The Coupled Perturbed Hartree-Fock Calculations of the Magnetic Susceptibility for Some Nonbenzenoid Aromatic Hydrocarbons

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The semi-empirical SCF MO method is applied to the calcutations of the magnetic susceptibility of the π-electron systems of several nonbenzenoid aromatic hydrocarbons. To avoid origin-dependent results, a method actually equivalent to Hall and Hardisson's one which is currently called the coupled perturbed Hartree-Fock method is used. With the best-fit parameters, the calculated results are in good agreement with the available experimental values except for the case of aceheptylene.

The diamagnetic susceptibilities of aromatic hydrocarbons are so anisotropic that they do not follow Pascal's sum rule. The first quantitative explanation of this anisotropy was given by Pauling,[1] who introduced the idea of the ring current in π-electron systems. The concept of the ring current, which should be replaced by the more suitable term "*delocalization susceptibility*,"[2] has survived in spite of corrections from the quantum-mechanical point of view.[3] The first attempt to treat the delocalization susceptibility quantum-mechanically was made by London.[4] In his method, the Hückel molecular orbital theory was generalized to include the gauge-invariant atomic orbitals, and the variation method was used to obtain the orbital energies in a magnetic field.

The semi-empirical aspect of the molecular orbital theory for conjugated molecules has been developed by Pariser and Parr[5] and by Pople.[6] They included the electron repulsion explicitly and used the zero-differential overlap approximation. All of the atomic integrals concerned were reduced to empirical parameters or were neglected completely. This semi-empirical scheme is quite simple, but it yields quantitative results which are in good agreement with the experimental values.

Advanced methods of the calculation of the anisotropy corresponding to the development of the molecular orbital theory should obtain more satisfactory results. However, it is well known that the self-consistent version of the molecular orbital theory leads to results which show an obvious origin-dependence[7] resulting from the approximate nature of wavefunctions. To overcome this diffrculty, two methods have been suggested. One is the coupled perturbed Hartree-Fock method which was first employed for aromatic hydrocarbons by Hall and Hardisson.[8] The other, simpler one is the uncoupled Hartree-Fock method,[7] in which the geometric approximation[9] is used instead of the complicated coupling procedure. These methods have given satisfactory results, mainly for benzenoid aromatic hydrocarbons.

The purpose of this paper is to show that, taking several examples, one can apply the above method to calculations of the delocalization susceptibility of nonbenzenoid aromatic hydrocarbons. It has been known that some of these molecules exhibit unusual magnetic properties, that is, a paramagnetic delocalization susceptibility. For actual calculations, the coupled perturbed Hartree-Fock method is adopted, though it is rather more tedious than the uncoupled one. The semi-empirical SCF MO method[10] combined with the variable bondlength technique, which is a variation of the Pariser-Parr-Pople theory, is adopted. The molecules examined are azulene, fulvene, heptafulvene, pentalene, heptalene, aceazulylene, and aceheptylene.

Theory

The Hamiltonian of a π-electron system in a magnetic field can be written as:

$$\mathscr{H} = \sum_a \left\{ -\frac{1}{2}(\nabla_a + i\alpha\mathbf{A}_a)^2 + \sum_\eta V_\eta(\mathbf{r}_a) \right\} + \sum_{a>b} \frac{1}{r_{ab}} \tag{1}$$

where $\mathbf{A}_a$ is the vector potential of the magnetic field at the point occupied by the a-th electron, α, the fine structure constant, V_η $(\mathbf{r}_a)$, the potential due to the σ-core associated with the atom, η, and the last term, the interaction energy between π-electrons. Atomic units will be used throughout this paper.

