Magnetic Properties of Nonbenzenoid Aromatic Hydrocarbons

Hiroyuki Yamaguchi* and Takeshi Nakajima
Department of Chemistry, Tohoku University, Sendai 980

(Received March 18, 1974)

The magnetic susceptibilities for nonbenzenoid aromatic hydrocarbons have been examined by using the modified London-Hoarau method in the framework of the Wheland-Mann-type SCF MO approximation. By taking into account the double-bond fixation quite common in these molecules, we obtained a general agreement between the calculated results and the available experimental values.

The diamagnetic delocalization susceptibility of a ring π-electron system, attributable to induced ring currents in its π-electron network, is one of the important quantities indicative of π-electron delocalization. A quantum-mechanical theory for the diamagnetic delocalization susceptibility was first developed by London.1) His method is based on the Hückel LCAO MO theory and has extensively been used for a variety of aromatic hydrocarbons.2,3) The calculated diamagnetic anisotropies for benzenoid hydrocarbons are usually in quite good agreement with the experimental values. On the other hand, the direct application o London's technique to nonbenzenoid aromatic hydrocarbons4,5) often brings about unsatisfactory results in view of the recently-reported experimental data.15)

It is probable that such unsatisfactory results arise mainly from the employment of molecular orbitals obtained using the simple Hückel MO theory which does not take into account the double-bond fixation quite common in nonbenzenoid hydrocarbons and, hence, proves to be less reliable when applied to these molecules, and partly from the shortcomings inherent in London's original theory. Hoarau6) has made improvements on the London theory by refining the calculation of the gauge factors.

It is the purpose of this paper to calculate the magnetic susceptibilities of several nonalternant hydrocarbons by using the modified London-Hoarau method in the framework of the Wheland-Mann-type SCF MO approximation.7) This approximation allows us to obtain equilibrium geometrical structures with respect to the C–C bond lengths of these molecules.

Method of Calculation

London's theory is not necessarily related to the simple Hückel MO approximation. It can naturally be extended to the Wheland-Mann-type SCF LCAO MO method.7) In this method, the Coulomb integral, α_μ, and the resonance integral, $\beta_{\mu\nu}$, are given by the following formulas, respectively:

$$\alpha_\mu = \alpha_0 + \omega(1-q_\mu)\beta_0 \tag{1}$$

where q_μ is the electron density and ω is taken to be unity, and:

$$\beta_{\mu\nu} = \beta_0 \exp\,[a(1.397-r_{\mu\nu})] \tag{2}$$

where $r_{\mu\nu}$ is the bond length and is correlated with the bond order, $p_{\mu\nu}$, by Eq. (3):8)

$$r_{\mu\nu} = 1.520 - 0.186p_{\mu\nu} \tag{3}$$

The value of a in Eq. (2) is taken to be 4.4 Å^{-1}. This value was determined so as to reproduce the observed C–C bond lengths of butadiene9) and naphthalene10) and the dipole moments of pentafulvene11) and heptafulvene.12)

Improving the correlation between the experimental and calculated relative anisotropies of diamagnetic susceptibility, Hoarau proposed an expression for the molar susceptibility which includes a dependence on the delocalization energy, DE:7)

$$\Delta K = \Delta K_{\mathrm{L}}/3 + A\times 10^{-18}DE \tag{4}$$

where ΔK_{L} is the molar susceptibility according to London's theory.1) The A parameter was fitted to ensure the best agreement with the experimental results; the value of 0.776 for the case of Hückel basis was found. Nakajima and Kohda13) proposed a different value for A, 0.940. However, in both papers rather inaccurate experimental values of diamagnetic susceptibility were used. Reconsidering their procedure by the use of the more recent experimental values of the diamagnetic susceptibilities given in Ref. 14, we obtain a different least-squares fit:**

$$\Delta K = \Delta K_{\mathrm{SCF}}/3 + 0.359\times 10^{-18}DE \tag{5}$$

where ΔK_{SCF} is the magnetic susceptibility calculated by using the Wheland-Mann-type SCF LCAO MO basis. Equation (5) can be used to calculate the magnetic susceptibilities of several nonbenzenoid aromatic hydrocarbons (Fig. 1).

