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# PHYSICAL CHEMISTRY

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## Abstract

## Full Text

PHYSICAL CHEMISTRY

R. M. AMINOVA

# ON THE MOLECULAR-ORBITAL THEORY OF THE DIAMAGNETISM OF CYCLIC MOLECULES. CALCULATION OF THE MAGNETIC ANISOTROPY OF CYCLOPROPANE

*(Presented by Academician B. A. Arbuzov, March 11, 1964)*

It is well known <sup>(1,2)</sup> that the cyclopropane ring exhibits a certain similarity to unsaturated compounds and behaves like a double bond. In addition, recent studies <sup>(3,4)</sup> of NMR spectra of compounds containing a cyclopropane ring indicate a significant diamagnetic influence of the ring on protons located above it. In this connection it was of interest to study in more detail the susceptibility of cyclopropane and to estimate the magnitude of its magnetic anisotropy. In the present work the molecular-orbital (M.O.) theory of diamagnetism, proposed by Pople <sup>(5)</sup> for simple noncyclic compounds, is developed for cyclic molecules, and, using the formulas obtained, calculations of the magnetic anisotropy of cyclopropane are carried out. The M.O. method is used in the one-electron LCAO approximation with allowance for the magnetic field. If, in the absence of a magnetic field, the LCAO theory gives approximate solutions  $\psi_i$  of the wave equation of Schrödinger in the form of a linear combination of atomic orbitals  $\Phi_\mu$  (which, for convenience, are taken to be real), then in a magnetic field it is necessary to use atomic orbitals of the form <sup>(6,7)</sup>

$$\chi_\mu = \Phi_\mu \exp [-(ie/\hbar c)\mathbf{A}_\mu \cdot \mathbf{r}], \quad (1)$$

where  $\Phi_\mu$  is the atomic orbital belonging to atom  $\mu$  with radius vector  $\mathbf{R}_\mu$ , and  $\mathbf{A}_\mu$  is the value of the vector potential at the nucleus of this atom. Using a series of approximations, Pople obtains the following expression for the change in the total energy of a molecule in a magnetic field in second-order perturbation theory:

$$E^{(2)} = \sum_{\mu\nu} P_{\mu\nu} \mathcal{H}_{\mu\nu}^{(2)} - 2 \sum_i^{\text{occ}} \sum_j^{\text{unocc}} \sum_{\mu\lambda\nu\sigma} c_{i\mu}^* c_{j\lambda}^* \left[ \mathcal{H}_{\mu\nu}^{(1)} \mathcal{H}_{\lambda\sigma}^{(1)} / (\varepsilon_j^{(0)} - \varepsilon_i^{(0)}) \right] c_{j\nu} c_{i\sigma}, \quad (2)$$

where

$$\mathcal{H}_{\mu\nu}^{(1)} = iL_{\mu\nu}\mathcal{H}_{\mu\nu}^{(0)} + \frac{e}{mc}\eta_{\mu\nu} \int \Phi_{\mu}^*(\mathbf{A} - \mathbf{A}_{\nu}) \cdot \mathbf{p} \Phi_{\nu} d\tau, \quad (3)$$

$$\mathcal{H}_{\mu\nu}^{(2)} = -\frac{1}{2}L_{\mu\nu}^2\mathcal{H}_{\mu\nu}^{(0)} + \frac{e^2}{2mc^2}\delta_{\mu\nu} \int \Phi_{\mu}^*(\mathbf{A} - \mathbf{A}_{\nu})^2\Phi_{\nu} d\tau, \quad (4)$$

$P_{\mu\nu}$  is the density matrix:

$$P_{\mu\nu} = 2 \sum_i^{\text{occ}} c_{i\mu}^* c_{i\nu}. \quad (5)$$

The remaining notation in expressions (3) and (4) is as follows:

$$L_{\mu\nu} = (e/2\hbar c)(\mathbf{A}_{\mu} - \mathbf{A}_{\nu}) \cdot (\mathbf{R}_{\mu} + \mathbf{R}_{\nu}), \quad (6)$$