We assume that the wavefunction for the ground state of a molecule with $2n$ π-electrons is the Hartree-Fock single determinant:

$$\Psi = \frac{1}{\sqrt{2n!}} |\tilde{\phi}_1(\mathbf{r}_1)\alpha\tilde{\phi}_2(\mathbf{r}_2)\beta \cdots \tilde{\phi}_{2n-1}(\mathbf{r}_{2n-1})\alpha\tilde{\phi}_{2n}(\mathbf{r}_{2n})\beta| \tag{2}$$

in which $\tilde{\phi}_i$ is the i-th molecular orbital with spin functions of α or β in the presence of the magnetic field. Following London, $\tilde{\phi}_i$ is written as a linear combination of the gauge-invariant atomic orbitals:

$$\tilde{\phi}_i = \sum_\mu \tilde{C}_{i\mu}\omega_\mu, \tag{3}$$

where:

$$\omega_\mu = \chi_\mu \exp(-i\alpha\mathbf{A}_\mu \cdot \mathbf{r}), \tag{4}$$

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[1] L. Pauling, *J. Chem. Phys.*, **4**, 673 (1936).

[2] D. W. Davies, "The Theory of the Electric and Magnetic Properties of Molecules," John Wiley and Sons, London, 1967.

[3] J. I. Musher, *J. Chem. Phys.*, **43**, 4081 (1965).

[4] F. London, *J. Phys. Rad.*, **8**, 397 (1937)

[5] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

[6] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

[7] A. T. Amos and H. G. Ff. Roberts, *J. Chem. Phys.*, **50**, 2375 (1969).

[8] G. G. Hall and A. Hardisson, *Proc. Roy. Soc.*, *Ser. A*, **268**, 328 (1962).

[9] J. M. Schulman and J. I. Musher, *J. Chem. Phys.*, **49**, 4845 (1968).

[10] H. Yamaguchi, T. Nakajima, and T. Kunii, *Theor. Chem. Acta*, **12**, 3491 (1968).

TABLE 1. EXPRESSIONS FOR QUANTITIES IN MATRIX ELEMENTS

$$F_{\mu\nu} = \beta_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{\mu\nu} + \delta_{\mu\nu}\Big(\sum_{\eta}P_{\eta\eta}\gamma_{\eta\mu} - \sum_{\eta(\neq\mu)}\gamma_{\eta\mu}\Big)$$

$$F_{\mu\nu}{}^{(1)} = \alpha L_{\mu\nu}\beta_{\mu\nu} - \frac{1}{2}P_{\mu\nu}{}^{(1)}\gamma_{\mu\nu}$$

$$F_{\mu\nu}{}^{(2)} = \frac{1}{2}\alpha^2 L_{\mu\nu}\beta_{\mu\nu} - \frac{1}{2}P_{\mu\nu}{}^{(2)}\gamma_{\mu\nu} + \delta_{\mu\nu}P_{\eta\eta}{}^{(2)}\gamma_{\eta\mu}$$

$$P_{\mu\nu} = 2\sum_{i}^{\text{occu}} C_{i\mu}C_{i\nu}$$

$$P_{\mu\nu}{}^{(1)} = 2\sum_{i}^{\text{occu}}(C_{i\mu}{}^{(1)}C_{i\nu} - C_{i\mu}C_{i\nu}{}^{(1)})$$

$$P_{\mu\nu}{}^{(2)} = 2\sum_{i}^{\text{occu}}(C_{i\mu}{}^{(2)}C_{i\nu} - C_{i\mu}{}^{(1)}C_{i\nu}{}^{(1)} + C_{i\mu}C_{i\nu}{}^{(2)})$$

where $\mathbf{A}_\mu$ is the vector potential at the μ-th atomic site. The equations for the coefficients, $\tilde{C}_{i\mu}$, are:

$$\sum_\mu \tilde{F}_{\mu\nu}\tilde{C}_{i\mu} = E_i\sum_\mu \tilde{S}_{\mu\nu}\tilde{C}_{i\mu}, \tag{5}$$

