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The Magnetic Properties of Several *Pseudo*-Jahn-Teller Nonbenzenoid Aromatic Hydrocarbons

By Takeshi NAKAJIMA and Susumu KOHDA

Department of Chemistry, Ibaraki University, Mito

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The effect of bond length alternation on the magnetic properties of several *pseudo*-Jahn-Teller nonbenzenoid aromatic hydrocarbons with 4ν carbon atoms will be investigated. The magnetic moment and the susceptibility of a cyclic polyene will first be formulated in terms of the bond alternation parameter. Appropriate cross-links for forming nonbenzenoid aromatic hydrocarbons, such as pentalene and heptalene, will then be treated as perturbations. It will be shown that the anomalously large paramagnetic susceptibilities of these molecules predicted by Pullman et al. ("Les Théories Electroniques de la Chimie Organique," Masson, Paris (1952), p. 527) arise mainly from the neglect of the bond alternation inherent in them. It will then be concluded that the magnetic susceptibility is a very sensitive indicator of the bond alternation, and that the diamagnetically-induced ring currents in these molecules are very much impeded.

The diamagnetic anisortopy of an aromatic hydrocarbon, attributable to induced ring currents in its π-electron network, is one of the important indications of π-electron delocalization. London(1) has developed a technique for calculating diamagnetic susceptibilities on the basis of the Hückel LCAO MO theory, and this method has since been used extensively for a variety of aromatic hydrocarbons.(2,3) The calculated diamagnetic anisotropies of benzenoid aromatic hydrocarbons are usually in quite good agreement with the experimental values.

As for nonbenzenoid aromatic hydrocarbons, on the other hand, the direct application of London's technique often brings about quite unsatisfactory results; Mayot et al.(4) and Pullman et al.(5) have, for instance, pointed out that the contribution to the magnetic susceptibility due to π-electron delocalization in the nonbenzenoid aromatic hydrocarbons with 4ν carbon atoms, such as pentalene and heptalene, turns out to be paramagnetic instead of diamagnetic. Wagnière and Gouterman(6) have recently interpreted such an anomalously-reduced diamagnetism as a quenched paramagnetism.

It has recently been shown that, as the result of a *pseudo*-Jahn-Teller distortion,(7) there exists a significant alternation in length in the peripheral C–C bonds of these nonbenzenoid aromatic hydrocarbons, the skew structure (C_{2h}) being more favorable energetically than the conventional symmetric structure (D_{2h}).(8-15) It is very probable that the unusually high paramagnetic susceptibilities obtained by the French authors are due mainly to the neglect of the bond alternation characteristic of these molecules.

The aim of this paper is to investigate the effect of bond length distortion on the magnetic susceptibilities of *pseudo*-Jahn-Teller nonbenzenoid aromatic hydrocarbons, such as pentalene, heptalene, *s*-indacene, and dibenzpentalene. The magnetic moment and the susceptibility of a cyclic polyene will first be formulated in terms of the bond alternation parameter, an external magnetic field being treated as a complex perturbation. The formulae will then be tested for cyclooctatetraene and [24]annulene. The formation of cross-links to yield the nonbenzenoid aromatic hydrocarbons will be considered further as a perturbation. The effect of this perturbation on the magnetic properties will then be investigated.

The Cyclic Polyenes, $C_{2n}H_{2n}$

In the presence of an external magnetic field, **H** assumed to be normal to the molecular plane,

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1) F. London, *J. Phys. Radium*, **8**, 397 (1937).

2) B. Pullman and A. Pullman, "Les Théories Electroniques de la Chimie Organique," Masson, Paris (1952).

3) R. McWeeny, *Proc. Phys. Soc.*, **A64**, 261, 921 (1951); ibid., **A65**, 839 (1952); ibid., **A66**, 714 (1953).

4) M. Mayot, G. Berthier and B. Pullman, *J. Phys. Radium*, **12**, 652 (1951); *J. Chim. Phys.*, **50**, 176 (1953).

5) B. Pullman, A. Pullman, E. D. Bergmann, G. Bertheir, E. Fischer, Y. Hirshberg and J. Pontis, ibid., **49**, 24 (1952).

6) G. Wagnière and M. Gouterman, *Mol. Phys.*, **5**, 621 (1962).

7) C. A. Coulson, *Chem. Soc.* (*London*) *Spec. Publ.*, No. 12 (1958), p. 85.