$\mathcal{H}^{(0)}$  is the Hamiltonian in the absence of a magnetic field,

$$\mathcal{H}^{(0)} = \frac{1}{2m}\mathbf{p}^2 + V, \quad (7)$$

$c_{i\mu}$  are the LCAO coefficients in the absence of perturbation, and  $\mathbf{p}$  is the electron momentum operator. Here Latin indices are used to denote molecular orbitals ( $i, j$ ), and Greek indices ( $\mu, \nu$ ), atomic orbitals. In expressions (3) and (4) the first term characterizes the interatomic contribution to the susceptibility, the second the intra-atomic contribution. Considering noncyclic molecules, Pople neglected the interatomic terms and obtained for the  $z$ -components of the diamag-

ic and paramagnetic atomic contributions are given by the formulas:

$$(\chi_d^A)_{zz} = -\frac{Ne^2}{4mc^2} \sum_{\mu}^A P_{\mu\mu} (x^2 + y^2)_{\mu\mu}, \quad (8)$$

$$\begin{aligned} (\chi_p^A)_{zz} = & \frac{Ne^2\hbar^2}{4m^2c^2} \langle (\Delta E)^{-1} \rangle \sum_B [P_{xAxB}(2\delta_{AB} - P_{yAyB}) + \\ & + P_{yAyB}(2\delta_{AB} - P_{xAxB}) + 2P_{xAyB}P_{yAxB}]. \end{aligned} \quad (9)$$

Let us consider what contribution to diamagnetism is made by the interatomic terms  $\mathcal{H}_{\mu\nu}^{(1)} = iL_{\mu\nu}\mathcal{H}_{\mu\nu}^{(0)}$  and  $\mathcal{H}_{\mu\nu}^{(2)} = -\frac{1}{2}L_{\mu\nu}^2\mathcal{H}_{\mu\nu}^{(0)}$ . Taking into account that in a uniform magnetic field  $\mathbf{H}$  the vector potential at a point with radius vector  $\mathbf{r}$  is equal to

$$\mathbf{A}(\mathbf{r}) = \frac{1}{2}(\mathbf{H} \times \mathbf{r}), \quad (10)$$

we obtain

$$L_{\mu\nu} = (e/4\hbar c) H_\alpha [\mathbf{R}_{\nu\mu} \times (\mathbf{R}_\mu + \mathbf{R}_\nu)]_\alpha, \quad (11)$$

$$L_{\mu\nu}^2 = (e^2/16\hbar^2 c^2)(\mathbf{R}_\mu + \mathbf{R}_\nu)^2 H_\alpha H_\beta (R_{\nu\mu}^2 \delta_{\alpha\beta} - R_{\nu\mu\alpha} R_{\nu\mu\beta}), \quad (12)$$

where  $R_{\nu\mu}$  is the distance between atoms  $\nu$  and  $\mu$ . Substituting (11) and (12) into (2), taking into account that  $\mathcal{H}_{\nu\mu}^{(0)} = \mathcal{H}_{\mu\nu}^{(0)}$ , and comparing with the susceptibility tensor

$$E^{(2)} = -\frac{1}{2}N^{-1}\chi_{\alpha\beta}H_\alpha H_\beta, \quad (13)$$

we find that the interatomic contribution to the diamagnetic susceptibility splits into two parts:

$$\chi_{\alpha\beta} = (\chi_d)_{\alpha\beta} + (\chi_p)_{\alpha\beta}, \quad (14)$$

where

$$(\chi_d)_{\alpha\beta} = \frac{Ne^2}{8\hbar^2 c^2} \sum_{\mu<\nu} P_{\mu\nu} (\mathbf{R}_\mu + \mathbf{R}_\nu)^2 (R_{\nu\mu}^2 \delta_{\alpha\beta} - R_{\nu\mu\alpha} R_{\nu\mu\beta}) \mathcal{H}_{\mu\nu}^{(0)}, \quad (15)$$

$$\begin{aligned} (\chi_p)_{\alpha\beta} = & \frac{Ne^2}{4\hbar^2 c^2} \sum_i \sum_j^{\text{unocc}} (\varepsilon_j^{(0)} - \varepsilon_i^{(0)})^{-1} \sum_{\mu<\nu} \sum_{\lambda<\sigma} (c_{i\mu} c_{j\nu} - c_{i\nu} c_{j\mu}) (c_{i\lambda} c_{j\sigma} - c_{i\sigma} c_{j\lambda}) \times \\ & \times [\mathbf{R}_{\nu\mu} \times (\mathbf{R}_\mu + \mathbf{R}_\nu)]_\alpha [\mathbf{R}_{\sigma\lambda} \times (\mathbf{R}_\lambda + \mathbf{R}_\sigma)]_\beta \mathcal{H}_{\mu\nu}^{(0)} \mathcal{H}_{\lambda\sigma}^{(0)*}. \end{aligned} \quad (16)$$