Following the Pariser-Parr-Pople approximation, we neglect the overlap integrals, $\tilde{S}_{\mu\nu}$, and the matrix elements, $\mathscr{H}_{\mu\nu}$, except for those between the nearest neighbours, unless $\mu=\nu$. Thus, the Fock element, $\tilde{F}_{\mu\mu}$, is expressed as:

$$\tilde{F}_{\mu\mu} = \tilde{\mathscr{H}}_{\mu\mu} + \frac{1}{2}\tilde{P}_{\mu\mu}\gamma_{\mu\mu} + \sum_{\eta(\neq\mu)}(\tilde{P}_{\eta\eta} - \zeta_\eta)\gamma_{\mu\eta}, \tag{6}$$

$$\tilde{F}_{\mu\nu} = \tilde{\mathscr{H}}_{\mu\nu} - \frac{1}{2}\tilde{P}_{\mu\nu}\gamma_{\mu\nu}, \qquad (\mu\neq\nu), \tag{7}$$

where:

$$\tilde{\mathscr{H}}_{\mu\nu} = \int w_\mu{}^*(\mathbf{r})\Big\{-\frac{1}{2}(\nabla + i\alpha\mathbf{A})^2 + \sum_\eta V_\eta(\mathbf{r})\Big\}w_\nu(\mathbf{r})d\mathbf{r}, \tag{8}$$

$$\begin{aligned}\gamma_{\mu\nu} &= \int w_\mu{}^*(\mathbf{r}_1)w_\nu{}^*(\mathbf{r}_2)\frac{1}{r_{12}}w_\mu(\mathbf{r}_1)w_\nu(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \int \chi_\mu{}^*(\mathbf{r}_1)\chi_\nu{}^*(\mathbf{r}_2)\frac{1}{r_{12}}\chi_\mu(\mathbf{r}_1)\chi_\nu(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2,\end{aligned} \tag{9}$$

$$\tilde{P}_{\mu\nu} = \sum_{i}^{\text{occu}} 2_i\tilde{C}_\mu\tilde{C}_{i\nu} \tag{10}$$

and where ζ_η is the effective charge of the σ-core of the ζ atom. For hydrocarbons, $\zeta_\eta=1$. According to London,[4)] the matrix element, $\mathscr{H}_{\mu\nu}$, is simplified as follows. The $(\mathbf{A}-\mathbf{A}_\mu)^2$ term is neglected and $\exp[(i\alpha(\mathbf{A}_\mu-\mathbf{A}_\nu)\cdot\mathbf{r}]$ is replaced by $\exp[i\alpha(\mathbf{A}_\mu-\mathbf{A}_\nu)-(\mathbf{r}_\mu+\mathbf{r}_\nu)/2]$, where $\mathbf{r}_\mu$ and $\mathbf{r}_\nu$ are the position vectors at the μ-th and ν-th atomic sites respectively. One thus obtains:

$$\begin{aligned}\tilde{\mathscr{H}}_{\mu\nu} &= \exp\{i\alpha(\mathbf{A}_\mu - \mathbf{A}_\nu)\cdot(\mathbf{r}_\mu + \mathbf{r}_\nu)/2\}\beta_{\mu\nu} \\ &= \exp(i\alpha HL_{\mu\nu})\beta_{\mu\nu},\end{aligned} \tag{11}$$

where $\beta_{\mu\nu}$ is the usual resonance integral:

$$\beta_{\mu\nu} = \int \chi_\mu{}^*(\mathbf{r})\Big\{-\frac{\nabla^2}{2} + \sum_\eta V_\eta(\mathbf{r})\Big\}\chi_\nu(\mathbf{r})d\mathbf{r}, \tag{12}$$

and where $L_{\mu\nu}$ is the signed area of the triangle formed by the point of origin and the nuclei, μ, ν. The diagonal matrix element, $\mathscr{H}_{\mu\mu}$, is also simplified by a similar approximation:

$$\tilde{\mathscr{H}}_{\mu\mu} = \int \chi_\mu{}^*(\mathbf{r})\Big\{-\frac{\nabla^2}{2} + V_\mu(\mathbf{r})\Big\}\chi_\mu(\mathbf{r})d\mathbf{r} = \alpha_\mu, \tag{13}$$

where α_μ is the Coulomb integral.

