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A NEW AROMATICITY INDEX AND ITS APPLICATION TO FIVE-MEMBERED RING HETEROCYCLES

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Abstract-A new index of aromatic character has been devised based upon a statistical evaluation of the deviations in peripheral bond orders. The latter can be derived readily from experimentally determined bond lengths. The utility of this index is exemplified by its application to five-membered ring heterocycles and their mesoionic derivatives.

The concept of aromaticity is virtually a tenet of faith to organic chemists yet its quantification has proved remarkably elusive. Of the wide range of experimental criteria which have been evaluated for this purpose[1] only resonance energies have proved to be of any general applicability in the case of heterocycles, and even these suffer from the difficulty of assigning appropriate energies to the hypothetical localised molecule, especially in the case of mesoionic compounds. A much neglected source of information has been the accurate molecular dimensions which have become available in recent years for an increasing number of heterocycles. Various workers have attempted to gain some insight into the aromaticity of a particular heterocycle by comparing its bond lengths with those of related molecules. Julg[2] has taken this approach one stage further by introducing an aromaticity index based upon the extent of uniformisation of the lengths of peripheral bonds. However, this treatment is only applicable to the carbon-carbon framework and hence of little use in discussing molecules like 1,2,4-oxadiazole which has no carbon-carbon bonds. Fringuelli et al.[3] have utilised the sum of the bond order differences as a criterion of aromaticity in comparing furan, thiophene, selenophene and tellurophene, but this becomes excessively complicated for less symmetrical molecules.

The present paper introduces a completely general aromaticity index based upon the statistical degree of uniformity of the bond orders of the ring periphery. The bond orders, N, were calculated from the bond length, R, using the Gordy relationship[4]:

$$N = a/R^2 - b$$

employing the values listed in Table 1 for the constants a and b. In several cases it was necessary to calculate values for these constants from covalent radii and electronegativity values[5] using the Shomaker-Stevenson equation[6]. The coefficient

TABLE 1 Values of constants *a* and *b* used in the calculation of bond orders

Bond	*a*	*b*	Bond	*a*	*b*
C-C	6.80	1.71[*]	N-N	5.28	1.41[*]
C-N	6.48	2.0[*]	N-O	4.98	1.45[*]
C-O	5.75	1.85[*]	N-S	10.53	2.50[+]
C-S	11.9	2.59[*]	N-Se	13.31	2.86[+]
C-Se	15.24	3.09[#]	O-S	17.05	5.58[+]
C-Te	21.41	3.81[#]	S-S	19.30	3.46[+]
C-P	13.54	3.02[+]			

[*]Ref. 4 ; [#]Ref. 3 ; [+]This paper

of variation for the bond orders of a particular heterocycle are given by the expression:

$$V = \frac{100}{\bar{N}} \sqrt{\frac{\Sigma(N-\bar{N})^2}{n}}$$

where $\bar{N}$ is the arithmetic mean of the various bond orders,N, and n is the number of bonds. In the case of a fully delocalised heterocycle V will have the value 0, whereas for a non-delocalised Kekulé form with alternating single and double bonds the value depends upon the type of ring system. Thus for a five-membered ring heterocycle $V_K = 35$, for a six-membered ring heterocycle $V_K = 33.3$, and for systems consisting of a five-membered and a six-membered ring fused together $V_K = 35$. In order to place the values of V on a more convenient scale than eg. 0 to 35, the calculated V is substituted into the equation:

$$\text{Aromaticity Index, } I = 100(1-V/V_K).$$

As index values are not necessarily comparable for differing ring systems it seems desirable to attach a guiding subscript as I_5, I_6 or $I_{5,6}$, to discourage inappropriate comparisons.

