Pergamon

Tetrahedron, Vol. 53, No. 9, pp. 3319-3324, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00041-0

Absolute Hardness as a Convenient Criterion of Heteroaromaticity

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Abstract: In contrast to the situation with theoretically calculated values of hardness, values of absolute hardness calculated from molecular refractions for a range of aromatic and heteroaromatic compounds show good linear correlations with well established aromaticity criteria such as resonance energies and the aromaticity index I_A. © 1997 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

A wide variety of criteria have been proposed for the assessment of aromaticity[1] and the past few years have seen considerable emphasis on establishing quantitative interrelationships[2-6]. One criterion so far omitted from these studies has been absolute hardness which Zhou, Parr and Garst proposed[7] could be used as a measure of aromaticity. Absolute hardness, η, is generally equated with half the HOMO-LUMO gap for the Hartree-Fock or Hückel theory[8] or (I - A)/2 where I is the vertical ionisation potential and A the electron affinity. Unfortunately there are very few appropriate electron affinity values recorded in the literature[9] and Parr *et al.*[7] exemplified their proposal, *vide infra*, by demonstrating the existence of a linear correlation between theoretically calculated values of hardness and resonance energy per π-electron (REPE, TREPE) scales for a range of carbocyclic and heterocyclic molecules. The work reported in the present paper arose out of attempts to correlate these hardness parameters with other quantitative aromatic criteria.

RESULTS AND DISCUSSION

Attempts to produce satisfactory linear correlations between the absolute hardness values reported by Zhou and Parr[7] and standard quantitative aromaticity criteria were disappointing. For example a correlation coefficient of 0.70 was obtained for the plot, Figure 1, of hardness versus experimental resonance energies for 25 ring systems using the data assembled in Table 1. Disturbingly a plot, Figure 2, of hardness versus REPE for 24 different ring systems listed in Table 1 indicated a virtually random relationship, r=0.053! A closer examination showed that, as reported[7], good correlations existed between the Zhou and Parr hardness scale and REPE, r=0.97, and also with their experimental hardness values for polycyclic benzenoid compounds, r=0.95. However, these correlations broke down on inclusion of their data for heterocyclic compounds and we noted that this was at least partly due to the assignment of hardness values to the five-membered heterocycles lower

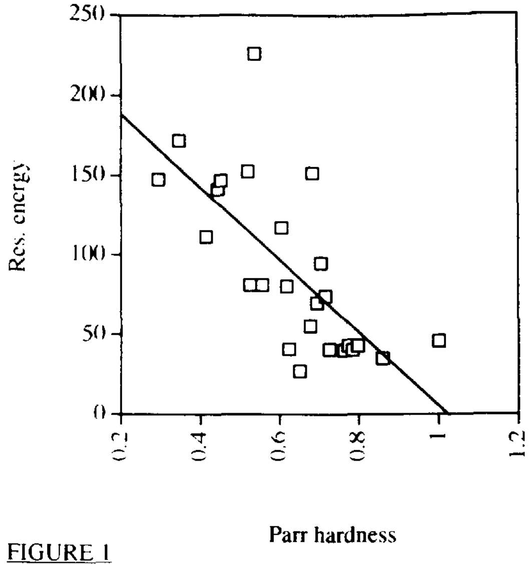


FIGURE 1

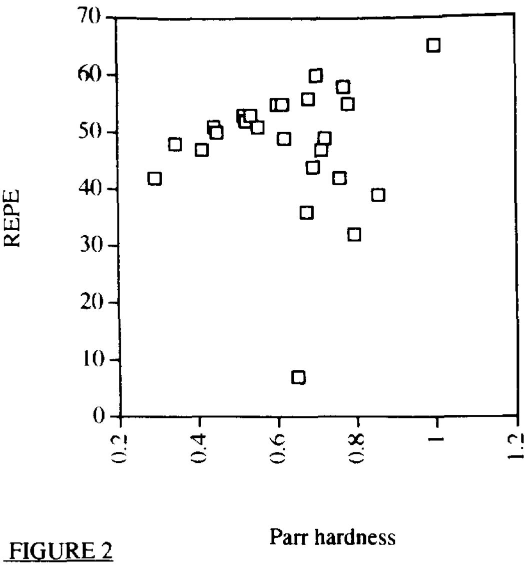


FIGURE 2

than that for benzene in contrast to simple minded expectations. Analogous observations were also made with attempted correlations employing TREPE rather than REPE values.