The interatomic contributions  $\chi_d$  and  $\chi_p$  to the total susceptibility can be decomposed into a sum of individual contributions from each bond  $A - B$  in the molecule. In doing so, expression (16) can be simplified by replacing  $(\varepsilon_j^{(0)} - \varepsilon_i^{(0)})^{-1}$  by the mean value  $\langle(\Delta E)^{-1}\rangle$ , and the sum over the molecular orbitals  $i$  and  $j$  by the generalized density matrix (equation (5)), since, if overlap integrals are neglected, then

$$\sum_i^{\text{occ}} c_{i\mu} c_{i\nu} + \sum_j^{\text{unocc}} c_{j\mu} c_{j\nu} = \delta_{\mu\nu}. \quad (17)$$

Fig. 1. Choice of coordinate axes for cyclopropane: a –in calculating atomic contributions to the susceptibility, b –in calculating interatomic contributions to the susceptibility

Figure 1: Fig. 1. Choice of coordinate axes for cyclopropane: a –in calculating atomic contributions to the susceptibility, b –in calculating interatomic contributions to the susceptibility

As a result we obtain

$$\chi_d = \sum_{A-B} \chi_d^{A-B},$$

$$(\chi_d^{A-B})_{\alpha\beta} = \frac{Ne^2}{8\hbar^2c^2} \sum_{\mu<\nu}^{A-B} P_{\mu A\nu B} (\mathbf{R}_A + \mathbf{R}_B)^2 (R_{AB}^2 \delta_{\alpha\beta} - R_{AB\alpha} R_{AB\beta}) \mathcal{H}_{\mu A\nu B}^{(0)}, \quad (18)$$

$$\chi_p = \sum_{A-B} \chi_p^{A-B},$$

$$(\chi_p^{A-B})_{\alpha\beta} = \frac{Ne^2}{16\hbar^2c^2} \langle (\Delta E)^{-1} \rangle \sum_{\mu<\nu}^{A-B} \sum_{S-T} \sum_{\lambda<\sigma}^{S-T} \{P_{\mu A\lambda S} (2\delta_{\mu A\lambda S} - P_{\nu B\sigma T}) +$$

\* The coefficients  $c_{i\mu}$  are assumed to be real.

$$+ P_{\nu B\sigma T} (2\delta_{\nu B\sigma T} - P_{\mu A\lambda S}) + 2P_{\mu A\sigma T} P_{\nu B\lambda S} \} \times \\ \times [\mathbf{R}_{AB} \times (\mathbf{R}_A + \mathbf{R}_B)]_{\alpha} [\mathbf{R}_{ST} \times (\mathbf{R}_S + \mathbf{R}_T)]_{\beta} \mathcal{H}_{\mu A\lambda B}^{(0)} \mathcal{H}_{\lambda S\sigma T}^{(0)}. \quad (19)$$

Here  $\sum_{\mu<\nu}^{A-B}$  is the sum over all atomic orbitals participating in the bond  $A - B$ . Expression (19) may be interpreted as the paramagnetic moment per unit field induced in the bond  $A - B$ . In contrast to the diamagnetic contribution (18), the paramagnetic term includes the sum  $\sum_{S-T}$  over all bonds in the molecule, since the magnetic field, acting on the bond  $S - T$ , also contributes to the susceptibility of the bond  $A - B$ .