The aromaticity indices,I_5, calculated for a wide range of five-membered heterocycles are assembled in Figure *1*. Where available the bond lengths recorded for the parent heterocycle were used for the calculation of these indices with preference being given to values derived by microwave spectroscopy. Otherwise data were preferentially selected for molecules bearing non-conjugating substituents. However, spot checks indicate that the index values are relatively insensitive to substituent effects causing variations of ±2 to 3. Qualitatively, the relative aromaticities deduced for these heterocycles agree with what would have been predicted from a knowledge of their chemical behaviour. Thus, the low aromaticity usually ascribed to the oxygen containing members is reflected in the low index numbers. 1-Benzylphosphole also has rather limited aromaticity, but the high index number calculated for p-dimethylaminophenylpentazole is rather unexpected. The I_5 values of 88 and 73 assigned to 2*H*- and 1*H*-1,2,3-triazole respectively correctly identify the former tautomer as the preferred species. Similarly the 1*H*-1,2,4-triazole tautomer with I_5=81 is indicated as being more favoured than the 4*H*-tautomer,I_5=66, in accord with observation[7]. As indicated in Figure *2* there is a reasonable parallel between these aromaticity indices and resonance energies, although the wide range of uncertainty in the latter precludes the establishment of a quantitative relationship. However, an excellent linear relationship is observed with the aromaticity parameter *A* determined by the dilution shift method for furan, thiophene, selenophene and tellurophene[3],

