

^1H NMR PATTERNS OF ANTIAROMATIC SYSTEMS: PARATROPIC
DISPLACEMENT DEPENDENCE UPON LUMO-HOMO ENERGY GAP

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Abstract: ^1H NMR chemical shifts of antiaromatic species reveal an enhanced paratropic displacement. The high-field shifts exhibited by doubly charged benzenoid polycycles were shown to be strongly related to the LUMO-HOMO energy gaps in these antiaromatic systems. As the gap decreases, a larger paratropic shift was observed.

It has been shown that the sign and magnitude of ring currents, estimated for cyclic conjugated systems, are sensitive to the energy gap between the lowest-vacant (LUMO) and highest-occupied (HOMO) molecular orbitals.¹ The magnitude of this energy splitting was also used to predict the extent of antiaromatic character of perturbed [12] annulenes^{1,2}, such as the pyracylene molecule. We wish to report the existence of a direct, unequivocal correlation between the extent of paratropic ^1H NMR chemical shift of charged, antiaromatic systems and the corresponding LUMO-HOMO gap, as estimated by $\omega\beta$ calculations.³

Doubly charged molecules, obtained by two-fold oxidation or reduction processes of polycyclic benzenoid hydrocarbons, are assumed to acquire an antiaromatic character. The assumption is based on Platt's Theory⁴ - the cyclic charged systems being planar or nearly so and having $4n\pi$ electrons in the path of conjugation. ^1H NMR spectra of such $4n\pi$ species reveal a substantial paratropic, high field shift.⁵

The reduction of five polycyclic catacondensed benzenoid hydrocarbons (1-5) was performed by exposing tetrahydrofuran solutions of the neutral systems to lithium or sodium metals.

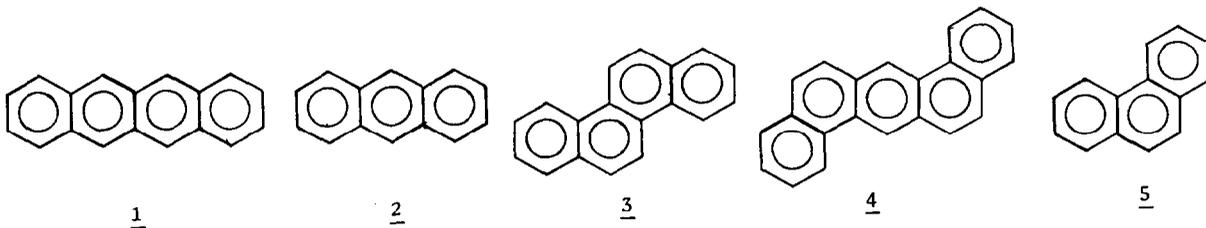


Table 1. ^1H NMR patterns and LUMO-HOMO energy gaps of catacondensed doubly charged systems 1-5.

Doubly charged systems	Calc. center of gravity ^a of NMR spectrum	Exptl. center of gravity ^a of NMR spectrum	Δ		LUMO-HOMO energy gaps ^c
			Calc.	Exptl.	
Tetracene (<u>1</u>) ⁼	6.68	4.13	2.55		0.414
Anthracene (<u>2</u>) ⁼	5.99	3.06	2.93		0.310
Chrysene (<u>3</u>) ⁼	6.48	2.42	4.06		0.272
Dibenzanthracene (<u>4</u>) ⁼	6.96	1.78	5.18		0.250
Phenanthrene (<u>5</u>) ⁼	6.13	0.80	5.33		0.232
Tetracene (<u>1</u>) ⁺⁺	9.28	8.61	0.67		0.414
Anthracene (<u>2</u>) ⁺⁺	9.82	8.39	1.43		0.310
Dibenzanthracene (<u>4</u>) ⁺⁺	9.19	6.51	2.68		0.250

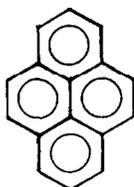
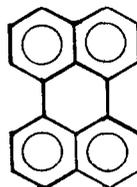
^appm down from SiMe_4 .

^bExcluding paramagnetic factors. For details, see text.

^c β units, as furnished by the $\omega\beta$ method.³

Three catacondensed polybenzenoid systems (1, 2, 4) were oxidized to the corresponding dications with SbF_5 in SO_2ClF as solvent (oxidation of 3 and 5 results in radical cations⁹). The ^{13}C NMR spectra revealed the expected low-field diatropic shifts which are due to deshielding by two positive charges. As for the ^1H NMR patterns, they are determined by two factors which operate in opposite directions: deshielding due to positive charge density, and shielding caused by the paramagnetic ring current. The net contribution of the paramagnetic effect was calculated as in the dianions - the average effect of charge density was added to the center of gravity of the ^1H NMR chemical shifts in the neutral molecule. A correlation between the value of LUMO-HOMO energy splittings and paratropic shift caused by ring current, analogous to the correlation indicated in the dianions - is obtained (Table 1).

We have studied the extent of paratropic shift in the doubly-charged pericondensed pyrene (6) dianion and perylene (7) dianion. The response of the high-field shift to the LUMO-HOMO energy splitting is found to be even more pronounced than in the catacondensed systems.

