

Ring Currents in Furan, Thiophen, and Pyrrole and the Aromaticities of these Compounds

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IN their comments,¹ on our suggestions² concerning a definition and the estimation of aromaticity, Abraham, Sheppard, and their colleagues have overlooked important points.

There are in organic chemistry two meanings of the term aromatic, which are distinct.³ One is "like benzene in chemical properties." The chemistry of a compound, however, at best provides only qualitative information and frequently is ambiguous. Our aim was to move away from chemical criteria (and their shortcomings) which, for example, fail to reveal the essential difference between [18]- and [24]-annulene, and are particularly ambiguous for furan.

The other established meaning is "having a low ground-state enthalpy."⁴ Our definition of an aromatic compound as "one that will sustain an induced ring current" is equivalent: it should therefore be acceptable.

The typically-aromatic benzene has a ground-state in which there is complete delocalisation of the six $p\pi$ -electrons (proved by the symmetry). Theory shows that π -localised cyclohexatriene would have a much higher enthalpy. A similar picture emerges from other planar fully-conjugated monocyclic systems with $(4n + 2)p\pi$ -electrons, at least where n is a small integer. If this Hückel rule⁵ is not satisfied, or if the molecule is restrained from being planar, then the ground state is one in which the π -bonds are localised and the enthalpy is not exceptionally low. The theoretically-based definition of aromaticity has the advantage that it can be extended by molecular orbital theory, even to heteromorphic systems.⁶ Moreover, it provides through the measurement of resonance energy, a quantitative assessment of the extent of delocalisation of the π -electrons.

Cyclically delocalised systems behave as though capable of sustaining an induced ring current.⁷ Cyclic olefins cannot. It is just the former systems

that are already defined on theoretical grounds as aromatic. Therefore the demonstration of a ring current is a good test of aromaticity. As an alternative to resonance energy (which is difficult to measure, *e.g.* for heterocyclic systems), we suggested measuring the extent of the π -electron delocalisation in terms of the magnitude of the induced ring current.² This appeared to be more practicable in general, making use of chemical shift or magnetic anisotropy data.

The use of chemical shifts is fraught with dangers. These we touched upon,² but the difficulties are not insuperable. In some situations, calculations may have advantages.⁸

Abraham, Sheppard, *et al.*¹ attempted to assess the aromaticity of furan and thiophen from chemical shift data. They rightly rejected the use of 3-H shifts. Their use of 2-H shifts alone is unwise, but reasonable results might be expected from the use of 2-methyl shifts. Their nonaromatic models, however, are bad: it is not sufficient that they look right. The correct non-aromatic model is strictly not attainable in these cases. The requirement is the fully conjugated system in which the bond hybridisation is the same as in the perfect aromatic model, but without the π -delocalisation. The best approximation is a very long polyene: bond alternation is minimal, yet there can be no ring current. Hence for the non-aromatic 2-methyl-furan, -thiophen, and -pyrrole models, one starts with a value of τ 8.18, this being the chemical shift (in CDCl_3) of an "end of chain" methyl in a polyene.⁹ The paramagnetic corrections for the inductive effects of the heteroatoms are best taken from models having purely σ -bonds. Values of 0.32, 0.37, and 0.15 p.p.m. are appropriate, derived from diethyl ether, ethyl methyl sulphide, and *s*-butylamine.¹⁰ $\tau(\text{Me})$ (calc.) values for the non-aromatic 2-methyl-heterocycles are, then, 7.86, 7.81, and 8.03,

¹ R. J. Abraham, R. C. Sheppard, W. A. Thomas, and S. Turner, *Chem. Comm.*, 1965, 43.

² J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 1961, 859.

³ D. Peters, *J. Chem. Soc.*, 1960, 1274.

⁴ G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, New York, 1955.

⁵ E. Hückel, *Z. Physik*, 1931, **70**, 204; 1932, **76**, 628.

⁶ D. P. Craig in "The Kekule Symposium," Butterworths Scientific Publications, London, 1959, p. 20.

⁷ See references cited in Ref. 2.

⁸ G. G. Hall, A. Hardisson, and L. M. Jackman, *Tetrahedron*, 1963, **19**, Suppl. 2, 101.

⁹ M. S. Barber, J. B. Davis, L. M. Jackman, and B. C. L. Weedon, *J. Chem. Soc.*, 1960, 2870.

¹⁰ N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, 1962, Nos. 46, 88.

respectively. Observed values are 7.70,¹ 7.52, and 7.82¹¹ so that the ring current shifts are 0.16, 0.29, and 0.21 p.p.m. The ring current contribution to the shielding of the methyl protons in toluene is 0.40 p.p.m.² Hence, from the equivalent dipole approximation,¹ and recognised molecular dimensions,¹² the following aromaticities are obtained: furan, $0.16 \times 1.39^2 \times 3.06^3/0.40 \times$

$1.18^2 \times 3.27^3 = 0.46$; thiophen, $0.29 \times 1.39^2 \times 3.21^3/0.40 \times 1.33^2 \times 3.27^3 = 0.75$; pyrrole, $0.21 \times 1.39^2 \times 3.08^3/0.40 \times 1.20^2 \times 3.27^3 = 0.59$. These aromaticities are in accord with experimental resonance energies.¹³

I conclude that our method is a reasonable one.

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¹¹ Ref. 10, Nos. 103, 131, 278.

¹² "Tables of Interatomic Distances," Special Publ. No. 11, The Chemical Society, London, 1958.

¹³ R. M. Acheson, "An Introduction to the Chemistry of Heterocyclic Compounds," Interscience Publishers, New York and London, 1962, pp. 52, 79, 105.