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Proton Magnetic Resonance Spectra of some Naphthalene Derivatives in DMSO-d_6

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ABSTRACT

The chemical shifts of the ring protons of 14 naphthalenesulfonic acid derivatives have been assigned from 250 MHz spectra. In addition, the spectra of a large number of monosubstituted naphthalenes were recorded using DMSO-d_6 as solvent. It is clear from this latter part of the study that DMSO-d_6 often causes an upfield (to a lower δ value) shift (relative to those in $CDCl_3$) in the δ values of the protons in this ring system. It is also clear that a number of signals are less resolved when DMSO-d_6 is used in lieu of $CDCl_3$, at the field strength of 250 MHz.

INTRODUCTION

In a recent paper from these laboratories, we presented[1] tables of chemical shifts of some monosubstituted naphthalenes resulting from a study using $CDCl_3$ as the ^{1}H-NMR solvent. Those data were then used to assist in the interpretation of the spectra of some more complex naphthalene derivatives such as H-acid and J-acid. It was concluded from the study that the chemical shift of protons on a naphthalene ring which are under the influence of two or more ring substituents could not always be predicted simply by adding the effects of the individual substituents. Although $CDCl_3$ was normally used as the solvent for the monosubstituted naphthalenes and DMSO-d_6 for the naphthalene-based dyestuffs intermediates (J-acid, γ-acid, S-acid, etc.), we did not believe that the difference in solvent polarity would account for

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the lack of a general correlation between the calculated and observed δ values for the protons of the more complex naphthalenes.

We thought it worthwhile to repeat the ^1H-NMR experiments using DMSO-d_6 as the solvent for the monosubstituted compounds studied and to generate new tables of parameters. In this way, the contribution of the NMR solvents to the δ values could be better assessed.

RESULTS AND DISCUSSION

Tables 1 and 2 contain the δ values in ppm for the ring protons of the naphthalenes examined in this study. Each compound was dissolved in DMSO-d_6 at a concentration of 5%, and tetramethylsilane (TMS) was employed as the internal reference. In general, changing the NMR solvent from $CDCl_3$ to DMSO-d_6 had little effect on the relative order in which the protons give rise to a signal in the spectrum of each compound; and in nearly each case the *peri* proton of the 1-substituted naphthalenes was found

TABLE 1

Chemical Shifts (δ, ppm) for the Ring Protons of 1-Substituted Naphthalenes

X	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-7*	*H-8*
H	7·52	7·52	7·92	7·92	7·52	7·52	7·92
Cl	7·69	7·53	8·03	7·96	7·69	7·69	8·21
Br	8·01	7·46	7·90	8·01	7·60	7·60	8·16
NMe_2	7·03	7·36	7·47	7·82	7·47	7·47	8·12
I	8·16	7·30	8·02	8·02	7·64	7·64	7·92
OH	6·91	7·32	7·32	7·80	7·46	7·46	8·17
OMe	6·93	7·49	7·49	7·86	7·49	7·49	8·17
NH_2	6·71	7·21	7·08	7·71	7·35	7·35	8·08
CHO	8·30	7·68	8·20	8·10	7·77	7·77	9·22
SO_2Cl	7·88	7·40	7·88	7·96	7·50	7·50	8·80
SO_3H	7·96	7·43	8·01	8·01	7·47	7·47	8·80
CH_2NH_2	7·51	7·51	7·79	7·92	7·51	7·51	8·12
OCOMe	7·35	7·56	7·88	7·96	7·62	7·62	8·02
Me	7·34	7·37	7·74	7·89	7·51	7·51	7·98
Et	7·32	7·41	7·74	7·89	7·51	7·51	8·02
NO_2	8·29	7·64	8·29	8·10	7·72	7·72	8·29
COMe	7·97	7·59	8·10	8·10	7·59	7·59	8·64
CN	8·07	7·61	8·07	8·07	7·69	7·69	8·24
CH_2Cl	7·58	7·46	7·92	7·92	7·58	7·58	8·19
C_6H_5	7·47	7·47	7·80	7·94	7·47	7·47	7·94
N=NPh	7·85	7·60	8·00	7·94	7·60	7·60	8·96