Following Hall and Hardisson, each term related to the magnetic field is expanded into a series in the descending order of the field strength, H:

$$\tilde{F}_{\mu\nu} = F_{\mu\nu} + iHF_{\mu\nu}{}^{(1)} - H^2F_{\mu\nu}{}^{(2)} - \cdots, \tag{14}$$

$$\tilde{C}_{i\mu} = C_{i\mu} + iHC_{i\mu}{}^{(1)} - H^2C_{i\mu}{}^{(2)} - \cdots, \tag{15}$$

$$\tilde{E}_i = E_i + iHE_i{}^{(1)} - H^2E_i{}^{(2)} - \cdots, \tag{16}$$

$$\tilde{\mathscr{H}}_{\mu\nu} = \beta_{\mu\nu}\Big\{1 + i\alpha L_{\mu\nu} - \frac{1}{2}\alpha^2H^2L_{\mu\nu}{}^2 + \cdots\Big\}, \tag{17}$$

$$\tilde{P}_{\mu\nu} = P_{\mu\nu} + iHP_{\mu\nu}{}^{(1)} - H^2P_{\mu\nu}{}^{(2)} - \cdots, \tag{18}$$

The actual expressions, say $F_{\mu\nu}{}^{1)}$, *etc.*, are shown in Table 1. The self-consistent Eq. (5) become, to the zeroth order:

$$\sum_\mu(F_{\mu\nu} - \delta_{\mu\nu}E_i)C_{i\mu} = 0 \qquad (\nu = 1, 2, \cdots, 2n), \tag{19}$$

to the first order:

$$\sum_\mu(F_{\mu\nu} - \delta_{\mu\nu}E_i)C_{i\mu}{}^{(1)} = \sum_\mu(E_i{}^{(1)}\delta_{\mu\nu} - F_{\mu\nu}{}^{(1)})C_{i\mu} \qquad (\nu = 1, 2, \cdots, 2n), \tag{20}$$

and to the second order:

$$\begin{aligned}\sum_\mu(F_{\mu\nu} - \delta_{\mu\nu}E_i)C_{i\mu}{}^{(2)} &= \sum_\mu(E_i{}^{(1)}\delta_{\mu\nu} - F_{\mu\nu}{}^{(1)})C_{i\mu}{}^{(1)} \\ &\quad + \sum_\mu(E_i{}^{(2)}\delta_{\mu\nu} - F_{\mu\nu}{}^{(2)})C_{i\mu} \\ &\qquad (\nu = 1, 2, \cdots, 2n).\end{aligned} \tag{21}$$

The expression of the π-electron energy, E_π, is:

$$\begin{aligned}\tilde{E}_\pi &= \frac{1}{2}\sum_{\mu\nu}\tilde{P}_{\mu\nu}\{\tilde{\mathscr{H}}_{\mu\nu} + \tilde{F}_{\mu\nu}\} \\ &= \sum_i\tilde{E}_i + \frac{1}{2}\sum_{\mu\nu}\{\tilde{\mathscr{H}}_{\mu\nu} - \sum_{\eta(\neq\mu)}\gamma_{\mu\nu}\delta_{\mu\nu}\}\end{aligned} \tag{22}$$

where the relation:

$$\sum_{i}^{\text{occu}}\tilde{E}_i = \frac{1}{2}\sum_{\mu\nu}\tilde{P}_{\mu\nu}\tilde{F}_{\mu\nu} \tag{23}$$

is used. As E_i is an eigenvalue of $F_{\mu\nu}$, Eq. (20) can be solvend only if:

$$\sum_{\mu\nu}C_{i\nu}(E_i{}^{(1)}\delta_{\mu\nu} - F_{\mu\nu}{}^{(1)})C_{i\mu} = 0, \tag{24}$$

but since $F_{\mu\nu}{}^{1)}$ is skew, this implies that

$$E_i{}^{(1)} = 0. \tag{25}$$

The corresponding relation for Eq. (21) is:

$$E_i{}^{(2)} = \sum_{\mu\nu}F_{\mu\nu}{}^{(2)}C_{\mu i}C_{\nu i} + \sum_{\mu\nu}F_{\mu\nu}{}^{(1)}C_{\mu i}{}^{(1)}C_{\nu i}, \tag{26}$$

so that:

$$\sum_{i}^{\text{occu}}E_i{}^{(2)} = \frac{1}{2}\sum_{\mu\nu}F_{\mu\nu}{}^{(2)}P_{\mu\nu} + \frac{1}{4}\sum_{\mu\nu}F_{\mu\nu}{}^{(1)}P_{\mu\nu}{}^{(1)}. \tag{27}$$

