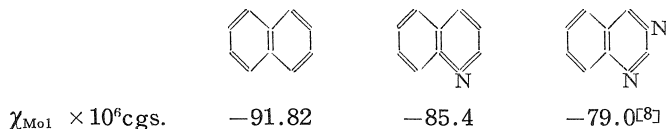
Thus the magnitude of the magnetic susceptibility of each substance decreases by -6.4×10^{-6} cgs., progressively. This value just corresponds to the above conclusion.

Summary

We treated the magnetic anisotropy of pyridine by means of London's theory. In

this paper, we adopted $\alpha+\beta$ and $\alpha+0.1\beta$ as the Coulomb integral of the nitrogen atom and that of the carbon atom neighbouring to the nitrogen atom, respectively, and 1.2β as exchange integral between carbon and nitrogen. In this case we obtained 0.971 as the value of the ratio of the anisotropy of pyridine to that of benzene. When $\alpha+0.5\beta$ was used as the Coulomb integral of the nitrogen atom, the result was rather small.

And it became evident that the replacement of the nitrogen atom into aromatic hydrocarbons gave no atomic increment of the diamagnetism.

Acknowledgments

References

[1] C. A. Coulson, "Valence", (Oxford University Press, 1952), p. 242.

[2] L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, Trans. Faraday Soc. 47, 113 (1951).

[3] F. London, J. de Phys. 8, 397 (1937).

[4] H. Brooks, J. Chem. Phys. 9, 463 (1941).

[5] K. S. Krishnan, B. C. Guha and S. Banerjee, Phil. Trans. 231A, 235 (1933).

[6] M. French, Trans. Faradey Soc. 47, 1056 (1951).

[7] H. Shiba and G. Hazato, Bull. Chem. Soc. Japan 22, 92 (1949).

[8] J. Maruha, read before the 10 th Annual Meeting of the Chem. Soc. Japan, April, (1957).