TABLE 2
Chemical Shifts (δ, ppm) for the Ring Protons of 2-Substituted Naphthalenes

X	*H-1*	*H-3*	*H-4*	*H-5*	*H-6*	*H-7*	*H-8*
H	7·92	7·52	7·92	7·92	7·52	7·52	7·92
Br	8·22	7·66	7·93	7·93	7·59	7·59	7·93
OH	7·15	7·11	7·74	7·74	7·23	7·36	7·67
OMe	7·32	7·15	7·81	7·81	7·35	7·45	7·81
CO_2H	8·62	7·98	7·98	7·95	7·59	7·59	8·09
CHO	8·60	7·94	8·05	8·05	7·72	7·72	8·19
SO_2Cl	8·26	7·80	7·93	7·93	7·57	7·57	8·02
SO_3H	8·19	7·74	7·88	7·88	7·51	7·51	7·95
CH_2OH	7·86	7·48	7·89	7·89	7·48	7·48	7·89
COCl	8·69	8·06	8·06	8·06	7·66	7·66	8·16
OCOMe	7·67	7·31	7·93	7·93	7·52	7·52	7·93
Me	7·66	7·35	7·84	7·84	7·45	7·45	7·84
Et	7·65	7·35	7·82	7·82	7·43	7·43	7·82
NO_2	8·95	8·09	8·17	8·17	7·73	7·73	8·24
COMe	8·63	7·95	7·95	7·95	7·62	7·62	8·09
NH_2	6·83	6·95	7·49	7·59	7·07	7·25	7·59
N═NPh	8·61	7·98	8·05	8·02	7·65	7·65	8·19

furthest downfield. Protons *ortho* to electron-donating groups in 1-substituted naphthalenes were found furthest upfield, as would be anticipated. Although the signals for protons H-6 and H-7 of 2-naphthylamine and 2-naphthol continue to be well-separated using DMSO-d_6 as solvent, the resolution of the signals for H-1 and H-3 is lost, since the two overlap. The signals furthest upfield in the spectra of 1-substituted naphthalenes in which an electron-withdrawing group is present (cf. H-3, 6, 7) were also noticeably less resolved using DMSO-d_6. It is possible that this loss in resolution would be circumvented by the use of a spectrometer of higher field strength.

Tables 3 and 4 depict changes in the δ value of the ring protons caused by introducing a substituent into the 1- or 2-position of naphthalene. We observed complex signals centered at δ 7·92 and δ 7·52 for the α and β protons, respectively, when DMSO-d_6 is used as the solvent for naphthalene itself. This represents a modest downfield change in the chemical shifts in DMSO-d_6 compared with $CDCl_3$ ($\alpha = 7{\cdot}81$; $\beta = 7{\cdot}46$). Most of the values in the two tables reflect a slight *upfield* shift in the positions of the signals for the ring protons relative to those reported when $CDCl_3$ was the solvent.

Table 5 contains δ values for the ring protons of 14 well-known dyestuffs intermediates, as a complement to the 12 compounds for which we reported data in our earlier paper.[1] Figure 1 contains the structures of the present

TABLE 3

Change in δ Value (ppm) of the Ring Protons Caused by Introducing a Substituent into the 1-Position of Naphthalene[a]