8) P. C. Boer-Veenendaal and D. H. W. Boer, *Mol. Phys.*, **4**, 33 (1961).

9) P. C. Boer-Veenendaal, J. A. Vliegenthart and D. H. W. Boer, *Tetrahedron*, **18**, 1325 (1962).

10) L. C. Snyder, *J. Phys. Chem.*, **66**, 2299 (1962).

11) T. Nakajima and S. Katagiri, *Mol. Phys.*, **7**, 149 (1963).

12) T. Nakajima, Y. Yaguchi, R. Kaeriyama and Y. Nemoto, This Bulletin, **37**, 272 (1964).

13) T. Nakajima, "Molecular Orbitals in Chemistry, Physics, and Biology," Ed. by P. O. Löwdin and B. Pullman, Academic Press, New York (1964), p. 451.

14) T. Nakajima, T. Saijo and H. Yamaguchi, *Tetrahedron*, **20**, 2119 (1964).

15) P. C. Boer, D. H. W. Boer, C. A. Coulson and T. H. Goodwin, ibid., **19**, 2163 (1963).

the MO's of the π-electrons are constructed from the AO's, χ_r^m, given by:

$$\chi_r^m = \chi_r \exp\{-2\pi i(e/hc)\mathbf{A}_r \cdot \rho\} \tag{1}$$

where χ_r is the $2p\pi$ atomic orbital for the rth atom and $\mathbf{A}_r$ is the value of the magnetic vector potential at the rth atom. For a uniform magnetic field, $\mathbf{A}$ is given by $-(1/2)\rho \times \mathbf{H}$, while at the rth atom we have $\mathbf{A}_r = -(1/2)\mathbf{R}_r \times \mathbf{H}$. According to London, the secular problem for the MO's is different from that without the field merely in the form of the resonance integrals, which now include the field-dependent phase factor:

$$\beta_{rs}^m = \beta_{rs}\exp\{\pi i(e/hc)(\mathbf{A}_r - \mathbf{A}_s)\cdot(\mathbf{R}_r + \mathbf{R}_s)\} \tag{2}$$

Using simple geometry, Eq. 2 may be rewritten as:

$$\beta_{rs}^m = \beta_{rs}\exp\{2\pi i(e/hc)S_{rs}H\} \tag{3}$$

where S_{rs} is the singed area of a triangle formed by the origin (where $A=0$) and the bond $r \to s$ (S_{rs} is positive if the direction $r \to s$ is right-handed about the direction of the magnetic field). By expanding the exponential function and writing $(e/hc)S_{rs}H = f_{rs}$, we obtain the change in the resonance integral due to the presence of the field as:

$$\varDelta_{rs} = \beta_{rs}(2\pi i f_{rs} - 2\pi^2 f_{rs}^2 + \cdots) \tag{4}$$

The total perturbation due to the presence of the field is represented by:

$$\varDelta = \sum_{r<s} \varDelta_{rs} \tag{5}$$

It is assumed that $\beta_{rs}=0$ if the atoms r and s are not bonded in a conventional structure.

Now let us consider a cyclic polyene, $C_{2n}H_{2n}$, the MO's of which are assumed to be expressed in the following form:

$$\left.\begin{aligned} \varphi_l &= a_l\varphi_l^{\circ} + b_l\varphi_l^{\bullet} \quad (l=0, \pm 1, \pm 2, \cdots, n) \\ \varphi_l^{\circ} &= \frac{1}{\sqrt{n}}\sum_{r=1}^{n} \chi_{2r-1}\exp\{i\theta_l(r-1)\} \\ \varphi_l^{\bullet} &= \frac{1}{\sqrt{n}}\sum_{r=1}^{n} \chi_{2r}\exp\left\{i\theta_l\left(r-\frac{1}{2}\right)\right\} \end{aligned}\right\} \tag{6}$$

where:

$$\theta_l = 2\pi l/n \tag{7}$$

Allowing for the possibility of a two-fold bond length alternation, we denote by β the resonance integrals for bonds between atoms $2r-1$ and $2r$, and by $k\beta$ ($k \leqq 1$), those for bonds between atoms $2r$ and $2r+1$, including the bond between the $2n$th atom and the first atom. Then we have:

$$\left.\begin{aligned} \int \varphi_l^{\circ *}\mathbf{H}\varphi_l^{\bullet}dv &= (e^{i\theta_l/2} + ke^{-i\theta_l/2})\beta = \gamma_l\beta \\ \int \varphi_l^{\bullet *}\mathbf{H}\varphi_l^{\circ}dv &= (e^{-i\theta_l} + ke^{i\theta_l/2})\beta = \gamma_l^*\beta \\ \int \varphi_l^{\circ *}\mathbf{H}_l{}^{\circ}dv = \int \varphi_l^{\bullet *}\mathbf{H}\varphi_l^{\bullet}dv &= \alpha \end{aligned}\right\} \tag{8}$$