At this stage our attention was directed to the contributions of Komorowski[10,11] who has reformulated hardness in terms of molar refractivity (R_D) so that the relationship becomes;-

$$\eta = 19.6\ R_D^{-1/3}$$

This reformulation makes the criterion of hardness much more readily accessible to the experimental chemist since molar refractivities have been recorded for many molecules as an adjunct to dipole moment measurements. Alternatively, the molar refractivity may be obtained from the refractive index, n_D , the density, ρ, and M, the molecular weight, employing the equation;-

$$R_D = (n_D^2 - 1) / (n_D^2 + 2)\ .\ M/\rho$$

Application of this relationship has enabled us to calculate values of hardness from molar refractivities[12] for a wide range of aromatic and heteroaromatic ring systems. These are listed in Table 1 along with, where available, corresponding resonance energies, aromaticity indices, I_A[4,13], theoretical resonance energies per electron (REPE)[7], and delocalisation energies per π-electron[14]. Of particular note is that these values ascribe higher magnitudes of hardness to five-membered heterocycles than benzene. As will be evident from Figures 3 and 4 these values of molecular hardness show good linear relationships with both experimental resonance energies (40 compounds), R.E. = 322.2 - 40.7η, and aromaticity indices (43 compounds), I_A = 429.2 - 49.5η, with correlation coefficients of 0.93 and 0.92 respectively.The present hardness values for polybenzenoid hydrocarbons show roughly linear relationships with the hardness scale of Zhou and Parr, r=0.79, REPE , r=0.72, and with TREPE , r=0.60, values. However, as shown in Figure 5, these new hardness values show a good linear relationship, r=0.92, with delocalisation energies per π-electron electron obtained from HMO calculations[14].

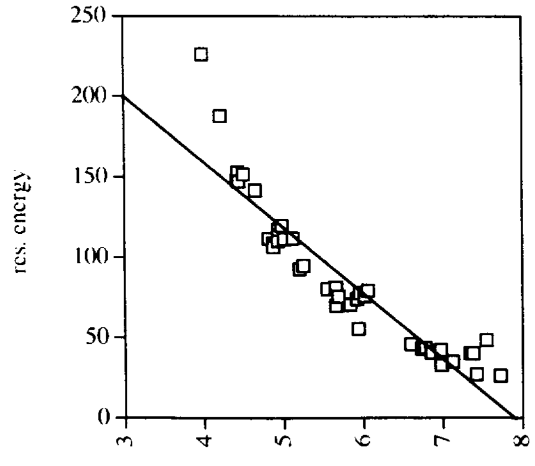
It is important to emphasise that values of hardness derived in this manner are markedly modified by ring substituents. This is of particular concern in the case of azoles where tautomers are often only isolatable as N-substituted species. Values of hardness calculated for a variety of N-methyl and N-ethylazoles are provided in Table 2. A disappointing feature of these values is that they do not differentiate between the tautomers of any particular ring system.

TABLE 1. Aromaticity Criteria for Aromatic and Heteroaromatic Compounds

Compound	η (ZP)[7]	REPE[7] $\times 10^3$(β)	R.E.[4,13] Kcals mole^{-1}	D.E.per π[14] electron (β)	I_A[4,13]	η
Furan	0.650	7	27.2	-	53	7.42
Thiophene	0.796	32	43.0	-	81.5	6.74
Pyrrole	0.859	39	34.8	-	85	7.12
Isoxazole	-	-	34.0	-	52	7.71
Oxazole	-	-	26.2	-	47	7.72
Thiazole	-	-	42.0	-	79	6.97
Isothiazole	-	-	-	-	91	7.0
Pyrazole	0.783	55	40.4	-	90	7.345
Imidazole	0.762	42	40.0	-	79	7.38
1,2,4-Thiadiazole	-	-	-	-	79	7.215
1,3,4-Thiadiazole	-	-	-	-	80	7.16
1H-1,2,4-Triazole	-	-	48.3	-	100	7.55
Benzene	1.000	-	45.8	0.333	100	6.60
Pyridine	0.773	58	43.3	-	86	6.78
Pyridazine	-	-	32.7	-	79	6.98
Pyrimidine	0.725	49	40.6	-	84	6.86
Pyrazine	0.622	49	40.9	-	89	6.85
1,2,4-Triazine	-	-	-	-	79	6.85
Benzofuran	0.676	36	55.4	-	94	5.94
Benzothiophene	0.695	44	69.8	-	119	5.66
Indole	0.716	47	73.8	-	146	5.92
Benzoxazole	-	-	-	-	79	6.13
1,2-Benzisoxazole	-	-	-	-	108	6.12
2,1-Benzisoxazole	-	-	-	-	113	5.76
1,2-Benzisothiazole	-	-	-	-	142	5.75
2,1-Benzisothiazole	-	-	-	-	142	5.69
Benzimidazole	-	-	78.9	-	148	6.06
1H-Indazole	-	-	75.7	-	144	6.02
1H-Benzotriazole	-	-	77.6	-	148.5	5.96
Naphthalene	0.618	55	80.3	0.365	142	5.55
Quinoline	0.525	52	81.0	-	134	5.65
Isoquinoline	0.556	51	81.0	-	133	5.66

Table 1 (cont.)