X	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-7*	*H-8*
Cl	0·17	0·01	0·11	0·04	0·17	0·17	0·29
Br	0·49	−0·06	−0·02	0·09	0·08	0·08	0·24
NMe_2	−0·49	−0·16	−0·45	−0·10	−0·05	−0·05	0·20
I	0·35	−0·22	0·21	0·10	0·12	0·12	0·12
OH	−0·61	−0·30	−0·60	−0·12	−0·06	−0·06	0·25
OMe	−0·59	−0·03	−0·43	−0·06	−0·03	−0·03	0·25
NH_2	−0·81	−0·31	−0·84	−0·21	−0·17	−0·17	0·16
CHO	0·77	0·16	0·28	0·18	0·25	0·25	1·30
SO_2Cl	0·36	−0·12	−0·04	0·04	−0·02	−0·02	0·88
SO_3H	0·44	−0·09	0·09	0·09	−0·05	−0·02	0·88
CH_2NH_2	−0·01	−0·01	−0·13	0·00	−0·01	−0·01	0·20
OCOMe	−0·17	0·04	−0·04	0·04	0·10	0·10	0·10
Me	−0·18	0·15	−0·15	−0·03	−0·01	−0·01	0·06
Et	−0·20	−0·11	−0·18	−0·04	−0·01	−0·01	0·10
NO_2	0·77	0·12	0·37	0·18	0·20	0·20	0·37
COMe	0·45	0·07	0·18	0·18	0·07	0·07	0·72
CN	0·55	0·09	0·15	0·15	0·17	0·17	0·34
CH_2Cl	0·06	−0·06	0·00	0·00	0·06	0·06	0·27
C_6H_5	−0·05	−0·05	−0·12	0·02	−0·05	−0·05	0·02
N=NPh	0·33	0·08	0·08	0·02	0·08	0·08	1·04

[a] A positive value denotes a downfield shift relative to TMS.

naphthalenesulfonic acids (**1–14**), and Figs 2 and 3 depict some representative spectra. A summary of the spectral data of these naphthalene derivatives would be the following.

(1) A β-proton between OH and SO_3H groups that are 1,3 to each other (*cf.* H-7 in **1–8**) gives rise to a signal near 7 ppm.

(2) Acylation of the amino group of a naphthylamine to give derivatives like **3**, **7**, **8** causes a substantial downfield shift in the δ value of an adjacent proton (*cf.* H-2 in **7**, **8**, and H-4 in **3**). No doubt these protons lie within the deshielding zone of the carbonyl groups (*cf.* **15**, **16**). This would be consistent with previous reports[2−7] that describe the anisotropy of compounds **17** and **18**.

(3) The low-field positions of the chemical shifts of the protons *ortho*/*para* to the amino groups of Peri acid (**13**) and Cleve's acid (**14**) suggest that these two compounds are zwitterionic.

(4) Proton H-1 of an *N*-substituted J-acid derivative appears invariably at 8 ppm (*cf.* **1**, **3**, **4** and **5**).

TABLE 4

Change in δ Value (ppm) of the Ring Protons Caused by Introducing a Substituent into the 2-Position of Naphthalene[a]

X	*H-1*	*H-3*	*H-4*	*H-5*	*H-6*	*H-7*	*H-8*
Br	0·30	0·14	0·01	0·01	0·07	0·07	0·01
OH	−0·77	−0·41	−0·18	−0·18	−0·29	−0·16	−0·25
OMe	−0·60	−0·37	−0·11	−0·11	−0·17	−0·07	−0·11
NH_2	−1·08	−0·57	−0·43	−0·33	−0·45	−0·27	−0·33
CHO	0·68	0·42	0·13	0·13	0·20	0·20	0·27
SO_2Cl	0·34	0·28	0·01	0·01	0·05	0·05	0·10
SO_3H	0·27	0·22	−0·04	−0·04	−0·01	−0·01	−0·03
CH_2OH	−0·06	−0·04	−0·03	−0·03	−0·04	−0·04	−0·03
OCOMe	−0·25	−0·21	0·01	0·01	0·00	0·00	0·01
Me	−0·26	−0·17	−0·08	−0·08	−0·07	−0·07	−0·08
Et	−0·27	−0·07	−0·10	−0·10	−0·09	−0·09	−0·10
NO_2	1·03	0·57	0·25	0·25	0·21	0·21	0·32
COMe	0·71	0·43	0·03	0·03	0·10	0·10	0·17
N=NPh	0·69	0·46	0·13	0·13	0·13	0·13	0·27
COCl	0·77	0·54	0·14	0·14	0·14	0·14	0·24
CO_2H	0·70	0·46	0·06	0·03	0·07	0·07	0·17

[a] A positive value denotes a downfield shift relative to TMS.