By solving the quadratic secular equation, we obtain, for the orbital binding energies:

$$\begin{aligned} x_l^{(0)} = (\varepsilon_l - \alpha)/\beta &= \pm(1 + 2k\cos\theta_l + k^2)^{1/2} \\ &= \pm(\gamma_l^*\gamma_l)^{1/2} \end{aligned} \tag{9}$$

where + and − should be taken for the bonding and antibonding orbitals respectively.

The partial π-bond orders for the $2r-1$—$2r$ bonds (double bonds) and the $2r$—$2r+1$ bonds (single bonds) are given respectively by the forms[16]:

$$\left.\begin{aligned} p_{l,d} &= \frac{1}{n}(a_l^* b_l e^{i\theta_l/2} + a_l b_l^* e^{-i\theta_l/2}) \\ &= \pm\frac{1 + k\cos\theta_l}{n(1 + 2k\cos\theta_l + k^2)^{1/2}} \\ p_{l,s} &= \frac{1}{n}(a_l b_l^* e^{i\theta_l/2} + a_l^* b_l e^{-i\theta_l/2}) \\ &= \pm\frac{k + \cos\theta_l}{n(1 + 2k\cos\theta_l + k^2)^{1/2}} \end{aligned}\right\} \tag{10}$$

In order to take account of the imaginary perturbation due to an external magnetic field, we define in this connection the imaginary partial π-bond orders, which are given by:

$$\left.\begin{aligned} \bar{p}_{l,d} &= \frac{1}{n}(a_l^* b_l e^{i\theta_l/2} - a_l b_l^* e^{-i\theta_l/2}) \\ &= \pm\frac{ik\sin\theta_l}{n(1 + 2k\cos\theta_l + k^2)^{1/2}} \\ \bar{p}_{l,s} &= \frac{1}{n}(a_l b_l^* e^{i\theta_l/2} - a_l^* b_l e^{-i\theta_l/2}) \\ &= \pm\frac{i\sin\theta_l}{n(1 + 2k\cos\theta_l + k^2)^{1/2}} \end{aligned}\right\} \tag{11}$$

According to the LCAO perturbation theory, the first-order change in the energy of the lth MO due to the presence of a magnetic field is expressed in terms of bond orders. Using Eqs. 10 and 11, we obtain:

$$\begin{aligned} \delta x_l^{(1)} &= \langle \psi_l^* | \varDelta | \psi_l \rangle \\ &= -2\pi i f n(\bar{p}_{l,d} + k\bar{p}_{l,s}) \\ &\quad -2\pi^2 f^2 n(p_{l,d} + kp_{l,s}) \\ &= \pm\left\{\frac{2}{n}\,\frac{k\sin\theta_l}{(1 + 2k\cos\theta_l + k^2)^{1/2}}\,\omega \right. \\ &\quad \left. -\frac{1}{2n}(1 + 2k\cos\theta_l + k^2)^{1/2}\omega^2\right\} \end{aligned} \tag{12}$$

where:

$$\omega = 2n\pi f = (e/hc)\pi SH \tag{13}$$

in which S is the total area of the molecular plane.

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[16] Y. Ooshika, *J. Phys. Soc. Japan*, **12**, 1246 (1957).

