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HETEROAROMATICITY.5. A UNIFIED AROMATICITY INDEX

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Abstract - A unified aromaticity scale is presented based upon the family of aromaticity indices previously introduced for differing ring systems. The resonance energies of a range of heterocycles have been calculated, on a common basis, from experimental heats of formation and correlated with the foregoing indices.

Several years ago[1] the present author introduced a new index of aromatic character based upon a statistical evaluation of the extent of variation of ring bond order as given by the expression $I_n = 100(1-V/V_K)$, where $V = 100\sqrt{\bar{N}/\Sigma(N-\bar{N})^2/n}$. $\bar{N}$ is the arithmetic mean of the n various ring bond orders, N, which are readily calculated[2] from the individual bond lengths (R) using the relationship $N = a/R^2 - b$ where a and b are constants. V_K is the value of V for the corresponding non-delocalised Kekule form with alternating single and double bonds. Indices have been reported for five-membered[1], six-membered[3], and fused five and six-membered heterocycles[4] and shown to provide a rationale for some characteristic properties and reactions. Recent statistical evaluations[5] of a range of criteria that have been proposed for the assessment of heterocyclic aromaticity have indicated the particular value of these indices as a measure of classical aromaticity.

The principle disadvantage of the indices as originally derived is that they are unique to different sized rings so that direct comparison between five and six-membered heterocycles for example is not possible. The observation[2] of the relation $E = 1/R^2 + m$ between bond energy (E) and bond length (R), paralleling that between bond order and bond length (vide supra) indicated that there should be a direct linear relationship between these aromaticity indices and resonance energies. However, at the time of the original publication[1] the best that could be discerned was a general parallelism between the indices and available experimental resonance energies. Subsequently, the aforementioned statistical evaluation[5] has indicated a good correlation between the aromaticity indices and, inter alia, Dewar resonance energies. These observations have suggested

Table I Unified Aromaticity Indices (I_A) for a Range of Heterocycles.

Compound	I_A	Compound	I_A
Oxazole	47	1,2,4,5-Tetrazine	98
1,2,4-Oxadiazole	48	Benzene	100
Isoxazole	52	1,3,5-Triazine	100
Furan	53	1*H*-1,2,4-Triazole	100
1,2,5-Oxadiazole	53	1,2,5-Thiadiazole	104
Selenazole	54	Benzo[c]furan	106
1,2,5-Selenadiazole	58	2*H*-1,2,3-Triazole	109
Tellurophene	59	Pentazole	109
1,3,4-Oxadiazole	62	Benzo[c]isoxazole	113
1,3,4-Selenadiazole	65	Benzo[d]isoselenazole	115
Pyrylium cation	66	1,2,3-Benzothiadiazole	115
1,2,3-Thiadiazole	67	Indolizine	115
Selenophene	73	Benzo[b]pyrylium cation	118
1,2,3-Triazine	77	Benzo[b]thiophene	119
Imidazole	79	Benzothiazole	119
Thiazole	79	Cinnoline	130
Pyridazine	79	Quinoxaline	132
Benzoxazole	79	Isoquinoline	133
1,3,4-Thiadiazole	80	Quinoline	134
Thiophene	81.5	Phthalazine	136
Pyrimidine	84	1*H*-benzotriazole	140
Pyrrole	85	Naphthalene	142
Pyridine	86	Benzo[c]isothiazole	142
1,2,4-Triazine	86	Benzo[d]isothiazole	142
1,2,4-Thiadiazole	89	Quinazoline	143
1*H*-Tetrazole	89	Indazole	144
Pyrazine	89	Indole	146
Pyrazole	90	Benzimidazole	148
1*H*-1,2,3-Triazole	90	Isoindole	150
Isothiazole	91	2*H*-Benzotriazole	152
Benzo[b]furan	94		

a solution to our impasse.

Simple Hueckel molecular orbital theory derives delocalisation energies of 2β, 2.47β, 3.68β and 4.17β for benzene, the cyclopentadienyl anion, naphthalene and the indenyl anion respectively[6]. As these are the nominal parents of the I_6, I_5, $I_{6,6}$ and $I_{5,6}$ systems it is then possible to define a unified aromaticity index $I_A = I_6 = 1.235I_5 = 1.34I_{6,6} = 2.085I_{5,6}$.