TABLE 5

Chemical Shifts (δ, ppm) for the Ring Protons of Some Naphthalene-Based Dyestuffs Intermediates

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-7*	*H-8*
1 Phenyl J-acid	7·97	7·24	—	7·41	7·41	—	6·98	—
2 Phenyl γ-acid	7·70	—	7·20	7·72	7·51	—	7·10	—
3 *N*-Acetyl J-acid	8·00	7·60	—	8·16	7·50	—	7·09	—
4 J-acid imide	7·99	7·33	—	7·51	7·45	—	6·99	—
5 J-acid urea	8·00	7·55	—	8·02	7·51	—	7·04	—
6 K-acid	—	7·28	7·91	—	8·71	—	7·28	—
7 *N*-Acetyl H-acid	—	8·64	—	7·61	7·29	—	7·01	—
8 *N*-Benzoyl H-acid	—	9·00	—	7·80	7·62	—	7·27	—
9 Schaeffer's acid	7·65	7·65	—	8·08	7·82	7·13	—	7·16
10 R-acid	7·61	7·61	—	8·05	8·05	—	—	7·14
11 G-acid	—	7·99	—	8·13	7·78	7·05	—	8·20
12 Chicago acid	—	—	8·32	—	8·28	7·35	6·93	—
13 Peri acid	—	8·14	7·65	8·34	8·14	7·65	7·65	—
14 1,6-Cleve's acid	—	7·79	7·55	7·95	8·18	—	7·79	7·95