On the other hand, from Eq. (23), we obtain:

$$\begin{aligned}\sum_{i}^{\text{occu}}E_i{}^{(2)} &= \frac{1}{2}\sum_{\mu\nu}F_{\mu\nu}{}^{(2)}P_{\mu\nu} + \frac{1}{2}\sum_{\mu\nu}F_{\mu\nu}{}^{(1)}P_{\mu\nu}{}^{(1)} \\ &\quad + \frac{1}{2}\sum_{\mu\nu}F_{\mu\nu}P_{\mu\nu}{}^{(2)},\end{aligned} \tag{28}$$

therefore:

$$\sum_{\mu\nu}F_{\mu\nu}{}^{(1)}P_{\mu\nu}{}^{(1)} = -2\sum_{\mu\nu}F_{\mu\nu}P_{\mu\nu}{}^{(2)}. \tag{29}$$

Since the magnetic susceptibility is of the second order in H, we need the energy expression of this order. From Eq. (22), we may express it as:

$$E_\pi{}^{(2)} = \sum_i^{\text{occu}} E_i{}^{(2)} + \frac{1}{2}\sum_{\mu\nu}[\{\beta_{\mu\nu} - \sum_{\eta(\neq\mu)} \gamma_{\eta\nu}\delta_{\mu\nu}\}P_{\mu\nu}{}^{(2)}$$
$$+ L_{\mu\nu}\beta_{\mu\nu}P_{\mu\nu}{}^{(1)} + \frac{1}{2}L_{\mu\nu}{}^2\beta_{\mu\nu}P_{\mu\nu}. \tag{30}$$

This expression can be simplified by the use of Eqs. (27) and (29) to:

$$E_\pi{}^{(2)} = \frac{1}{2}\alpha^2\sum_{\mu\nu}L_{\mu\nu}{}^2H_{\mu\nu}P_{\mu\nu} + \frac{1}{2}\alpha^2\sum_{\mu\nu}L_{\mu\nu}H_{\mu\nu}P_{\mu\nu}{}^{(1)}. \tag{31}$$

Therefore, in the presence of the magnetic field, the total π-electron energy of the molecule is:

$$E_\pi = E_\pi - H^2E_\pi{}^{(2)} + \cdots\cdots, \tag{32}$$

since the linear term in H vanishes for a normal molecule with doubly-occupied orbitals. The magnetic susceptibility of a π-electron system is:

$$K_z^\pi = -\partial^2E_\pi/\partial H^2 = 2E_\pi{}^{(2)}$$
$$= 2\alpha^2\sum_{\mu\nu}L_{\mu\nu}{}^2\beta_{\mu\nu}P_{\mu\nu} + 2\alpha\sum_{\mu\nu}L_{\mu\nu}\beta_{\mu\nu}P_{\mu\nu}{}^{(1)}. \tag{33}$$

This gives the delocalization susceptibility required.

Method of Calculation

The first step of our calculations is to solve the zeroth-order Eq. (19). The method used here is a modification of the Pariser-Parr-Pople method, in which the bond lengths and, consequently, the resonance and Coulomb repulsion integrals are allowed to vary with the bond order at each iteration until self-consistency is reached. The bond length is calculated from the bond order by the relationship:[10]

$$r_{\mu\nu}(\text{Å}) = 1.520 - 0.186P_{\mu\nu} \tag{34}$$

The Coulomb repulsion integrals are calculated using the Nishimoto-Mataga formula. The resonance integrals are evaluated by the relation:

$$\beta_{\mu\nu} = \beta_0 \exp\{a(r_0 - r_{\mu\nu})\} \tag{35}$$

where β_0 and r_0 are the resonance integral and the C–C bond distance for benzene respectively. The a=2.5 value has been adopted, because it reproduces well the experimental C–C bond distances and dipole moments of a number of aromatic hydrocarbons.[10]