**Fig. 1.** Choice of coordinate axes for cyclopropane:  $a$  –in calculating atomic contributions to the susceptibility,  $b$  –in calculating interatomic contributions to the susceptibility

We shall use formulas (18) and (19) to calculate the magnetic anisotropy of cyclopropane. Let us choose the coordinate axes as shown in Fig. 1. Then the diamagnetic and paramagnetic interatomic contributions to the anisotropy of cyclopropane will be, respectively,

$$\begin{aligned} \Delta\chi_d^{C_3H_6} &= \chi_{\parallel} - \chi_{\perp} = \chi_{zz} - \frac{1}{2}(\chi_{xx} + \chi_{yy}) = \\ &= \frac{Ne^2}{16\hbar^2c^2} \sum_{\text{bonds}} \sum_{\mu < 0}^{A-B} (X_{A-B}^2 + Y_{A-B}^2) P_{\mu A\nu B}(\mathbf{R}_A + \mathbf{R}_B)^2 \mathcal{H}_{\mu A\nu B}^{(0)}, \end{aligned} \quad (20)$$

$$\begin{aligned} \Delta\chi_p^{C_3H_6} &= \sum_{\text{bonds}} (\chi_p^{A-B})_{zz} = \frac{Ne^2}{\hbar^2c^2} \langle (\Delta E)^{-1} \rangle \sum_{\text{bonds}} \sum_{\mu < \nu}^{A-B} \sum_{\lambda < \sigma}^{S-T} S_{AB} S_{ST} \times \\ &\times \{ P_{\mu A\lambda S} (2\delta_{\mu A\lambda S} - P_{\nu B\sigma T}) + P_{\nu B\sigma T} (2\delta_{\nu B\sigma T} - P_{\mu A\lambda S}) + \\ &+ 2P_{\mu A\sigma T} P_{\nu B\lambda S} \} \mathcal{H}_{\mu A\nu B}^{(0)} \mathcal{H}_{\lambda S\sigma T}^{(0)}. \end{aligned} \quad (21)$$

Here  $S_{AB}$  is the area of the triangle formed by the bond  $A - B$  with the origin of coordinates. Calculations by formulas (20) and (21) can be carried out if sufficient information is available on the molecular orbitals of the molecule. Here we shall carry out the calculations following the ideas of Coulson and Moffitt (8) on the “bent” bonds of cyclopropane (Fig. 1). As molecular orbitals we use localized molecular orbitals of the form

$$\Psi(C_A - C_B) = \frac{1}{\sqrt{2}} \left[ \Phi(C_A; 2p\sigma_{C_A}^{C_B}) + \Phi(C_B; 2p\sigma_{C_B}^{C_A}) \right], \quad (22)$$

$$\Psi(C_A - H_{1,2}) = \frac{1}{\sqrt{2}} \left[ \Phi(C_A; 2p\sigma_{H_A^1, H_A^2}) + \Phi(H; 1s) \right],$$

where  $\Phi(C_A; 2p\sigma_{C_A}^{C_B})$  is the hybrid atomic wave function of carbon  $C_A$ , forming a bond with the neighboring atom  $C_B$  in the ring, and  $\Phi(C_A; 2p\sigma_{H_A^1})$  is the atomic

function participating in the bond with H. Let us write them in general form:

$$\begin{aligned} \Phi(C_A; 2p\sigma_{C_A^B, C_A^D}) &= (1 + \lambda^2)^{-1/2} \{ \Phi(2s) + \lambda \sin \xi \cdot \Phi(2p\sigma_x) \pm \lambda \cos \xi \cdot \Phi(2p\sigma_y) \}; \\ \Phi(C_{B,D}; 2p\sigma_{C_B^A, C_D^A}) &= (1 + \lambda^2)^{-1/2} \{ \Phi(2s) - \lambda \cos(30^\circ - \theta) \cdot \Phi(2p\sigma_{x',x''}) \mp \\ &\mp \lambda \sin(30^\circ - \theta) \cdot \Phi(2p\sigma_{y',y''}) \}; \\ \Phi(C_{B,D}; 2p\sigma_{C_B^B, C_D^B}) &= (1 + \lambda^2)^{-1/2} \{ \Phi(2s) + \lambda \sin \theta \cdot \Phi(2p\sigma_{x',x''}) \mp \\ &\mp \lambda \cos \theta \cdot \Phi(2p\sigma_{y',y''}) \}; \end{aligned} \quad (23)$$

