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The H-1 NMR Solvent Shifts and Reactivity Parameters of Several Aromatic Compounds

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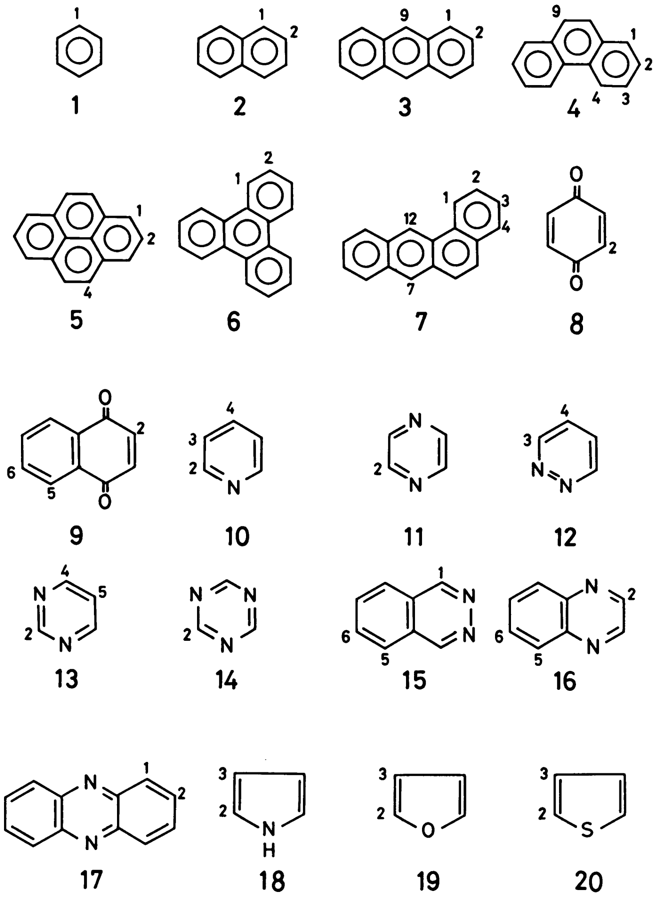
Synopsis. H-1 NMR solvent shifts were measured for 7 aromatic hydrocarbons and 13 heteroaromatic compounds. The chemical shifts can be correlated to the self-polarizabilities of the carbon atoms attached to the hydrogens in the aromatic hydrocarbons and will be of use in predicting the reactivities of the compounds. However, in the case of heteroaromatic compounds, no good correlation has been found between the reactivity parameters and the H-1 NMR solvent shifts.

The orientaion or, more quantitatively, the partial rate factor is an important problem in aromatic substitution reactions. The reactivities of the aromatic compounds can be expressed by various parameters. Several useful parameters are derived from the Hückel molecular orbital treatment.[1] Kuthan sought to present some correlation between the NMR chemical shifts and the reactivities.[2–6] However, Bartle and Jones[7,8] and Mallion[9] pointed out that the NMR shifts can be explained by the ring current and cannot be correlated with any reactivity parameters. We ourselves thought that the polarizability of the reaction center would be reflected in the solvent shifts of the relevant H-1 NMR and so have studied the correlation of the latter with various reactivity parameters.



Scheme 1.

Experimental

The reagents and solvents are from commercial sources. The reagents used and their numberings are given in Scheme 1. Three solvents, acetone, carbon tetrachloride, and cyclohexane, were used (hereafter they will be abbreviated as **S1**, **S2**, and **S3**). The H-1 NMR chemical shifts were obtained by extrapolating to an infinitely diluted state in the solvents. The values were referred to an internal TMS, with errors of ±0.03 ppm. If the solution was measured at a concentration under 0.3 mol%, its singly measured value was taken as the infinitely diluted one. Here, D is defined as $D=\delta(\mathbf{S1})-\delta(\mathbf{S3})$. Therefore, D is the difference between two infinitely diluted shifts in acetone and cyclohexane. The H-1 NMR spectra were recorded on a Hitachi R-20B spectrometer at 60 MHz and 31.5 °C. The Hückel MO calculations were carried out by a HITAC-8400 computer system installed in this Institute. The parameters used in the calculation are mostly taken from Streitwieser's book.[1]

Results and Discussion

The chemical shifts and D's of 7 alternant aromatic hydrocarbons and 13 heteroaromatic compounds are tabulated in Tables 1 and 2, along with several calculated reactivity parameters. The chemical-shift data shown in the tables are almost entirely consistent with those previously reported.[10–19]