This particular scaling exercise assigns the archaromatic compound benzene an I_A value of 100. A list of I_a's for a range of commonly encountered heterocycles is assembled in Table I. Other values can be derived readily from the previously reported indices by applying the above relationships. A particular merit of this unified index is its energetic basis since a unitary increment corresponds to 0.02β.

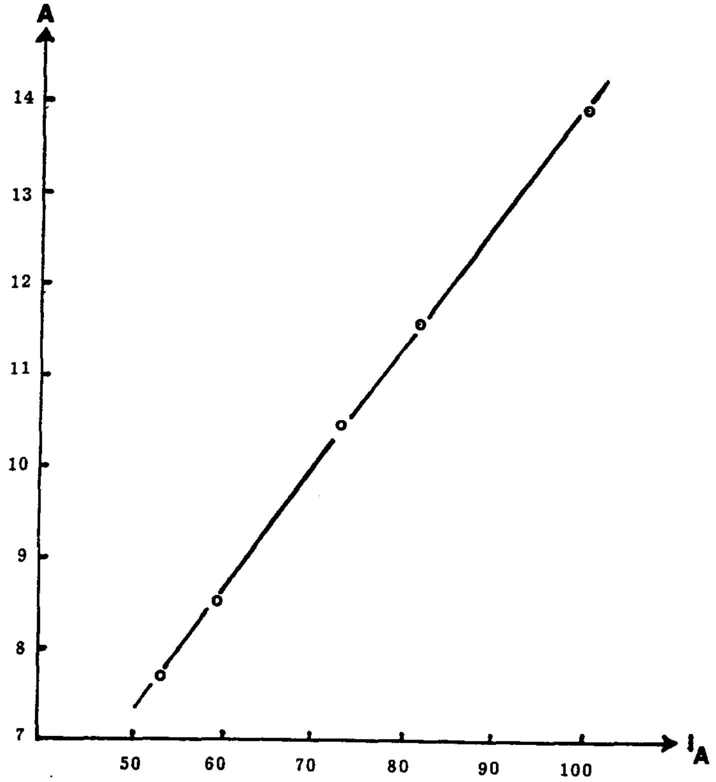

FIGURE I Plot of I_A versus Dilution Shift Parameter (A)

An initial quantitative indication of the validity of this treatment is the observation of an excellent linear relationship ($r = 0.99$) between I_A and the aromaticity parameter A determined by the dilution shift method for benzene, furan, thiophene, selenophene and tellurophene[7]. In view of the energetic basis of these indices a direct correlation with experimental resonance energies would be even more desirable. Although heats of formation are now available in the literature for a variety of heteroaromatic compounds widely divergent sets of reference bond energies have been used for the derivation of resonance energies, resulting in strictly noncomparable values. Consequently we have used the original data to calcul-

TABLE II Resonance Energies of Heterocycles.

Compound	R.E.Kcals.	Ref.*	Compound	R.E.Kcals.	Ref.*
Oxazole	26.2	11	1,2,4-Triazole	48.3	13
Furan	27.2	11	1*H*-Tetrazole	49.9	11
Pyridazine	32.7	9	Benzo[b]furan	55.4	5
Isoxazole	34.3	11	Benzo[b]thiophene	69.8	14
Imidazole	40.0	12	Cinnoline	70.3	5
Pyrazole	40.4	12	Indole	73.8	11
Pyrrole	40.5	11	Quinoxaline	75.3	5
Pyrimidine	40.6	9	Indazole	75.7	12
Pyrazine	40.9	9	Benzotriazole	77.6	13
Thiazole	42.0	11	Benzimidazole	78.9	12
Thiophene	43.0	11	Naphthalene	80.3	11
Pyridine	43.3	9	Quinoline	81.0	11
1,3,5-Triazine	44.9	9	Isoquinoline	81.0	11
Benzene	45.8	9			

*References are to sources of thermodynamic data.