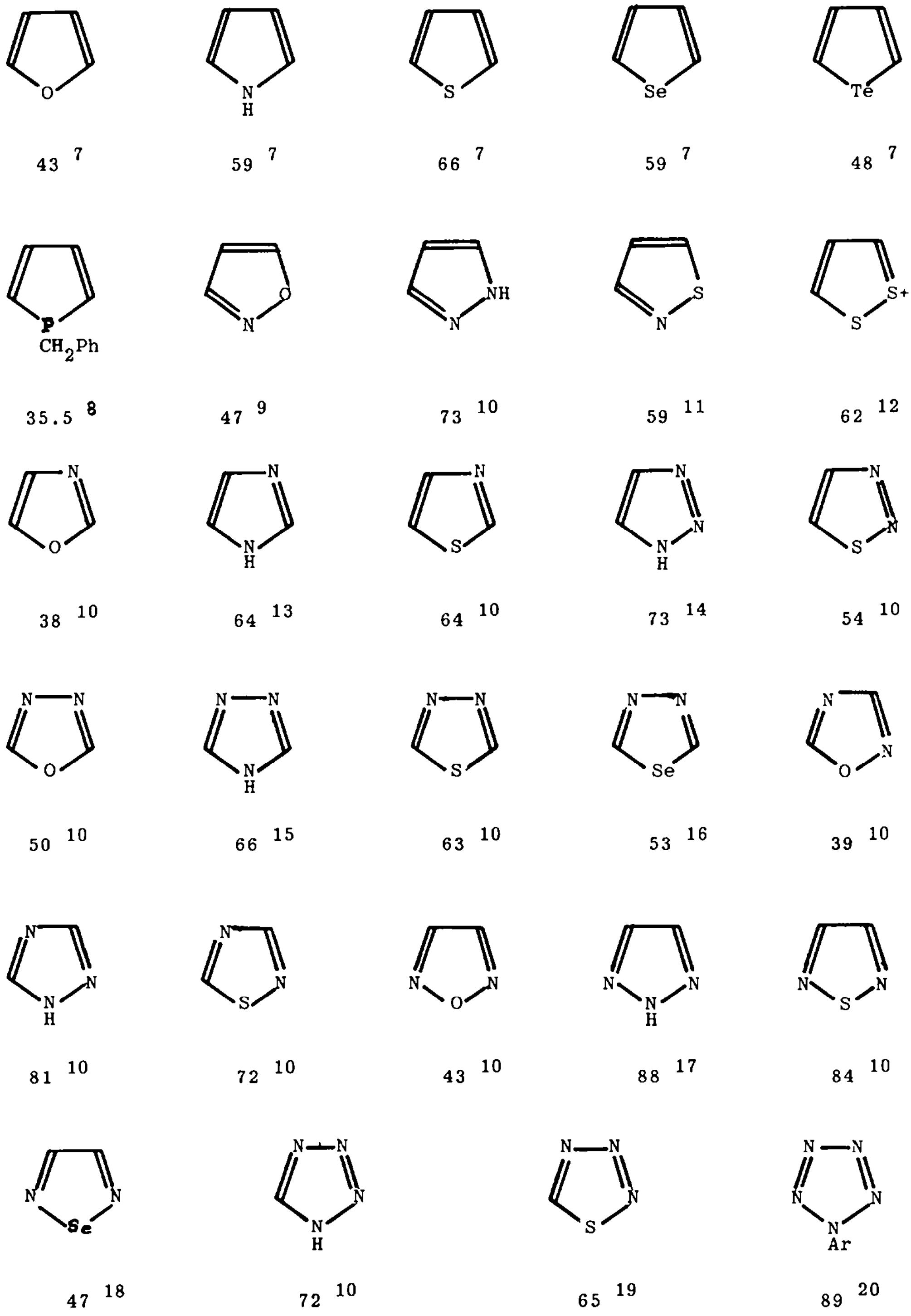

FIGURE 1 Aromaticity indices for five-membered ring heterocycles.(The references are to the source of bond lengths used for their calculation).

TABLE 2 Comparison of aromaticity indices with experimental resonance energies(ERE)

Heterocycle	Aromaticity Index	ERE kJ/mole	Reference
Furan	43	34-96	1
Isoxazole	47	4-46	21
1,3,4-Oxadiazole	50	167	22
Pyrrole	59	59-130	1
Imidazole	64	51-134	1
Thiazole	64	42-50	23
Thiophene	66	84-117	1
Tetrazole	72	231-293	24
Pyrazole	73	112-174	1
1,2,4-Triazole	81	84-206	1

having a correlation coefficient of 0.999. Linear relationships of A for these heterocycles with several other aromaticity criteria have been reported previously[3].

Structural data are presently available for some nineteen monocyclic mesoionic ring systems and the derived aromaticity indices are assembled in Figure 2. In view of the appreciable charge separation encountered in these molecules the indices might be expected to be more influenced by substituent effects than in the normal heterocycles dealt with above, but there is no evidence available on this point at present. Inspection of the data in Figure 2 permits some generalisations. Firstly, compounds with a ring oxygen atom have appreciably lower aromaticities than their sulphur or nitrogen counterparts whereas the relative effects of the latter atoms depend upon their disposition in the ring. Thus replacement of sulphur by nitrogen adjacent to the carbon bearing the exocyclic oxygen (B →C) results in an appreciable increase in the aromaticity index whereas a similar change at the more remote position (D →A) causes a decrease. Again the indices indicate that changing the exocyclic atom(s) results in decreasing the aromaticity of a particular ring system in the sequence $S^- > NCOR^- > NR^- > O^-$. Some of these conclusions are supported by observations on the interconversion of Class A meso-ionic isomers[25].

Overall these indices appear to provide an experimentally based means of comparing the relative aromaticities of a wide range of five-membered ring heterocycles. Doubtless the values recorded here for some ring systems will be modified as dimensions for more appropriate representatives become available. In particular X-ray structural determinations are available for only a third of the known meso-ionic ring systems and hopefully the present usage will inspire the collection of a much wider range of molecular dimensions so as to facilitate a more detailed analysis of the relationship between structure and aromaticity.

