NOTES

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The NMR Chemical Shifts of Aromatic Ring Protons. II. The Substituent Chemical Shift of the Ring Protons of 1-Substituted Naphthalenes

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We have shown, in the preceding paper, that the chemical shift of *o*-, *m*-, and *p*-ring protons of a number of monosubstituted benzenes could be determined without any difficulty and that they could be assigned without ambiguity by means of the statistically-distributed deuterium substitution method.[1] In the present paper, we will report the application of the same technique to the naphthalene-series, for which few systematic studies seem to have been reported.[2]

Ring hydrogens of naphthalene were about 85% statistically replaced by deuteriums through the hydrogen-deuterium exchange reaction of naphthalene in the presence of a small amount of aluminum trichloride as a catalyst. The extent of the substitution was checked by IR analysis at appropriate intervals. The NMR spectrum of the deuterated naphthalene showed only two singlets corresponding to α and β protons; the intensities of both signals were nearly the same. Since there is little possibility that more than two hydrogens remain at vicinal positions, the spectra are very much simplified to give only two signals, without any splitting of the signals caused by spin-spin interactions. Although the direct assignment of two peaks from the spectrum was impossible, it was made possible by changing chemically their relative intensities up to *ca.* 3: 2, as is shown in Fig. 1-A. This modification was done by heating the above deuterio-naphthalene under reflux with trifluoroacetic acid. As the dedeuteration occurs much more rapidly at the α-position than at the β-position in trifluoroacetic acid, the more intense signal must be assigned to α-protons, and the less intense one, to β-protons. A series of 1-substituted naphthalenes (X in 1-X-Naph-d_6; NO_2, CN, Br, COOH, H, OH, NH_2) were prepared from this partially-deuterated naphthalene. The NMR spectra of Naph-X are generally made up of seven singlets, four of which are little smaller in their intensities than the other three singals, as is shown in Fig. 1-B and 1-C. From this difference in intensity, the smaller four signals can be assigned to β-protons, or 2, 3, 6, and 7-protons, and the rest, to α-protons, or 4, 5, and 8-protons. In some cases, more than two signals overlapped, but it was still possible to analyse the spectra rather precisely by considering the ratio of the intensities of the signals in detail. All the measurements were carried out with a Hitachi R-20 NMR spectrometer at 60 MHz. The chemical shifts were measured at 5 mol% in a *N,N*-dimethylacetamide solution from the internal standard TMS. The chemical shifts of each signal can be determined precisely, within ±0.5 Hz in most cases, but the accuracy may fall as much as to ±1.5 Hz in the worst case. The equal intensities of the four signals belonging to the β-protons unfortunately provided us with a serious disadvantage in making further unambiguous assignments of the individual signals, and the same is also true for the three signals corresponding to the α-protons. Nevertheless, plausible assignments can be done by comparison with the data for mono-substituted benzenes and also with their solvent effects.

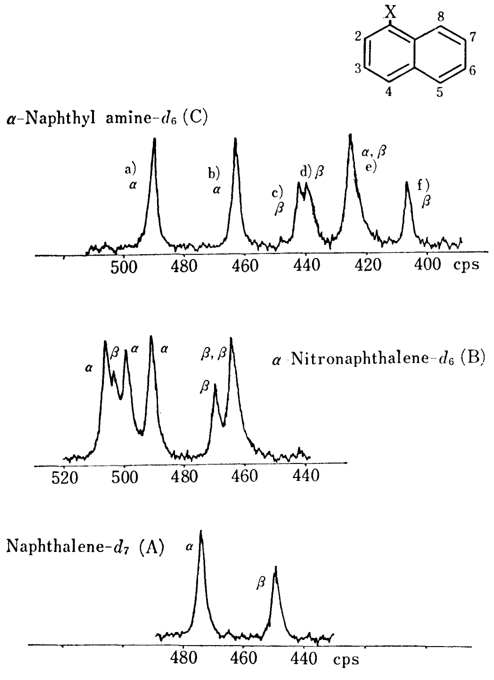

Fig. 1. NMR spectra of deuterated naphthalenes.

In the case of α-naphthylamine in a *N,N*-dimethylacetamide solution, for instance, the individual signals could be assigned as follows; one (signal *a*) of the three signals belonging to the α-protons is more deshielded than that of unsubstituted naphthalene ($\Delta = -15.8$ Hz). Since the amino group has a large shielding effect in the benzene series, the *a* signal must be assigned to the 8-proton, of the other two, *e* (two signals overlapped) at a high field ought to be assigned to the 4-proton, and *b*, to the 5-proton. The *f* and *e* signals referred to β-protons can be assigned to 2- and 3-protons respectively by analogy with the relative chemical shifts of the aniline protons. It should also be possible to assign the *d* signal to the proton at the conjugate 7-

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[1] Y. Yukawa, Y. Tsuno, and N. Shimizu, This Bulletin, **44**, 2843 (1971).