The second step is to solve the first-order perturbation, Eq. (20). We must consider the additional condition that the perturbed eigenfunction is orthogonal to the unperturbed one, *i.e.*:

$$\sum_\mu C_{\mu i}{}^{(1)}C_{\mu i} = 0 \tag{36}$$

If the matrix, $F_{\mu\nu}{}^{1)}$, is assumed to be known, the set of Eqs. (20) and (36) can be solved as linear equations for various $C_{i\mu}$ values. These $C_{i\mu}$ values are then used to produce a new $F_{\mu\nu}{}^{1)}$ and the linear equations are iteratively solved until this matrix element becomes self-consistent.

The computations were done on the NEAC-2200 computer at Tohoku University.

Results and Discussion

The calculations following the method given in the previous sections have been carried out by varying the positions of the point of origin. These positions, shown in Fig. 1, are various H-atomic sites, C-atomic sites, the midpoint of the C–C bond, and the center of an odd-membered ring. The calculated delocalization susceptibilities, K_z^π, are given in Table 2 in units of the K_z^π of benzene. It turns out that, for all of the molecules concerned, K_z^π is actually origin-independent. The small variation in the values with the displacement

TABLE 2. ORIGIN DEPENDENCE OF THE DELOCALIZATION SUSCEPTIBILITY

Molecule	Position of origin[a]	K_z^π/K_z^π (benzene)
Azulene	1	2.30
	2	2.30
	3	2.30
	4	2.30
	5	2.30
	6	2.30
	7	2.30
Fulvene	1	0.02
	2	−0.01
	3	−0.03
	4	−0.02
	5	−0.03
Heptafulvene	1	−0.07
	2	−0.06
	3	−0.06
	4	−0.05
	5	−0.06
	6	−0.06
Pentalene	1	−1.31
	2	−1.24
	3	−1.37
	4	−1.35
	5	−1.39
Heptalene	1	−1.85
	2	−1.86
	3	−1.86
	4	−1.89
	5	−1.89
Aceazulylene	1	2.24
	2	2.25
	3	2.24
	4	2.22
	5	2.14
	6	2.15
	7	2.27
Aceheptylene	1	1.74
	2	1.85
	3	1.93
	4	1.82
	5	1.71
	6	1.74
	7	1.71
	8	1.71

[a] Each position is shown in Fig. 1.

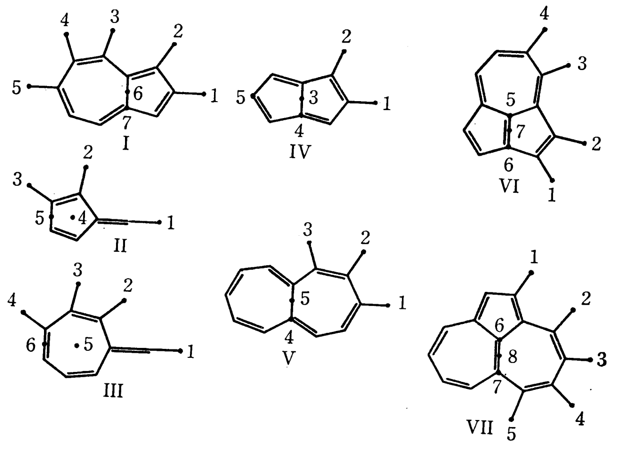

Fig. 1. The positions of the origin taken in this work.
I: Azulene, II: Fulvene, III: Heptafulvene, IV: Pentalene, V: Heptalene, VI: Aceazulylene, VII: Aceheptylene.

of the point of origin seems to be within the limits of unavoidable error arising from the termination of higher-order terms in the calculating processes. Azulene, aceheptylene, and aceazulylene are predicted to be diamagnetic, while heptalene and pentalene, classified as the $4n$-electron system, are predicted to be paramagnetic so far as the delocalization susceptibility is concerned. There exists an uncertainty about the sign of K_z^π of fulvene. However, this does not indicate a serious defect of the method, because the variation in the sign may be due to unavoidable errors since the absolute value of K_z^π is approximately zero. Contrary to the predictions of earlier works,[11,12] heptafulvene has a paramagnetic K_z^π. For azulene, the value (2.30) is in good agreement with the result (2.28) obtained by Hall and Hardisson. The discrepancy may be due to slightly different integral values in the two calculations.