Alternant Hydrocarbons. The hydrogens in question will hereafter be divided into two groups. One is a sterically compressed hydrogen (i.e., "angular protons" in Kuthan's nomenclature[4]), while the other is an ordinary one. The former is hydrogen which has a mutual interaction, such as the H-4 and the H-5 of phenanthrene.[4] The D values can be correlated with the self-polarizability, (π_{rr}),[20,21] of the carbon atom carrying the hydrogen in question, as is shown in Fig. 1. The compressed hydrogens are situated under a correlation line in Fig. 1. This means that the compressed hydrogens have small π_{rr} values or large D's. A correlated equation is derived for π_{rr} and D as follows: $\pi_{rr}=0.85D+0.26$. The correlation coefficient is about 0.885 for 15 data points except for three compressed hydrogens. The data show that the relative reactivities of the positions in a molecule can be evaluated well from the D values, but that those between different molecules are difficult to evaluate. For example, the calculated order of the π_{rr} values of three similarly positioned carbons is **3**-1>**2**-1>**4**-1, but the experimentally

Table 1. H-1 Chemical Shifts of Several Alternant Aromatic Hydrocarbons in ppm[a)] and Their Reactivity Parameters[b)]

No.	δ(**S1**)	δ(**S2**)	δ(**S3**)	D	π_{rr}	$L_r(E)$	$L_r^*(E)$	$S_r(E)$
1	7.35	7.27	7.22	0.14	0.398	2.536	1.603	0.833
2-1	7.90	7.74	7.70	0.20	0.443	2.299	1.305	0.994
2-2	7.51	7.40	7.34	0.17	0.405	2.480	1.519	0.873
3-1	8.08	7.94	7.87	0.21	0.454	2.25	1.23	1.072
3-2	7.50	7.39	7.32	0.18	0.411	2.40	1.44	0.922
3-9	8.55	8.35	8.28	0.27	0.526	2.013	0.91	1.312
4-1	7.98	7.83	7.77	0.22	0.439	2.318	1.247	0.977
4-2	7.58	7.45	7.39	0.18	0.403	2.498	1.469	0.860
4-3	7.58	7.45	7.39	0.18	0.409	2.454	1.375	0.893
4-4	8.82	8.62	8.59	0.23	0.429	2.366	1.343	0.939
4-9	7.82	7.66	7.60	0.22	0.442	2.299	1.347	0.997
5-1	8.29	8.10	8.05	0.24	0.466	2.190	0.990	1.115
5-2	8.07	7.92	7.87	0.20	0.395	2.55	1.500	0.829
5-4	8.18	8.00	7.95	0.22	0.445	2.28	1.309	1.026
6-1	8.81	8.58	8.56	0.26	0.427	2.378	1.311	0.888
6-2	7.72	7.58	7.52	0.20	0.406	2.477	1.398	0.928
7-7	8.51	8.29	8.21	0.30	0.496	2.101	1.02	1.325
7-12	9.39	9.09	9.05	0.34	0.514	2.049	0.91	1.250

a) The chemical-shift values was obtained by extrapolation to the infinitely diluted state in each solvent, with an error of 0.03 ppm. b) The values and notations of the reaction parameters are mostly from Ref. 1, the others were calculated by the present authors.

Table 2. Infinitely Diluted H-1 Chemical Shifts of Heteroatom Compounds in ppm and Their Reactivity Parameters

No.	δ(**S1**)	δ(**S2**)	δ(**S3**)	D	π_{rr}	q_r
8	6.83	6.71	6.57	0.26	0.493	0.927
9-2	7.04	6.90	6.78	0.27	0.483	0.910
9-5	8.05	7.88	7.68	0.37	0.442	0.925
9-6	7.90	7.74	7.54	0.36	0.418	0.959
10-2	8.58	8.54	8.52	0.06	0.399	0.923
10-3	7.35	7.19	7.07	0.28	0.398	1.004
10-4	7.65	7.47	7.35	0.30	0.397	0.950
11	8.59	8.50	8.40	0.19	0.401	0.926
12-3	9.20	9.13	9.02	0.18	0.396	0.923
12-4	7.64	7.32	7.12	0.52	0.400	0.953
13-2	9.16	9.12	9.09	0.07	0.385	0.844
13-4	8.78	8.64	8.54	0.23	0.392	0.874
13-5	7.48	7.23	7.02	0.46	0.397	1.009
14	9.24	9.10	9.01	0.23	0.372	0.797
15-1	9.61	9.42	9.34	0.27	0.434	0.899
15-5	8.16	7.87	7.75	0.40	0.442	0.986
15-6	8.04	7.87	7.75	0.29	0.405	0.984
16-2	8.92	8.76	8.66	0.27	0.407	0.902
16-5	8.11	8.06	8.02	0.09	0.443	1.002
16-6	7.87	7.71	7.59	0.28	0.406	0.987
17-1	8.26	8.20	8.17	0.09	0.454	1.001
17-2	7.96	7.77	7.65	0.31	0.414	0.980
18-2	6.78	6.64	6.57	0.20	0.485	1.035
18-3	6.07	6.07	6.11	−0.04	0.380	1.106
19-2	7.54	7.36	7.28	0.26	0.504	1.015
19-3	6.42	6.29	6.24	0.18	0.382	1.090
20-2	7.48	7.26	7.18	0.29	0.451	1.000
20-3	7.15	7.05	6.99	0.16	0.400	1.000