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^{13}C NMR spectra, obtained after four to six days of exposure to the metal, revealed a total high field shift relative to the chemical shifts of the neutral hydrocarbons. The substantial paratropic displacement of the ^{13}C NMR absorptions clearly indicates the formation of dianion species.⁶ The ^1H NMR spectra of the doubly charged systems also exhibited a high field shift with respect to the neutral molecules. Yet, in contrast with ^{13}C NMR spectra, in which charge densities contribute the main cause of the paramagnetic shifts, proton chemical shifts reflect the contribution of two different mechanisms:

- (i) The shielding due to electron density at the carbon atoms to which the protons are attached. The ^1H NMR chemical shifts in conjugated systems were found to relate linearly with the corresponding π -electron density, with a correlation constant of 10.7 ppm.⁷
- (ii) Ring currents which are induced by external magnetic fields. While aromatic systems reveal a diamagnetic ring current, antiaromatic species sustain a paramagnetic current which causes an increased shielding of the protons outside the ring.^{5,8}

We turned to $\omega\beta$ semiempirical calculations as a means to assess the portion of chemical shift that is due to the charge-density factor, and isolate thereby the contribution of the paramagnetic ring current. In each of the charged species, the theoretical charges on hydrogen-bearing carbon atoms were summed and the sum was multiplied by the shift-charge correlation constant⁷ (10.7 ppm). The product was then divided by the number of protons and this average subtracted from the center of gravity of the ^1H NMR chemical shifts exhibited by the neutral polycyclic hydrocarbon. An estimate is thus derived of the displacement in center of gravity that is due to shielding by the negative charges. An observed high-field deviation from this estimate is taken as the contribution of the antiaromatic, paramagnetic ring current.

When ^1H NMR chemical shifts of the doubly charged systems 1-5 were processed as described, the paratropic deviations were found to vary over a large range of values (A values in table 1). While species such as phenanthrene and dibenzanthracene dianions revealed a large high-field shift beyond the values expected by charge density considerations, the shift in tetracene dianion was much smaller. We found that the extra paratropic shift correlates with the calculated energy gap between the lowest unoccupied and the highest occupied molecular orbitals of the dianion. Thus, when a large LUMO-HOMO splitting is predicted, a relatively small paratropic shift is estimated, and conversely.

A relatively small change in the gap (as on going from pyrene to perylene dications) corresponds to a large difference in the magnitude of the paratropic shift (Table 2).

Table 2. ^1H NMR patterns and LUMO-HOMO energy gaps of pericondensed doubly charged systems.

Doubly charged systems	Calc. center of gravity ^a of the NMR spectrum	Exptl. center of gravity ^a of the NMR spectrum	Δ Calc.-Exptl.	LUMO-HOMO energy gaps ^c
Pyrene (6) ⁼	6.18	0.82 ^d	5.36	0.354
Pyrene (6) ⁺⁺	9.92	5.95	3.97	0.354
Perylene (7) ⁺⁺	9.23	8.59	0.64	0.446

^appm down from SiMe_4 .

^bExcluding paramagnetic factors. For details, see text.

^c β units, as furnished by the $\omega\beta$ method.³

^dsee ref. 11.

By using the London theory, Pople et al.,^{8a} and Longuet-Higgins,^{8b} showed that the paramagnetic contribution to the magnetic susceptibility of $4n\pi$ conjugated systems has to do with the narrowness of the LUMO-HOMO energy gap. The narrow gap enhances the probability of transitions from the ground to the excited state, the excited orbital making a large positive contribution to the overall magnetic susceptibility.¹⁰ On the basis of our findings we suggest that the calculated LUMO-HOMO gaps in $4n\pi$ systems be used for a direct prediction of their ^1H NMR patterns. Moreover, we believe that the correlation, once examined in a large number of systems, and by methods more sophisticated than $\omega\beta$, might serve as a quantitative criterion for antiaromaticity and therefore deepen our understanding of this phenomenon.

REFERENCES AND NOTES

- Mallion, R.B., *Pure Appl. Chem.*, **52**, 1541 (1980).
- (a) Trost, B.M., Kinson, P.L., *J. Am. Chem. Soc.*, **97**, 2438 (1975).
(b) Gomes, J.A.N.F.; Mallion, R.B., *J. Org. Chem.*, **46**, 719 (1981).
- Modified calculations on Coulomb integrals (a) Berson, J.A., Evleth, E.M. Hamlet, Z., *J. Am. Chem. Soc.*, **87** 2901 (1965). (b) Boyd, G.V., Singer, N., *Tetrahedron*, 2901 (1966).
- Platt, J.R.T., *Chem. Phys.*, **22**, 1448 (1954).
- (a) Bates, R.B. in "Comprehensive Carbanion Chemistry", Elsevier, New York, 1980; Part A, pp. 1-54, and references cited therein.
(b) O'Brien, D.H. *ibid.*, pp. 271-322.
- Spiesecke, H.; Schneider, W.G., *Tetrahedron Lett.*, 468 (1961).
- Schaefer, T.; Schneider, W. G., *Can. J. Chem.*, **41**, 966 (1963).
- (a) Pople, J.A.; Untch, K.G., *J. Am. Chem. Soc.*, **88**, 4811 (1966).
(b) Longuet-Higgins, H.C. *Aromaticity: Chemical Society Special Publications*, London, No. 21, 109 (1967).
- (c) Haddon, R.C.; Haddon, V.R.; Jackman, L.M., *Fortsch. Chem. Fors.*, **16**, 103 (1970).
- Forsyth, D.A.; Olah, G.A., *J. Am. Chem. Soc.*, **98**, 4086 (1976).
- Van Vleck, J.H. "Electric and Magnetic Susceptibilities", Oxford University Press, Oxford, 1932, pp. 262-276.
- Mullen, K., *Helv. Chim. Acta*, **61**, 2307 (1978).