ate resonance energies on a common basis employing a Laidler bond energy scheme[8,9]. Ideally values for $(C_{sp}2 - C_{sp}2)$ etc. should be employed but there is as yet not even an agreed value for this bond[10] let alone for corresponding C - N and N - N ones. Following recent practice[9] the principle bond energies used were E(C-C) = -4.62, E(C=C) = 37.90, E(C-N) = 6.39, E(C=N) = 32.27, E(C-O) = -18.50, E(C-S) = 5.29, E(C-H) = -5.70, E(N-H) = -0.47, E(N-N) = 28.89, E(N=N) = 39.56, and E(N-O) = 23.13 Kcal/mole. The resulting resonance energies are listed in Table II along with the sources of thermochemical data. In most cases the values were derived from the heat of formation of the parent heterocycle when available. The principle exceptions are furan, thiophene and pyrrole where modern data for furfuraldehyde, 2- and 3-methylthiophene, and *N*-methylpyrrole provide resonance energies more in keeping with expectations than the elderly data for the parent heterocycles.

Graphical comparison of these resonance energies with the unified aromaticity indices, Figure II, shows a very satisfactory correlation between the two sets of data. A least squares treatment leads to the relation R.E. = $0.53I_A$ with a correlation coefficient of 0.76. The value of the latter is somewhat misleading as inspection of the graph shows that deviations from the line correspond in most cases to variations in resonance energies of ±5Kcals/mole which are well within experimental accuracy.

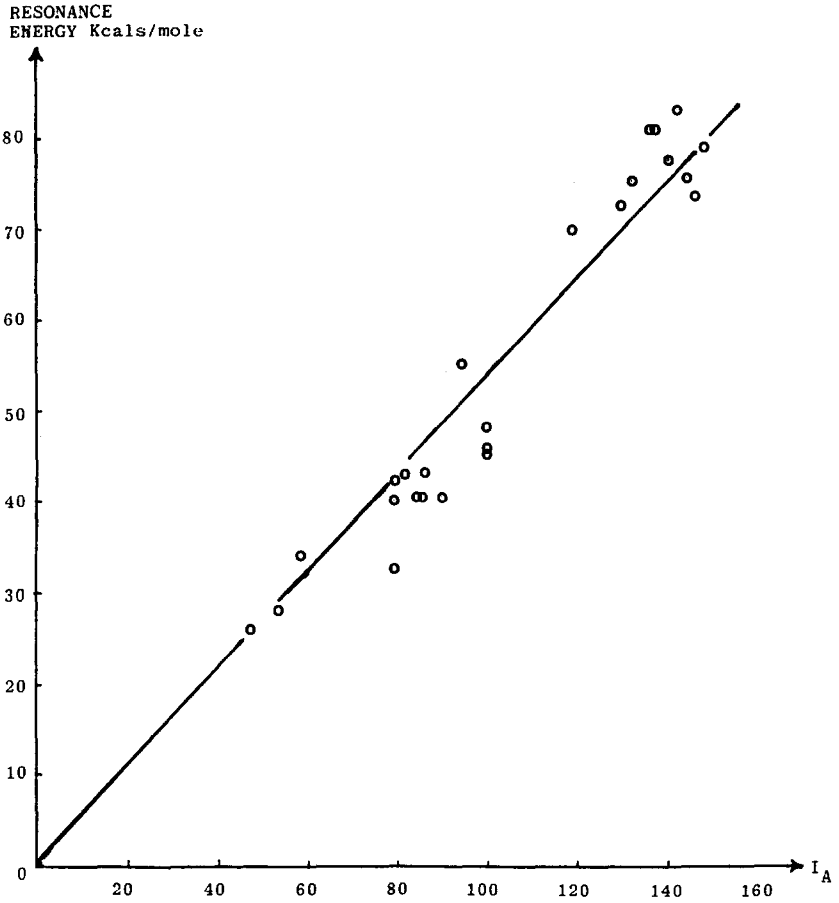

FIGURE II Plot of I_A versus Resonance Energies

In conclusion it is now possible for the first time to assign a well-defined rank in the aromaticity stakes to any heterocycle for which ring bond lengths are available and to estimate its resonance energy. Subsequent papers will explore some pertinent applications.

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