REFERENCES

1. M. J. Cook, A. R. Katritzky and P. Linda, Adv. Heterocycl. Chem.,1974,17,255.
2. A. Julg,'Aromaticity, Pseudoaromaticity, Antiaromaticity',eds. E. D. Bergmann and B. Pullman, Israel Academy of Sciences and Humanities (Academic Press), Jerusalem, 1971, 383.
3. F. Fringuelli, G. Marino, A. Taticchi and G. Grandolini, J. Chem. Soc., Perkin Trans. 2, 1974, 332.
4. W. Gordy, J. Chem. Phys., 1947, 15, 305.
5. L. Pauling,'The Nature of the Chemical Bond', Cornell University Press, Ithaca, 3rd. edn., 1960.
6. V. Shomaker and D. P. Stevenson, J. Am. Chem. Soc., 1941, 63, 37.

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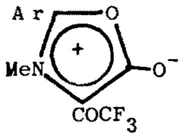

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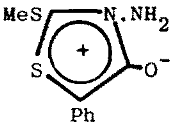

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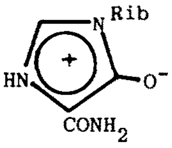

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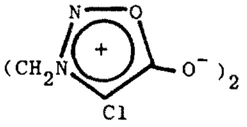

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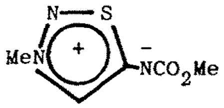

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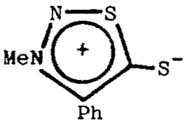

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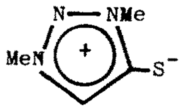

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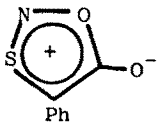

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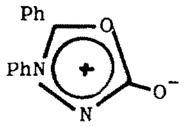

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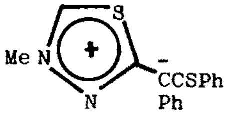

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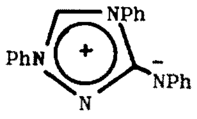

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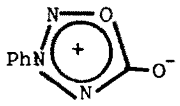

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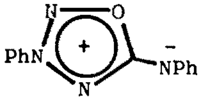

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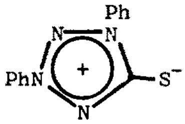

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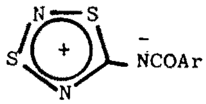

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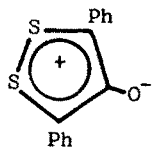

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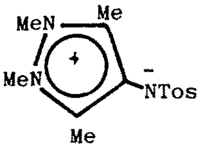

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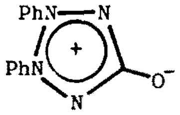

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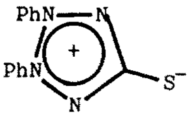

88[42]

FIGURE 3 Aromaticity indices for mesoionic heterocycles.(The references are to the source of bond lengths used for their calculation).