TABLE I. MO ENERGIES, MAGNETIC MOMENTS, AND MAGNETIC SUSCEPTIBILITIES OF C_8H_8

	$x_l^{(0)}$		λ_l		μ_l	
l	$k=1$	$k<1$	$k=1$	$k<1$	$k=1$	$k<1$
-2	0.0000	$k-1$	-0.5000	0.0000	0.0000	$1/32\{(1-k)-(1+k)^2(1-k)^{-1}\}$
2	0.0000	$1-k$	0.5000	0.0000	0.0000	$-1/32\{(1-k)-(1+k)^2(1-k)^{-1}\}$ $(\geqq 0)$
-1	1.4142	$(1+k^2)^{1/2}$	-0.3536	$-k/2(1+k^2)^{1/2}$	-0.0442	$-1/32\{(1+k^2)^{1/2}-(1-k^2)^2(1+k^2)^{-3/2}\}$ $(\leqq 0)$
1	1.4142	$(1+k^2)^{1/2}$	0.3536	$k/2(1+k^2)^{1/2}$	-0.0442	$-1/32\{(1+k^2)^{1/2}-(1-k^2)^2(1+k^2)^{-3/2}\}$ $(\leqq 0)$
0	2.0000	$1+k$	0.0000	0.0000	-0.0625	$-1/32\{(1+k)-(1-k)^2(1+k)^{-1}\}$ $(\leqq 0)$
$2\sum\limits_l$*	9.6568	$4+4(1-k^2)^{1/2}$	1.0000	0.0000	-0.3018	$(k^2/2)\{(1-k^2)^{-1}-(1+k^2)^{-3/2}\}$ $(\geqq 0)$
$2\sum\limits_l^{2-}$†	9.6568	$2(1+k)+4(1+k^2)^{1/2}$	0.0000	0.0000	-0.3018	$-(k/4)\{(1+k)^{-1}+2k(1+k^2)^{-3/2}\}$ $(\leqq 0)$

* The summation is over $l=0, \pm 1, 2$.
† The summation is over $l=0, \pm 1, \pm 2$.

McWeeny[17] has already shown that the second-order energy change of the lth MO due to complex perturbations is related to the imaginary partial mutual bond polarizability defined as:

$$\bar{\pi}_{l,rs,tu} = \pi_{l,rs,tu} - \pi_{l,rs,ut} + \pi_{l,sr,ut} - \pi_{l,sr,tu} \tag{14}$$

where:

$$\pi_{l,rs,tu} = \sum_{m(\neq l)} \frac{c_{rl}^{*} c_{sm} c_{tm}^{*} c_{ul}}{x_l^{(0)} - x_m^{(0)}} \tag{15}$$

The zero-field MO's are assumed to be $\psi_l = \sum\limits_r c_{rl} \chi_r$. The second-order energy change in the lth MO due to the presence of a magnetic field is thus given by:

$$\begin{aligned}\delta x_l^{(2)} &= \sum_{m(\neq l)} \frac{\langle \psi_l^{*} | \Delta | \psi_m \rangle \langle \psi_m^{*} | \Delta | \psi_l \rangle}{x_l^{(0)} - x_m^{(0)}} \\ &= -4\pi^2 f^2 n(\bar{\pi}_{l,d,d} + k\bar{\pi}_{l,d,s} \\ &\quad + k\bar{\pi}_{l,s,d} + k^2 \bar{\pi}_{l,s,s}) \\ &= \pm \frac{1}{2n^2} \Big\{ \frac{(1-k^2)^2}{(1+2k\cos\theta_l + k^2)^{3/2}} \\ &\quad + (n-1)(1+2k\cos\theta_l+k^2)^{1/2} \Big\} \omega^2 \end{aligned} \tag{16}$$

We can now formulate the magnetic moment and the magnetic susceptibility associated with the lth MO. The shifts in orbital energies due to the magnetic field being very small, we may in general expand the energy of a given MO as a function of H in Taylor's series in H:

$$x_l = x_l^{(0)} + \lambda_l \omega + \mu_l \omega^2 + \cdots \tag{17}$$

where, using Eqs. 12 and 16 respectively, λ_l and μ_l are given by (in β units):

$$\lambda_l = \mp \frac{2}{n} \frac{k\sin\theta_1}{(1+2k\cos\theta_l+k^2)^{1/2}} \tag{18}$$

$$\begin{aligned}\mu_l = \pm \frac{1}{2n^2} \Big\{ &(1+2k\cos\theta_l + k^2)^{1/2} \\ &- \frac{(1-k^2)^2}{(1+2k\cos\theta_l+k^2)^{3/2})} \Big\}\end{aligned} \tag{19}$$

The magnetic moment and the susceptibility, χ_l, associated with the lth MO are given, by $-\lambda_l(\omega/H)$ and $-2\mu_l(\omega/H)^2$, respectively. For the bonding MO's, the first term of Eq. 19 represents the pure diamagnetism (negative in β units), while the second term, which arises from the second-order perturbation, represents the induced paramagnetism (positive in β units).