$$\begin{aligned}
 \Phi(C_A; 2p\sigma_{H_A^1, H_A^2}) &= (1 + \mu^2)^{-1/2} \{ \Phi(2s) - \mu \sin \eta \cdot \Phi(2p\sigma_x) \pm \mu \cos \eta \cdot \Phi(2p\sigma_z) \}; \\
 \Phi(C_B; 2p\sigma_{H_B^1, H_B^2}) &= (1 + \mu^2)^{-1/2} \left\{ \Phi(2s) + \frac{1}{2} \mu \sin \eta \cdot \Phi(2p\sigma_{x'}) + \right. \\
 &\quad \left. + \frac{\sqrt{3}}{2} \mu \sin \eta \cdot \Phi(2p\sigma_{y'}) \pm \mu \cos \eta \cdot \Phi(2p\sigma_{z'}) \right\}; \\
 \Phi(C_D; 2p\sigma_{H_D^1, H_D^2}) &= (1 + \mu^2)^{-1/2} \left\{ \Phi(2s) + \frac{1}{2} \mu \sin \eta \cdot \Phi(2p\sigma_{x''}) - \right. \\
 &\quad \left. - \frac{\sqrt{3}}{2} \mu \sin \eta \cdot \Phi(2p\sigma_{y''}) \pm \mu \cos \eta \cdot \Phi(2p\sigma_{z''}) \right\}.
 \end{aligned}
 \tag{24}$$

In expressions (23) and (24) the values of the parameters were taken from Coulson' s work <sup>(8)</sup> and are:  $\lambda = 2.03$ ;  $\mu = 1.51$ ;  $\xi = 38^\circ$ ;  $\eta = 32^\circ$ ;  $\theta = 22^\circ$ .

Taking (22)–(24) into account, the intra-atomic and interatomic quantities  $P_{\mu\nu}$  were calculated from formula (5). Thus, for example, for atom  $A$  we have nonzero matrix elements:  $P_{x_{Ax}A} = 1.0004$ ,  $P_{y_{Ay}A} = 0.9993$ ,  $P_{S_{AS}A} = 1$ ,  $P_{z_{Az}A} = 0.9997$ ; for the  $A$ – $B$  bond we have  $P_{x_{Ax}B} = -0.4906$ ,  $P_{x_{Ay}B} = -0.069$ ,  $P_{y_{Ax}B} = -0.628$ ,  $P_{y_{Ay}B} = -0.088$ ,  $P_{S_{AS}B} = 0.1953$ . Here  $xA$ ,  $SA$ , etc. denote the  $2p_x$ ,  $2s$ -orbitals of atom  $A$ . We used atomic wave functions of the Slater type <sup>(9)</sup>. The matrix elements  $\mathcal{H}_{\mu\nu}^{(0)}$  of the energy operator in the absence of the magnetic field  $\mathbf{H}$ , required in the calculations, were computed by Roothaan' s method <sup>(10)</sup>.

The calculations showed that the contributions to the susceptibility of the molecule from the carbon atoms, calculated by Pople' s formulas (8) and (9), are almost isotropic and equal to:  $\chi_d^C \simeq 9 \cdot 10^{-6}$  cm<sup>3</sup>/mole, and  $\chi_p^C = 0.1034 \langle (\Delta E)^{-1} \rangle \cdot 10^{-15}$  cm<sup>3</sup>/mole. In doing this we did not take into account nonvalence electrons, which will not contribute to the anisotropy. The principal contribution to the anisotropy of cyclopropane is given by interatomic effects, and this contribution is equal to  $\Delta\chi_d^{C_3H_6} = -22.48 \cdot 10^{-6}$  cm<sup>3</sup>/mole,  $\Delta\chi_p^{C_3H_6} = 4.895 \cdot 10^{-17} \langle (\Delta E)^{-1} \rangle$ . Not having exact information on the average value of the energy  $\langle (\Delta E)^{-1} \rangle$ , we took it equal to 10 eV <sup>(5)</sup>. Then  $\Delta\chi_p^{C_3H_6} = 9.17 \cdot 10^{-6}$  cm<sup>3</sup>/mole, and, thus, the total anisotropy of cyclopropane will be  $\Delta\chi^{C_3H_6} = -13.3 \cdot 10^{-6}$  cm<sup>3</sup>/mole. It is of interest to calculate the anisotropy of  $C_3H_6$ , proceeding from M. E. Dyatkina' s ideas <sup>(11)</sup> on the electronic structure of this ring, and to compare the results using NMR spectra.

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