7. C. W. Bird and G. W. H. Cheeseman, Comprehensive Heterocyclic Chemistry, eds. A. R. Katritzky and C. W. Rees, Pergamon Press, Oxford, 1984, vol. 4, p.1.
8. P. Coggon and A. T. McPhail, J. Chem. Soc., Dalton Trans., 1973, 1888.
9. O. L. Stiefvater, J. Chem. Phys., 1975, 63, 2560.
10. A. R. Katritzky and J. M. Lagowski, Comprehensive Heterocyclic Chemistry, eds. A. R. Katritzky and C. W. Rees, Pergamon Press, Oxford, 1984, vol. 5, p.1.
11. W. H. Koster, J. E. Dolfini, B. Toeplitz and J. Z. Gougoutas, J. Org. Chem., 1978, 43, 79.
12. H. C. Freeman, G. H. W. Milburn, C. E. Nockolds, R. Mason, G. B.Robertson and G. A. Rusholme, Acta Crystallogr., Part B, 1974, 30, 886.
13. R. K. McMullan, J. Epstein, J. R. Ruble and B. M. Craven, Acta Crystallogr., Part B, 1979, 33, 688.
14. A. Kalman, K. Simon, J. Schawartz and G. Horvath, J. Chem. Soc., Perkin Trans. 2, 1974, 1849.
15. C. H. Stam and H. C. Van der Plas, Acta Crystallogr., Part B, 1976, 32, 1288.
16. D. M. Levine, W. P. Krugh and L. P. Gold, J. Mol. Spectrosc., 1969, 30, 450.
17. A. Kalman, L. Parkanyi, J. Schawartz and K. Simon, Acta Crystallogr., Part B, 1976, 32, 2245.
18. M. Mellini and S. Merlino, Acta Crystallogr., Part B, 1976, 32, 1074.
19. T. Ottersen, Acta Chem. Scand.,Ser. A, 1976, 30, 351.
20. J. D. Wallis and J. D. Dunitz, J. Chem. Soc., Chem. Commun., 1983, 910.
21. A. V. Chapman, M. J. Cook, A. R. Katritzky, M. H. Abraham, A. F. D. de Namor, L. Dumont and J. Reisse, Tetrahedron, 1978, 34, 1571.
22. J. Hill, Comprehensive Heterocyclic Chemistry, eds.A. R. Katritzky and C. W. Rees, Pergamon Press, Oxford, 1984, vol. 6, p. 427.
23. M. Mansson and S. Sunner, Acta Chem. Scand., 1966, 20, 845.
24. W. S. McEwan and M. W. Rigg, J. Am. Chem. Soc., 1951, 73, 4725.
25. W. D. Ollis and C. A. Ramsden, Adv. Heterocycl. Chem., 1976, 19, 1.
26. G. V. Boyd, C. G. Davies, J. D. Donaldson, J. Silver and P. Wright, J. Chem. Soc. Perkin Trans. 2, 1975, 1280.
27. S. Abrahamsson, A. Westerdahl, G. Isaksson and J. Sandström, Acta Chem. Scand. 1967, 21, 442.
28. H. Yoshioka, K. Nakatsu, M. Hayashi and K. Mizuno,Tetrahedron Lett.,1975,4031.
29. W. E. Thiessen and H. Hope, J. Am. Chem. Soc., 1967, 89, 5977.
30. S. Bruckner, G. Fronza, L. M. Giunchi, V. A. Kozinski and O. V. Zelenskaja, Tetrahedron Lett., 1980, 21, 2101.
31. S. Auricchio, S. Bruckner, L. M. Giunchi and V. A. Kozinski, Heterocycles, 1980, 14,1757.
32. K. Nielsen,Acta Chem. Scand.,Ser. A, 1975, 29, 647.
33. G. D. Andreetti, D. Bocelli, L. Cavalca and P. Sgarabotto, Gazz. Chim. Ital., 1972, 102, 23.
34. T. J. King, P. N. Preston, J. S. Suffolk and K. Turnbull, J. Chem. Soc., Perkin Trans. 2, 1979, 1751.
35. R. M. Moriarty, R. Mukherjee, J. L. Flippen and J. Karle, J. Chem. Soc., Chem. Commun., 1971, 1436.
36. J. R. Cannon, C. L. Raston and A. H. White, Aust. J. Chem., 1980, 33, 2237.
37. T. Ottersen, Acta Chem. Scand., Ser. A, 1975, 29, 799.
38. T. Ottersen, C. Christophersen and S. Treppendahl, Acta Chem. Scand., Ser. A, 1975, 29, 45.
39. A. Gieren and B. Dederer, Acta Crystallogr.,Part B, 1978, 34, 2046.
40. J. R. Cannon, K. T. Potts, C. L. Raston, A. F. Sierakowski and A. H. White, Aust. J. Chem., 1978, 31, 297.
41. P. F. Lindley, M. M. Mahmoud, C. Dodd, C. H. Smith, G. V. Boyd and T. Norris, Acta Crystallogr., Part B, 1977, 33, 2160.
42. Y. Kushi and Q. Fernando, J. Am. Chem. Soc., 1970, 92, 1965.