Compound	η (ZP)[7]	REPE[7] $x10^3$(β)	R.E.[4,13] Kcals $mole^{-1}$	D.E.per π[14] electron (β)	I_A[4,13]	η
Cinnoline	-	-	70.3	-	130	5.84
Quinoxaline	-	-	75.3	-	132	5.69
Biphenyl	0.704	60	94.7	0.365	-	5.25
Dibenzofuran	-	-	92.5	-	162	5.20
Dibenzothiophene	-	-	111.0	-	210	5.01
Carbazole	-	-	111.7	-	207	5.12
Anthracene	0.414	47	111.5	0.380	206	4.82
Acridine	-	-	108.3	-	198	4.87
Phenazine	-	-	110.3	-	188	4.93
Phenanthrene	0.605	55	117.1	0.389	210	4.94
Phenanthridine	-	-	119.6	-	206	4.98
Benzo[c]cinnoline	-	-	106.3	-	194	4.87
Pyrene	0.445	51	141.4	0.407	-	4.65
Tetracene	0.295	42	147.6	0.385	-	4.42
1,2-Benzanthracene	0.452	50	147.2	0.394	-	4.44
Chrysene	0.520	53	152.8	0.400	-	4.43
Triphenylene	0.684	56	151.7	0.404	-	4.50
Dibenz[a,h]anthracene	0.473	51	187.6	0.404	-	4.21
Coronene	0.539	53	226.0	0.441	-	3.99



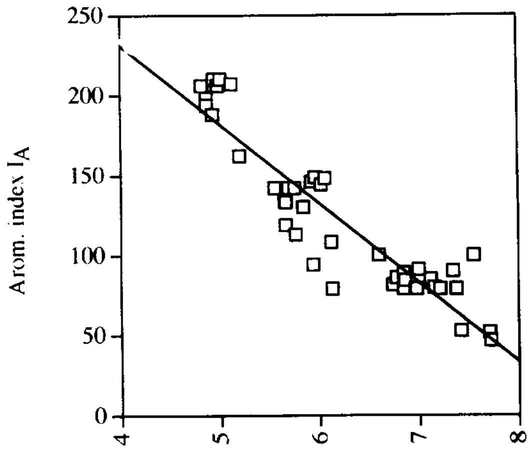


FIGURE 3 FIGURE 4

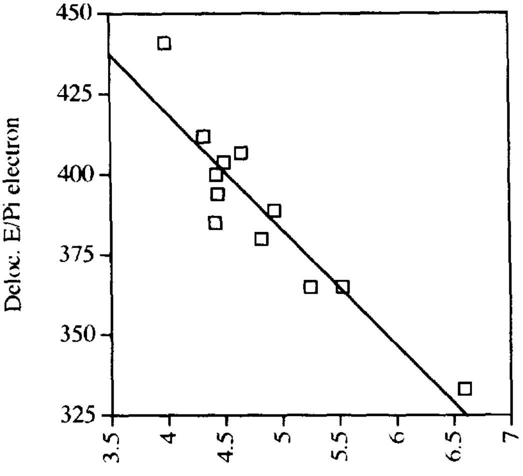


FIGURE 5

Table 2. Values of hardness, η, for N-substituted azoles.

Azole	N-H	N-Me	N-Et
Pyrrole	7.12	6.63	6.26
Imidazole	7.38	6.86	6.44
Pyrazole	7.35	6.86	6.45
1H-1,2,3-Triazole	7.67	7.04	-
2H-1,2,3-Triazole	-	7.04	-
1H-1,2,4-Triazole	7.55	7.13	-
1H-Tetrazole	-	-	6.80
2H-Tetrazole	-	-	6.80
Indole	5.92	5.68	5.41
Benzimidazole	6.06	5.80	5.51
1H-Indazole	6.02	5.76	5.50
2H-Indazole	-	5.76	5.47
1H-Benzotriazole	5.96	5.71	5.59
2H-Benzotriazole	-	5.71	5.56
Carbazole	5.12	-	4.84

Acknowledgement. I am indebted to Dr. A.W. Parkins for his helpful comments.

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(*Received in UK* 16 *December* 1996; *accepted* 9 *January* 1997)