Salem[18] has derived a formula similar to Eq. 19 for the effect of a bond alternation on the magnetic susceptibility of a cyclic polyene. However, the pure diamagnetic term and the second-order paramagnetic term are not separated in his expression, and the origin of the paramagnetic susceptibility is not clearly explained.

The usefulness of Eqs. 18 and 19 may also be demonstrated for cyclooctatetraene and [24]-annulene.

Cyclooctatetraene (C_8H_8).—The orbital energies and the magnetic contributions, λ_l and μ_l, calculated using Eqs. 9, 18, and 19 are presented in Table I. When $k=1$, all the MO's except for the lowest and the highest (vacant) ones are doubly degenerate. The bond alternation lifts the degeneracy of the nonbonding orbitals (with $l=\pm 2$), the top two electrons being both placed in the lower level. As we are concerned with the effect of the bond length distortion on the magnetic properties, we adopt for the case when $k=1$ the electron configuration in which the top two electrons are both placed into one of the degenerate nonbonding orbitals. This gives rise to a molecular paramagnetic moment due to the non-compensating orbital angular

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[17] R. McWeeny, *Mol. Phys.*, **1**, 311 (1958).

[18] L. Salem, *Proc. Cambridge Phil. Soc.*, **57**, 353 (1961); H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.*, **A257**, 445 (1960).

momentum.* The magnetic moment of the occupied nonbonding orbital disappears if the bond alternation is introduced, and, at the same time, the magnetic susceptibility turns out to be paramagnetic. In other words, the first-order paramagnetism is quenched by the bond length distortion and transferred to the susceptibility as an induced paramagnetism. This second-order paramagnetism greatly predominates over the diamagnetism originating from all other, lower-lying electrons, giving rise to a molecular paramagnetic susceptibility. The molecular susceptibility is very sensitive to the value of k; the value of $2\sum_{l}\mu_{l}$ varies from ∞ to 0 as k varies from 1 to 0.

In the dianion of cyclooctatetraene that forms a closed electron shell when $k=1$, no such an anomalous paramagnetic susceptibility is predicted.

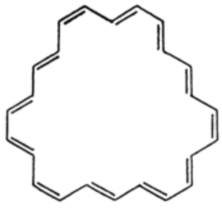
Hoarau[19] has recently made improvements on the London method by refining the calculation of the gauge factors. According to him, the molar magnetic anisotropy is given by:

$$\varDelta K = (1/3)\varDelta K_{\mathrm{London}} + \mathrm{A}\times 10^{-18}R \qquad (20)$$

where $\varDelta K_{\mathrm{London}}=\boldsymbol{N}\chi_{\pi}$, in which $\boldsymbol{N}$ is Avogadro's number and $\chi_{\pi}=2\sum_{l}\chi_{l}$; R is the π-electron delocalization energy as calculated using the Hückel-type MO method. The value adopted for the proportionality constant, A, is 0.940.**

The magnetic susceptibilities as a function of the k of C_8H_8 calculated using Eq. 20 indicate that, within the range $0.2\geq k>0$, the susceptibility turns out to be diamagnetic, if only slightly so. Actually, it has been shown that the molecule exhibits a marked bond length alternation, as revealed by its tub form, and that it has a weak diamagnetism.[20] On the other hand, the $C_8H_8{}^{2-}$ dianion has been known to show the normal diamagnetism, as in benzenoid aromatic hydrocarbons, and no bond length alternation.[21]

[24]annulene ($C_{24}H_{24}$).—The molecule, if the molecular symmetry group is D_{3h}, possesses an open-shell electronic configuration in the sense that the top two degenerate MO's are filled with two electrons. The bond length distortion lifts the degeneracy of these MO's and results in the achievement of a closed electron shell, the situation being quite similar to the case of C_8H_8.



$C_{24}H_{24}$

In order to determine the equilibrium bond length alternation, we employ the minimum energy method, in which the effects of σ-bond compression are taken into account.[11] The total binding energies, V, taken to be the sum of the π-bond energy and the σ-bond energy, are calculated for a series of k values (1–0), and then the equilibrium bond alternation, k_{min}, is given by the minimum of the V-k curve. The k_{min} value thus calculated for [24]annulene turns out to be 0.61, which indicates that in this molecule there exists a significant bond length alternation, one which is comparable in extent to that in butadiene (with $k_{\mathrm{min}}=0.55$).