In order to compare the calculated results with the experimental ones, we should add the local contributions to K_z^π. The most direct result obtained from the experiment on gaseous molecules is the mean susceptibility, K^m, which can be written as:

$$K^m = \frac{1}{3}(K_x+K_y+K_z+K_z^\pi), \tag{37}$$

where we assume that:

$$K_x = K_y = N_C K_C^m + N_H K_H^m, \tag{38}$$

and that:

$$K_z = N_C K_C^\perp + N_H K_H^\perp. \tag{39}$$

In these expressions, N_H and N_C are the numbers of hydrogen and carbon atoms in a molecule respectively. For the Pascal constants of carbon and hydrogen atoms for the field perpendicular to the plane, we have used the Amos[7] values, $K_C^\perp = -8.5$, $K_H^\perp = -2.1$ (in units of 10^{-6} cgs emu), which are obtained from the original Hoarau[13] values by slight modifications. For the local values of the in-plane susceptibility, we take the values of $K_C^m = -3.23$, and $K_H^m = -2.69$. These values have been successfully used elsewhere.[7] The mean susceptibilities thus obtained are given in Table 3, together with the experimental results. For aceazulylene and aceheptylene, experimental values are available only for their derivatives. The calculations of the mean susceptibilities of these molecules were carried out on the assumptions that the methyl group contributes only to local effects and that the phenyl group gives one-half of the mean susceptibility of biphenyl. We have no experimental values for heptafulvene and pentalene.

TABLE 3. MEAN SUSCEPTIBILITY χ_m
(cgs emu 10^{-6}cm^3 mol^{-1})

Molecule	Theoretical	Experimental[a]
Benzene	54.94	54.8
Azulene	93.10	91.0
Fulvene	42.40	43.0
Heptafulvene	56.69	
Pentalene	41.93	
Heptalene	65.93	72±7
Aceazulylene	102.48	
its derivative[b]	(170.44)	179±4
Aceheptylene	113.10	
its derivative[c]	(131.35)	112±3

a) H. J. Dauben *et al.*, *J. Amer. Chem. Soc.*, **91**, 1991 (1969).
b) 2-phenyl-5,7-demethylaceazulylene.
c) 3, 5-dimethylaceheptylene.

A comparison of the theoretical and experimental values shows a good agreement in general, except for the case of aceheptylene. As for aceheptylene, no accurate comparison is possible unless the delocalization susceptibility of the derivative can be calculated on a reasonable basis. Moreover, there still remains an ambiguity in the allocated values of the local effects. Subtracting their own local effects, Dauben *et al.*[14] obtained 0.0 as the exaltation value (corresponding to the delocalization susceptibility) of aceheptylene. However, our calculation does not support this conclusion, because no choice of parameters could lead to the vanishing of the exaltation. It is, therefore, hoped that the experimental value of aceheptylene will be reexamined.

Finally, we may conclude that the coupled perturbed Hartree-Fock method gives satisfactory and gauge-invariant results on the delocalization susceptibility, K_z^π, for nonbenzenoid aromatic hydrocarbons as well as benzenoid ones.

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[11] B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique, " Masson et Cie., Paris, 1952.

[12] T. Nakajima, T. Toyota, and H. Yamaguchi, "Aromaticity, Pseudo-Aromaticity, Antiaromaticity," Eds. E. D. Bergmann and B. Pullman, Academic Press, New York, 1971, p. 227.

[13] J. Hoarau, *Ann. Chem.*, **13**, 544 (1956).

[14] H. J. Dauben, J. D. Wilson, and J. L. Laity, *J. Amer Chem. Soc.*, **71**, 1991 (1969).