Results and Discussion

In Table 1, the theoretical diamagnetic susceptibilities, ΔK, for nonalternant hydrocarbons are listed (in units of $\Delta K_{\mathrm{benzene}}$) and compared with the experimental exaltations (in units of $\Lambda_{\mathrm{benzene}}$).15) The theoretical values are in good agreement with the experimental data, except for the case of aceheptylene (IX), whose experimental exaltation has been reported, unbelievably, to be zero. Recently, using the coupled perturbed Hartree-Fock method, Mikami *et al.*16) have calculated the magnetic susceptibility of IX. The calculated value is almost the same as that obtained in this paper. It is, therefore, hoped that the experimental value of this molecule should be re-examined. In pentalene (I), heptalene (II), *s*-indacene (III), py-

---

* Present address: Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami-machi, Kumamoto 860.

** We have re-examined the A value using the experimental values of benzene, naphthalene, anthracene, naphthacene, phenanthrene, chrysene, pyrene, perylene, triphenylene, and coronene, which do not exhibit any significant bond-length variation.

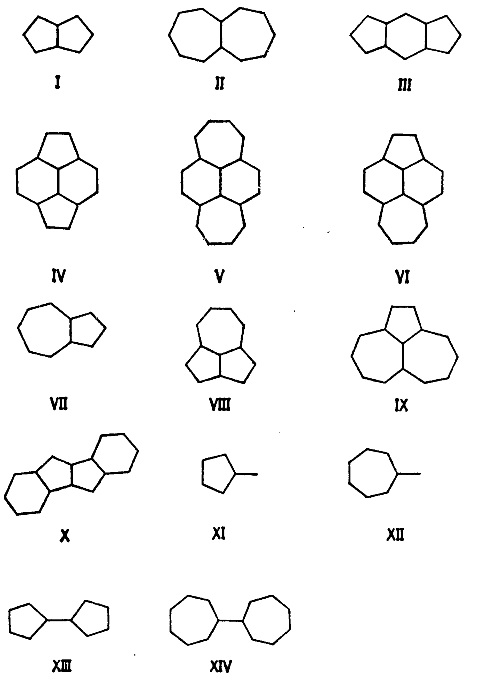

Fig. 1. Nonbenzenoid aromatic hydrocarbons.

Table 1. DIAMAGNETIC SUSCEPTIBILITIES OF NONALTERNANT HYDROCARBONS

Molecule	Theoretical $\Delta K/\Delta K_{\mathrm{benzene}}$	Experimental $\Lambda/\Lambda_{\mathrm{benzene}}$
Pentalene (I), D_{2h}	-1.35	
Pentalene (I), C_{2h}	-0.41	
Heptalene (II), D_{2h}	-4.41	
Heptalene (II), C_{2h}	-0.61	-0.45[a]
s-Indacene (III), D_{2h}	-0.88	
s-Indacene (III), C_{2h}	-0.38	
Pyracylene (IV)	-0.40	
Dipleiadiene (V)	-0.34	
Acepleiadylene (VI)	3.92	3.87[a]
Azulene (VII)	2.04	2.16[a]
Aceazulylene (VIII)	2.14	2.18[a,c]
Aceheptylene (IX)	1.72	0.0[a,d]
Dibenzopentalene (X)	1.10	1.00,[a,d] 0.87[b,d]
Fulvene (XI)	0.10	0.08[a]
Heptafulvene (XII)	0.16	
Fulvalene (XIII)	0.075	
Heptafulvalene (XIV)	0.18	0.15[a]

a) Ref. 15. b) Ref. 6. c) The value for a dimethylphenyl derivative. d) The value for a dimethyl derivative.

racylene (IV), and dipleiadiene (V), the last of which is yet unknown, the magnetic susceptibilities are predicted to be negative. Such an anomalously-reduced diamagnetism may be interpreted as an induced paramagnetism.[13,17–19]