The molar anisotropy, $\varDelta K/\varDelta K_{\mathrm{benzene}}$, calculated for the skew form with $k=0.61$ turns out to be 0.012. This indicates that the induced diamagnetic ring current in this molecule is highly impeded. It has recently been shown that the proton NMR spectrum of this molecule consists of one single band at 3.16 τ, which is close to that observed for the olefinic protons of linear-conjugated polyenes, showing an absence of the ring current as in the benzenoid aromatic hydrocarbons.[22]

The Introduction of Cross-Links

Now let us consider a cata-condensed aromatic hydrocarbon formed by the introduction of certain cross-links into a cyclic polyene, the formation of cross-links being treated as a perturbation.

Let us consider the formation of a cross-link between the odd-numbered atoms, $2r-1$ and $2r'-1$, of a cyclic polyene, and let us denote the change in the π-electron Hamiltonian by $\mathbf{H}^{\circ}$. We then have:

$$\langle\varphi_{l}^{\circ *}|\mathbf{H}|\varphi_{l}^{\circ}\rangle = (2k^{\circ}\beta/n)\cos\theta_{l}(r'-r) = \delta_{l}^{\circ}\beta \qquad (21)$$

where we set $\int\chi_{2r-1}\mathbf{H}^{\circ}\chi_{2r'-1}\mathrm{d}v=k^{\circ}\beta$. Similarly, for the cross-link between the even-numbered atoms, $2r$ and $2r'$, we have:

$$\langle\varphi_{l}^{\mathrm{e}*}|\mathbf{H}^{\mathrm{e}}|\varphi_{l}^{\mathrm{e}}\rangle = (2k^{\mathrm{e}}\beta/n)\cos\theta_{l}(r'-r) = \delta_{l}^{\mathrm{e}}\beta \qquad (22)$$

where $\int\chi_{2r}\mathbf{H}^{\mathrm{e}}\chi_{2r'}\mathrm{d}v=k^{\mathrm{e}}\beta$. Further, for the cross-

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* We may place alternatively each of the top two electrons in one of the degenerate levels. This gives rise to a triplet spin paramagnetism.

[19] J. Hoarau, *Ann. Chim.*, **1**, 544 (1956).

** The value of A has been determined so that the $\varDelta K/\varDelta K_{\mathrm{benzene}}$ values calculated using Eq. 20 fit the experimental ones. Hoarau has proposed a value of 0.776 calculated using the experimental anisotropies of a number of aromatic hydrocarbons, including biphenyl and stilben, which show a remarkable bond length variation. We have re-examined the value using the experimental values of benzene, naphthalene, anthracene, phenanthrene, and naphthacene, which do not exhibit any significant bond length variation.

[20] S. Shida and S. Fujii, This Bulletin, **24**, 173 (1951).

[21] T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960); T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, **32**, 1873 (1960).

[22] L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky and A. A. Bothner-By, *J. Am. Chem. Soc.*, **84**, 4307 (1962).

TABLE II. MO ENERGIES, MAGNETIC MOMENTS, AND MAGNETIC SUSCEPTIBILITIES OF PENTALENE*

	x_l		λ_l		μ_l	
l	$k=k^o=1$	$k=k^o=0.55$	$k=k^o=1$	$k=k^o=0.55$	$k=k^o=1$	$k=k_o=0.55$
−2	0.0000	−0.3330	0.0000	0.0000	−0.5000	−0.1461
2	0.5000 (0.4707)	0.6080 (0.5950)	0.0000 (0.0000)	0.0000 (0.0000)	0.5000 (0.4968)	0.1461 (0.1423)
−1	1.1861 (1.0000)	1.0120 (0.8989)	−0.3482 (0.0000)	−0.2392 (0.0000)	−0.0422 (−0.3333)	−0.0249 (−0.2605)
1	1.1861 (1.4142)	1.0120 (1.1413)	0.3482 (0.0000)	0.2392 (0.0000)	−0.0422 (0.2500)	−0.0249 (0.2111)
0	2.0000 (2.3429)	1.6936 (1.7247)	0.0000 (0.0000)	0.0000 (0.0000)	−0.0620 (−0.0549)	−0.0442 (−0.0412)
$2\sum_l$	9.7444 (10.4556)	8.6512 (8.7198)	0.0000 (0.0000)	0.0000 (0.0000)	0.7072 (0.7172)	0.1042 (0.1034)