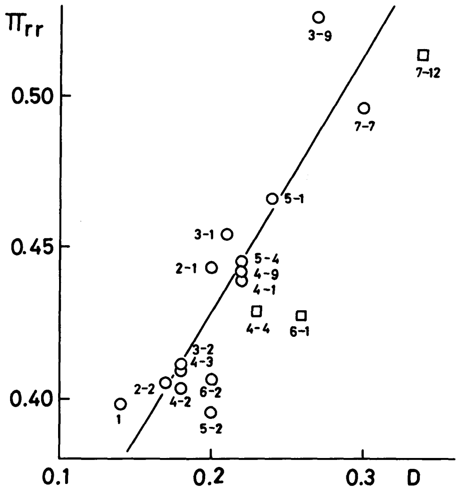


Fig. 1. Plot of self-polarizaility (π_{rr}, ordinate vs. solvent induced shift (D, abscissa). Rectangular show the values for the compressed hydrogens.

observed one of the D values is **4**-1>**3**-1>**2**-1. Here, **m**-n denotes the reference number of the compound (**m**) and the position (n) as given in Scheme 1. Large deviations of the self-polarizability from the correlation line in Fig. 1 were found for the hydrogens of **1**(0.019), **3**-9(0.037), **5**-2(−0.032), **6**-2(−0.024), and **7**-7(−0.019). It is strange that H(**3**-9) and H(**7**-7) show different signs for the deviation, although the hydrogens seem to be similar in their locations. The large deviation of **1** comes from its large π_{rr} value. Mallion stated that H(**5**-2) has a large deviation in the correlation between the chemical shifts and the free valences (F_r).[9)] Bartle and Jones considered the

Table 3. Correlation between Solvent-Induced Shifts (*D*) and Reactivities (*R*) with 15 Data of 7 Alternant Hydrocarbons in the $R=aD+b$ Equation

R	*a*	*b*	$r^{a)}$	$e^{b)}$
π_{rr}	0.85	0.26	0.885	0.018
$L_r(E)$	−3.56	3.09	−0.877	0.081
$L_r^{w}(E)$	−4.56	2.26	−0.898	0.093
$S_r(E)$	3.59	0.25	0.924	0.062

a) Correlation coefficients. b) Standard deviations.

Table 4. Correlation between Solvent-Induced Shifts (*D*) and Reactivity Parameters (*R*) of 8 Nitrogen-containing Aromatic Compounds in the $R=aD+b^{a)}$ Equation

R	*a*	*b*	*r*	*e*
$L_r(E)$	−2.03 (2.44)	2.72 (1.55)	−0.551 (0.447)	0.45 (0.43)
$L_r^{w}(E)$	−1.66 (1.84)	0.98 (0.16)	−0.393 (0.310)	0.57 (0.50)
$S_r(E)$	−0.41 (0.06)	0.97 (0.67)	−0.645 (0.063)	0.07 (0.28)
q_r	−0.061 (−0.039)	1.004 (0.893)	−0.412 (−0.071)	0.020 (0.049)
π_{rr}	−0.098 (0.080)	0.445 (0.383)	−0.616 (0.364)	0.018 (0.018)

a) The values are given for 10 sites except for those adjacent to the hetero atom, whose values are given separately in parentheses.

cause of the deviation to be the ring-current effect in the case of **5**.[7] On the other hand, Haigh et al. stated that the deviation of H(**5**-2) is smaller than either H(**5**-1) or H(**5**-4) in the correlation of the chemical shifts and ring current.[22] Therefore, the abnormally large deviation of H(**5**-2)(−0.032 in π_{rr}) cannot be explained only by the ring-current effect, as has been stated by Bartle and Jones.[7]

There are many reactivity parameters in addition to π_{rr}; several of them are given in Table 1, the values of which are mostly cited from Streitwieser's book.[1] The correlations between such parameters and *D* can, then, be evaluated by the following linear equation: $R=aD+b$, where *R* is a reactivity parameter and where *a* and *b* are constant parameters. The results are shown in Table 3. Among the four parameters in the table, $S_r(E)$ has the best correlation coefficient, while π_{rr} has the smallest standard deviation. The latter parameters can now be evaluated from the H-1 NMR chemical shifts in order to compare the local positions in a molecule or those of several related molecules.[23]

Hetroaromatic Compounds. The heteroaromatic compounds studied are divided into 3 types: (A) 2 quinones (**8** and **9**), (B) 8 nitrogen-containing compounds (**10**—**17**), and (C) 3 five-membered compounds (**18**—**20**). The hydrogens adjacent to heteroatoms sometimes give abnormal *D* values. The correlations between the reactivity parameters and *D* are given in Table 4. As the table shows, the correlations are poor. One of the reasons for this is that the reactivity parameters are derived by the Hückel MO method, the simplest MO method, which may not be suitable even for a qualitative discussion of the properties of heteroaromatic compounds. One of the other reasons is the heteroatom effect. The heteroatoms considered here have lone-pair electrons. These will significantly affect the *D* values in various complex manners.

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