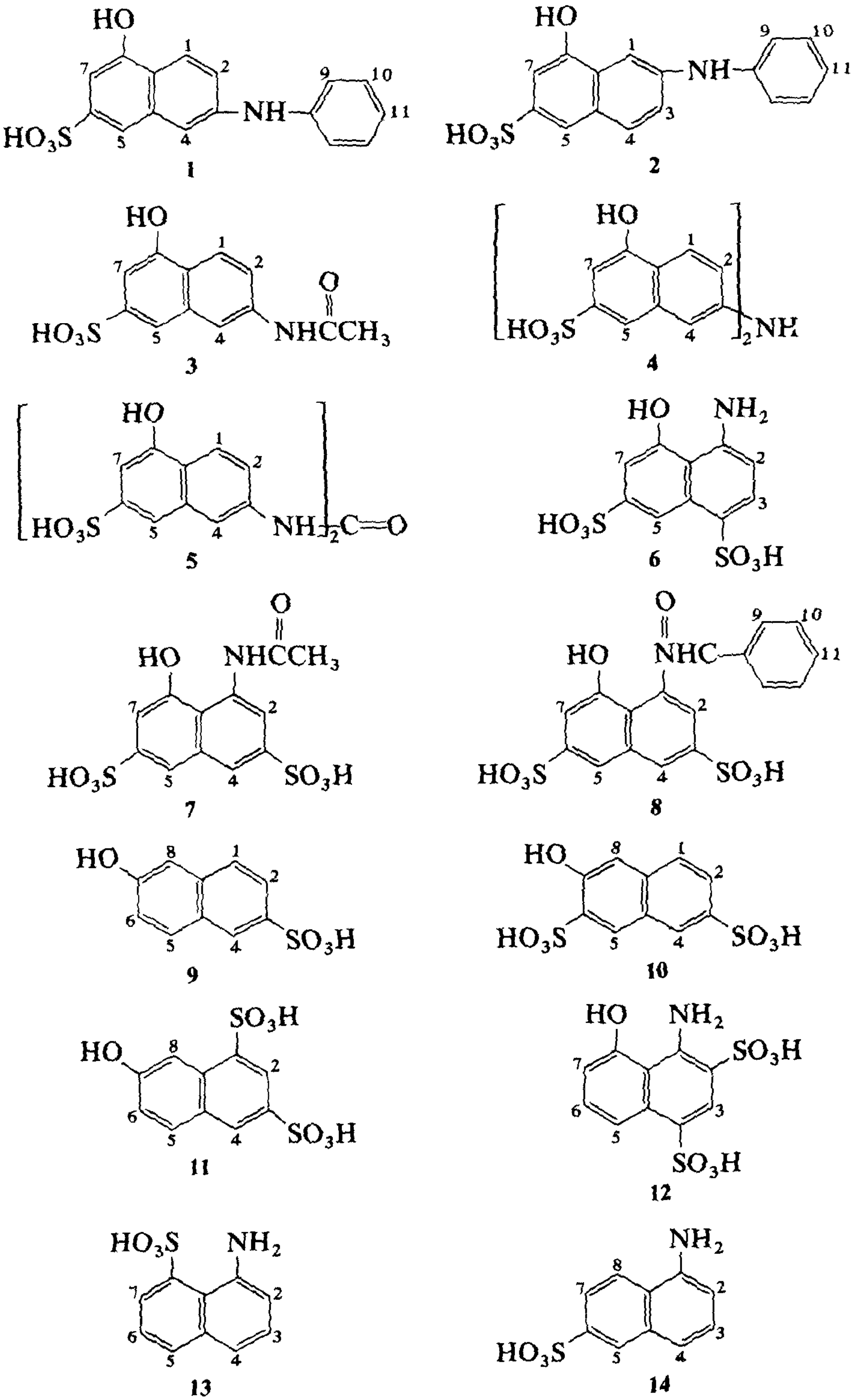


Fig. 1. Naphthalene-based dyestuffs intermediates examined in this investigation.

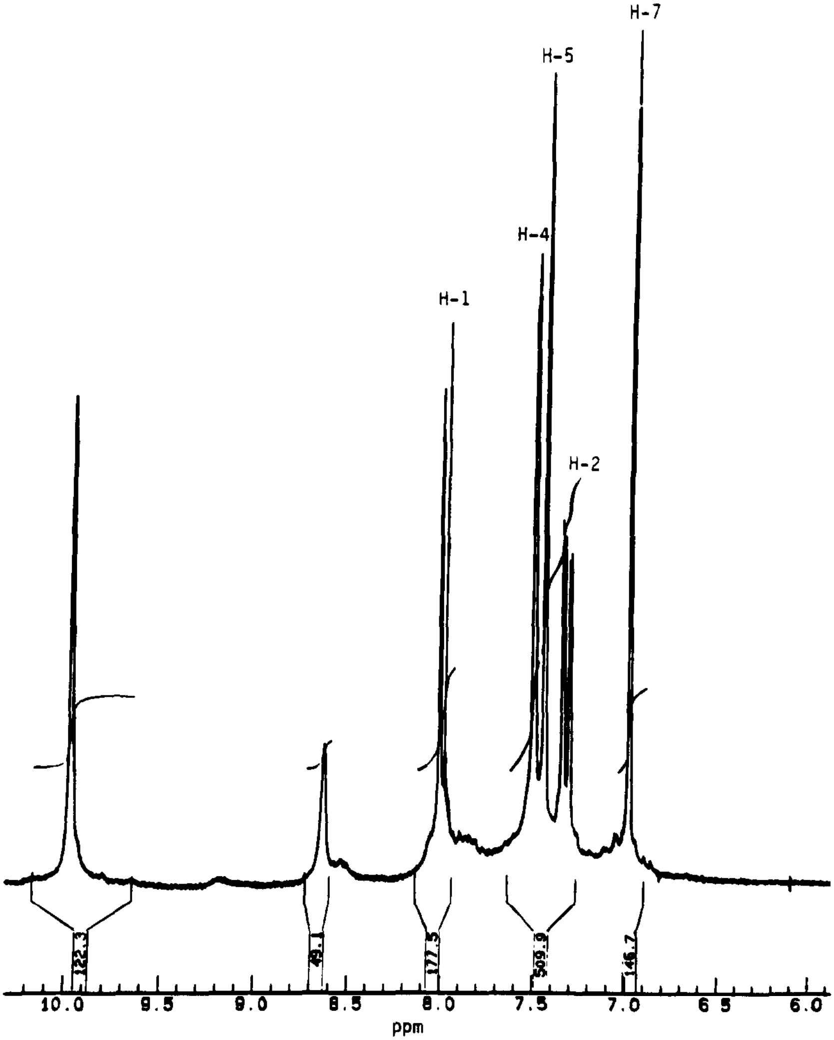
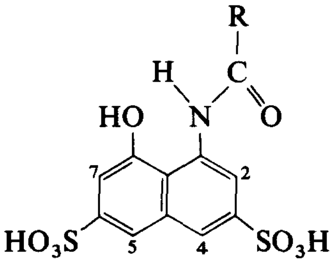