* The values in parentheses for x_l are calculated by solving the secular equation, and those for λ_l and μ_l are calculated by using London's method.

link between an odd-numbered atom, $2r-1$, and an even-numbered atom, $2r'$, we have:

$$\langle\varphi_l^{\circ *}|\mathbf{H}'|\varphi_l^{\bullet}\rangle = (k'\beta/n)\mathrm{e}^{i\theta_l(r'-r+1/2)} = \delta_l'\beta \quad (23)$$

where $\int \chi_{2r-1}\mathbf{H}'\chi_{2r'-1}\mathrm{d}v=k'\beta$.

Assuming the perturbations due to the three types of cross-links to be additive, and solving the quadratic secular equation, we then obtain the energy of the $l$the MO as (in β units):

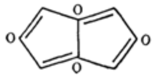
$$x_l = \frac{1}{2}\left[\left(\delta_l^{\circ}+\delta_l^{\bullet}\right) \pm\left\{\delta_l^2+4\left(\gamma_l^*+\delta_l'^*\right)\left(\gamma_l+\delta_l'\right)\right\}^{1/2}\right]$$
$$\left(\delta_l=\delta_l^{\circ}-\delta_l^{\circ}\right) \quad (24)$$

Using the LCAO perturbation theory generalized to take account of the imaginary perturbation due to a magnetic field, as described in the preceding chapter, we obtain the magnetic contributions, λ_l and μ_l, as:

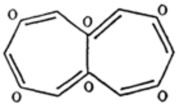
$$\lambda_l = \pm\{4k\sin\theta_l-i(e^{i\theta_l/2}-k\mathrm{e}^{-i\theta_l/2})\delta_l'^* +i(\mathrm{e}^{-i\theta_l/2}-k\mathrm{e}^{i\theta_l/2})\delta_l'\}/n\{\delta_l^2 +4(\gamma_l^*+\delta_l'^*)(\gamma_l+\delta_l')\}^{1/2} \quad (25)$$

$$\begin{aligned}\mu_l = \pm\frac{1}{2n^2}\Bigg[&\frac{2\gamma_l^*\gamma_l+\gamma_l^*\delta_l'+\delta_l'^*\gamma_l}{\{\delta_l^2+4_l^*(\gamma_l+\delta_l'^*)(\gamma_l+\delta_l')\}^{1/2}} \\ &-\frac{2}{\{\delta_l^2+4(\gamma_l^*+\delta_l^*)(\gamma_l+\delta_l')\}^{3/2}} \\ &\times\{4(1-k^2)^2+(1-2k\cos\theta_l+k^2) \\ &\times(\delta_l^2+2\gamma_l^*\delta_l'+2\delta_l'^*\gamma_l+2\delta_l'^*\delta_l') \\ &+(\mathrm{e}^{i\theta_l}-2k+k^2\mathrm{e}^{-i\theta_l})(2\gamma_l^*\delta_l'^*+\delta_l'^{*2}) \\ &+(\mathrm{e}^{-i\theta_l}-2k+k^2\mathrm{e}^{i\theta_l})(2\gamma_l\delta_l'+\delta_l'^2)\}\Bigg]\end{aligned} \quad (26)$$

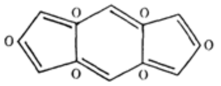
For the bonding MO's, the first term in the bracket of Eq. 26 represents the pure diamagnetism, while the second term, which arises from the second-order perturbation due to the magnetic field, represents the induced paramagnetism. Equations 25 and 26 will first be tested for pentalene, and then applied to heptalene, *s*-indacene, and dibenzpentalene.



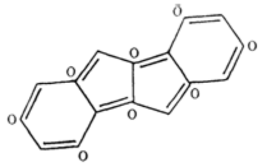
(I)



(II)



(III)



(IV)

Pentalene (I).—The molecule is formed from cyclooctatetraene by the introduction of a cross-link between the atoms of a like parity with $r'-r=4$. The perturbation is given by $\delta_l^{\circ}=(k^o/2)-\cos\pi l$, the cross-linked atoms being assumed to be odd-numbered. The values of x_l, λ_l, and μ_l calculated using Eqs. 24—26 are presented in Table II. By comparing Table II with Table I, we can see how the introduction of the cross-link influences these quantities. By examining the figures of the case when $k(=k^o)=1$, it may be seen that the cross-link perturbation lifts the degeneracy of the non-bonding orbitals of the parent cyclic polyene. At the same time, the magnetic moment of the non-bonding orbitals is quenched and reproduced as the second-order susceptibility; namely, the first-order magnetic moment, λ_2, of the parent polyene is transferred to the second term of μ_2 as an induced paramagnetism. This paramagnetism greatly overshadows the diamagnetism from all other, lower-lying orbitals, giving rise to a large molecular paramagnetic susceptibility.