[2] P. R. Wells, *Aust. J. Chem.*, **17**, 967 (1964). Y. Sasaki, M. Suzuki, T. Hibino, K. Karai, M. Hatanaka, and I. Shiraishi, *Chem. Pharm. Bull.* (Tokyo), **16**, 1367 (1968).

Table 1. Relative chemical shift of the ring protons of α-monosubstituted naphthalenes

Subst.	2	3	4	5	6	7	8
NO_2	−54.1	−21.0	−27.0	−17.0	−15.2	−15.2	−30.2
CN	−39.7	−19.8	−26.0	−14.0	−11.4	−13.4	−14.9
COOH	−47.1	−8.9	−15.7	−7.1	−4.9	−4.9	−69.2
Br	−22.6	4.0	−4.8	−4.8	−7.0	−10.4	−16.3
OH	31.0	9.8	34.6	7.6	4.2	9.8	−21.6
NH_2	41.2	22.9	47.7	11.4	7.6	9.6	−15.8

Relative values of 2,3,6, and 7-protons were determined from the chemical shift of the β-proton of naphthalene and those of 4, 5, and 8-protons from that of α-proton.

position, and *c*, to the 6-proton, considering the fact that the resonance effect is mostly responsible for the determination of the chemical shifts. The assignments for the other compounds were obtained in a similar manner. In most cases, the resulting assignment for the protons on the substituted ring is believed to be highly reliable, because of the rigorous agreement of the relative variations of the substituent chemical shifts between the corresponding protons of benzene and naphthalene. However, for the β-protons on the other ring, certain ambiguities might unfortunately be involved in the tentative assignment. The relative chemical shifts are listed in Table 1.

The substituent effects in the substituted ring of the naphthalene serise are linearly correlated with those of the corresponding protons in the benzene series; $\Delta\Delta\delta^2 = 1.09\,\Delta\Delta\delta^o$, $\Delta\Delta\delta^3 = 0.98\,\Delta\Delta\delta^m$, and $\Delta\Delta\delta^4 = 0.89\,\Delta\Delta\delta^p$. This may indicate that there is not much difference in the substituent effect on the ring proton chemical shift between the benzene and naphthalene series. The substituent effects on the respective protons are expressed in terms of the σ_p^0 and $\Delta\bar{\sigma}_R^+$ in just the same way as for the benzene series;

$$\Delta\Delta\delta^3 = -27.7(\sigma_p^0 + 0.29\Delta\bar{\sigma}_R^+)$$

$$\Delta\Delta\delta^4 = -38.7(\sigma_p^0 + 0.87\Delta\bar{\sigma}_R^+)$$

$$\Delta\Delta\delta^5 = -22.7(\sigma_p^0 + 0.13\Delta\bar{\sigma}_R^+)$$

$$\Delta\Delta\delta^6 = -19.1(\sigma_p^0)$$

$$\Delta\Delta\delta^7 = -19.7(\sigma_p^0 + 0.17\Delta\bar{\sigma}_R^+)$$

In these treatments, σ_p^0 is used as a conventional measure of the unexalted polar effect throughout the series, since no σ^0 values for the respective naphthalene position are available. Perhaps, in view of the analogy to the benzene system, $\Delta\Delta\delta^3$ should be described in terms of the σ_m^0 parameter. This results in the correlation;

$$\Delta\Delta\delta^3 = -32.1(\sigma_m^0 + 0.45\Delta\bar{\sigma}_R^+)$$

Similarly, the chemical shifts of the non-conjugate 6-proton are given by;

$$\Delta\Delta\delta^6 = -21.0(\sigma_m^0 + 0.23\Delta\bar{\sigma}_R^+)$$

It is evident from these correlations that the protons on the substituted ring are more susceptible to both the polar and resonance effects of substituents than those on the other ring. The same treatment cannot be applied to the chemical shifts of the 8-proton. As the ordinary electronic effects of substituents could not be transmitted so effectively to this position, the behavior of this proton may give many valuable information about the particular interactions with substituents at the closest position.[3]

From the theoretical point of view, it should be more reasonable to treat these results in terms of the inductive σ_i and π-electronic σ_π parameters.[4] The results of this treatment and a comparison with recent results obtained by means of Taft and Dewar treatments[5] will be the subjects of a forthcoming paper.

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3) R. H. Martin, N. Defay, and F. Greets-Evard, *Tetrahedron*, **20**, 1505 (1964).

4) Y. Yukawa and Y. Tsuno, *Nippon Kagaku Zasshi*, **86**, 873 (1965).

5) P. R. Wells, S. Ehrenson, and R. W. Taft, "Progress in Physical Organic Chemistry," Vol. **6**, Interscience Publishers, N. Y. (1964), p. 147.