Molecules I, II, and III are predicted to possess two equilibrium geometrical structures, one belonging to the molecular symmetry, D_{2h}, and the other to C_{2h}.[20] In the former, the C–C bond lengths are quite equalized, while in the latter there is a considerable double-bond fixation. The equilibrium structures with the reduced-molecular symmetry (C_{2h}) were obtained by taking a distorted C nuclear arrangement with the C_{2h} symmetry as the starting geometry for the iterative calculation. It has been shown that, as a result of the *pseudo*-Jahn-Teller effect, in such a case the structure with reduced symmetry is energetically more stable than the fully-symmetrical one. We calculated the magnetic susceptibilities for two molecular symmetries of these molecules. It can be seen that the double-bond fixation brings about a considerable decrease in the paramagnetic susceptibility. The good agreement with theory and experiment in heptalene (II) provides further support for the molecular-symmetry reduction occurring in this molecule and in Molecules I and III as well.

In Molecules IV, V, and VI, it is predicted that the calculated bond lengths of the naphthalene core are almost the same as those in the free naphthalene molecule and that there are marked double-bond fixations in the other region of the periphery.[21] The periphery of IV and V may give a paramagnetic ring current characteristic of the $4n$ perimeter.[18] On the other hand, naphthalene core in IV and V may exhibit a diamagnetic ring current to the same extent as that of a free naphthalene molecule. Therefore, it may be expected that the paramagnetic ring current and the diamagnetic ring current cancel each other out to give a small magnetic susceptibility in IV and V.

It may be concluded that the magnetically-induced ring currents decrease sensitively with the double-bond fixation, and that in I, II, III, IV, and V they are extremely impeded. Part of the evidence for these reduced magnetic susceptibilities is given by the NMR spectra of II,[22] III,[23] and IV,[24] which show the proton signals in the olefinic region.

References

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), p. 527.
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) J. Hoarau, *Ann. Chim.*, **1**, 544 (1956).
7) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).
8) T. Nakajima and S. Katagiri, *Mol. Phys.*, **7**, 149 (1964).
9) A. Almeningen, O. Bastiansen, and M. Treattberg, *Acta Chem. Scand.*, **12**, 1221 (1958).
10) D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc.* (London), **A528**, 270 (1960); O. Bastainsen and P. N. Skanke, *Advan. Chem. Phys.*, **3**, 323 (1961).
11) J. Thiec and J. Wiemann, *Bull. Soc. Chim. Fr.*, **1956**, 177.
12) Y. Kurita, S. Seto, T. Nozoe, and M. Kubo, This Bulletin, **26**, 272 (1953).
13) T. Nakajima and S. Kohda, This Bulletin, **39**, 804 (1966).

14) J. Nowakowski, *Theor. Chim. Acta*, **10**, 79 (1968).

15) H. J. Dauben, Jr., J. D. Wilson, and J. L. Laity, *J. Amer. Chem. Soc.*, **91**, 1991 (1969).

16) Y. Mikami, S. Miyai, and T. Nakajima, This Bulletin, **46**, 787 (1973).

17) G. Wagnière and M. Couterman, *Mol. Phys.*, **5**, 621 (1962).

18) J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.*, **88**, 4811 (1966).

19) H. C. Longuet-Higgins, "Aromaticity," Spec. Publ. No. 21, The Chemical Society, London (1966), p. 109.

20) T. Nakajima, A. Toyota, and S. Fujii, This Bulletin, **45**, 1022 (1972); T. Nakajima, *Topics Current Chem.*, **32**, 1 (1972).

21) H. Yamaguchi and T. Nakajima, This Bulletin, **44**, 682 (1971).

22) H. J. Dauben and D. J. Bertelli, *J. Amer. Chem. Soc.*, **83**, 4659 (1961).

23) 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).

24) B. M. Trost and G. M. Bright, *J. Amer. Chem. Soc.*, **89**, 4244 (1967).