Table II includes the values of x_l, λ_l, and μ_l

for the case when $k(=k^{\circ})=0.55$, which is the $k_{\min}$ value of the parent polyene. It may be seen that the susceptibility is very senstive to the value of k.

The values of x_l calculated by solving the secular equation, and those of λ_l and μ_l calculated by the direct use of London's method, are also included in Table II. For the molecular susceptibility, $2\sum_l \mu_l$, there is a good agreement between the present perturbation calculations and the complete MO calculations, though as to μ_1 and μ_{-1} there is a large difference.

Pentalene has not yet been synthesized.

Heptalene (II).—The $k_{\min}$ value of the perimeter of this molecule, dodecahexaene, was calculated to be 0.59. The cross-link perturbation used to yield heptalene from the cyclic polyene is $\delta_l^{\circ}=(k^{\circ}/3)\cos\pi l$. Assuming $k^{\circ}=0.59$ and using Eq. 26, one obtains $\chi_{\pi}=0.803\times 10^{-17}\,\beta$. The $\Delta K/\Delta K_{\text{benzene}}$ value turns out to be -0.15 (cf. $\Delta K/\Delta K_{\text{benzene}}=-5.65$ when $k=k^{\circ}=1$). This indicates that, in heptalene, the magnetically-induced ring currents should be impeded considerably. A part of evidence for this conclusion is given by the proton NMR spectrum of this molecule, which exhibits the proton signals in the vinyl region (4–5τ).[23]

s-Indacene (III).—The cross-link perturbations used to form this molecule from the corresponding cyclic polyene are $\delta_l{}^{\circ}=(k^{\circ}/3)\cos(2\pi l/3)$. Assuming $k=k^{\circ}=0.59$, we obtain $\chi_{\pi}=0.377\times 10^{-17}\,\beta$, which in turn yields $\Delta K/\Delta K_{\text{benzene}}=0.007$. The magnetically-induced ring currents should be considerably impeded in this molecule also. Comparing the $\Delta K/\Delta K_{\text{benzene}}$ values of heptalene and *s*-indacene, it may be expected that the NMR proton signals of the latter should appear at lower fields than do those of the former. It has experimentally been shown that *s*-indacene exhibits signals between 2.4 and 3.7 τ.[24]

Dibenzpentalene (IV).—The $k_{\min}$ value of the perimeter of this molecule, the 16-membered cyclic polyene, is calculated to be 0.60. The cross-link perturbations used to form dibenzpentalene from the cyclic polyene are $\delta_l^{\circ}=(k^{\circ}/4)\cos\pi l$ for the central cross-link (between atoms of a like parity) and $\delta_l^{\prime}=(k'/8)\exp(5\pi il/8)$ for the other two cross-links (between atoms of a different parity). Assuming $k^{\circ}=k=0.60$ and $k'=(1+k)/2=0.80$, we obtain $\Delta K/\Delta K_{\text{benzene}}=0.99$. The calculated value is in good agreement with the observed value, 0.87, for dimethyldibenzpentalene.[19] The introduction of a methyl substituent would result in the reduction of the diamagnetic anisotropy.

In conclusion, it may be said that, in these catacondensed nonbenzenoid aromatic hydrocarbons with 4 ν carbon atoms, magnetically-induced ring currents are considerably impeded by the bond length alternation inherent in them, and that, hence, the π-electron delocalization is fairly restricted. In this sense these molecules can not be considered to belong to the "aromatic" category. They should have, rather, characteristics of a cyclic polyolefin.

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[23] H. J. Dauben and D. J. Bertelli, ibid., **83**, 4659 (1961).

[24] K. Hafner, K. H. Häfner, C. König, M. Kreuder, G. Ploss, G. Schulz, E. Sturm and K. H. Vöpel, *Angew. Chem.*, **75**, 35 (1963); K. Hafner, ibid., **75**, 1041 (1963).