Fig. 2. ^{1}H-NMR spectrum of J-acid imide.

(5) The 2,6-naphtholsulfonic acids Schaeffer's acid (**9**) and R-salt (**10**) give rise to a *single* degenerate signal for protons H-1 and H-2 (*cf.* Figs 4 and 5). The δ values for the protons in the phenyl ring of **1**, **2** and **8** were also recorded. The chemical shifts observed were 7·17–7·29 ppm (H-9, 10) and 6·88 ppm (H-11) for **1**, 7·16–7·27 ppm (H-9, 10) and 6·86 ppm (H-11) for **2**, and 7·96 ppm (H-9) and 7·62 ppm (H-10, 11) for **8**.

When Tables 1 and 2 were used to calculate the chemical shifts of the ring



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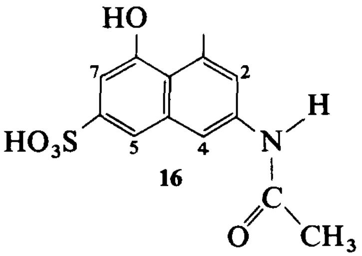
($R = CH_3, C_6H_5$)



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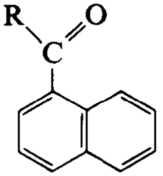

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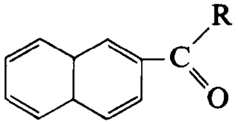

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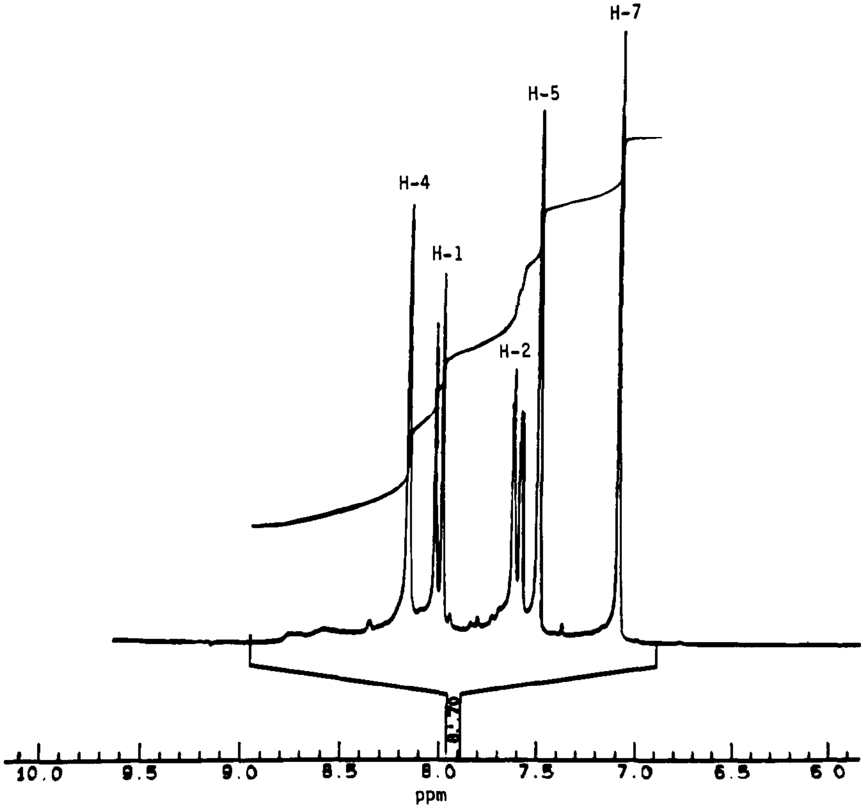

Fig. 3. ^{1}H-NMR spectrum of *N*-acetyl J-acid.

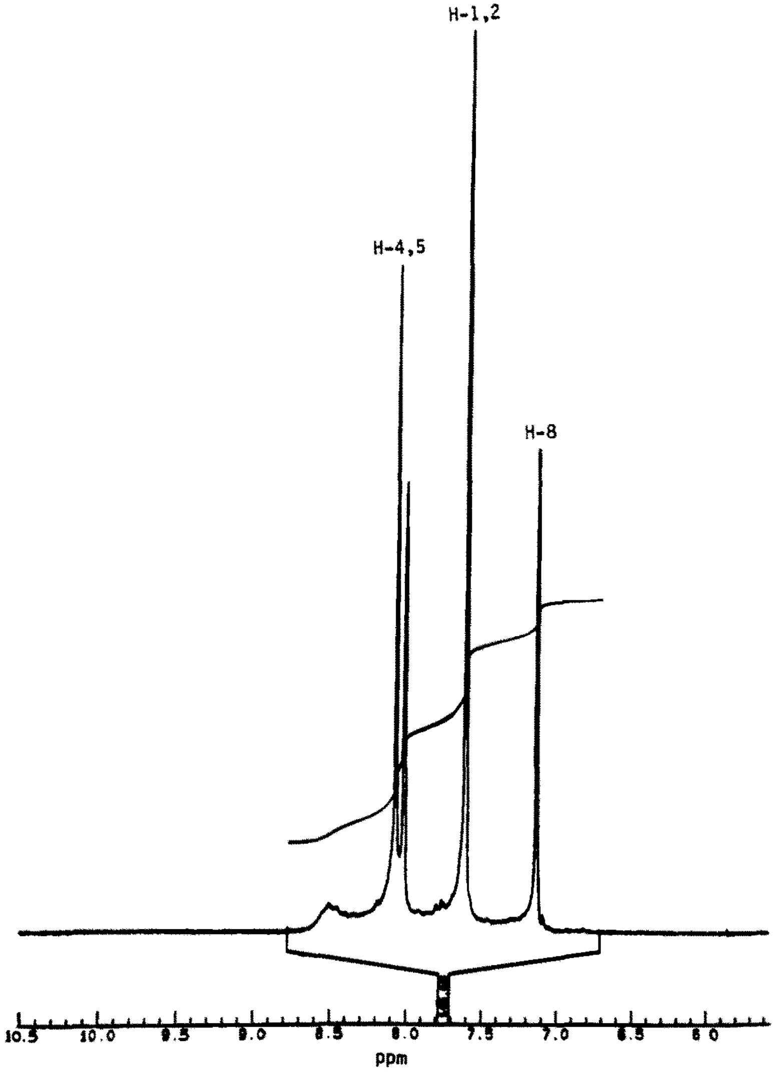

Fig. 4. ^{1}H-NMR spectrum of R-acid.

protons of compounds **1–14**, very good agreement with the observed values was obtained for **1**, **9–11**, and for **3**, **5**, **7–8** once the anisotropic effects of the acyl groups was taken into account. The remaining spectra were readily interpreted even though the chemical shifts of some of the protons were as much as a full ppm further downfield than the calculated values. In two of these latter cases (**13–14**), however, we believe that the aminonaphthalenesulfonic acids exist in a zwitterionic form with the resulting NH_3^+ group deshielding protons that are *ortho* and *para*. This explanation is supported

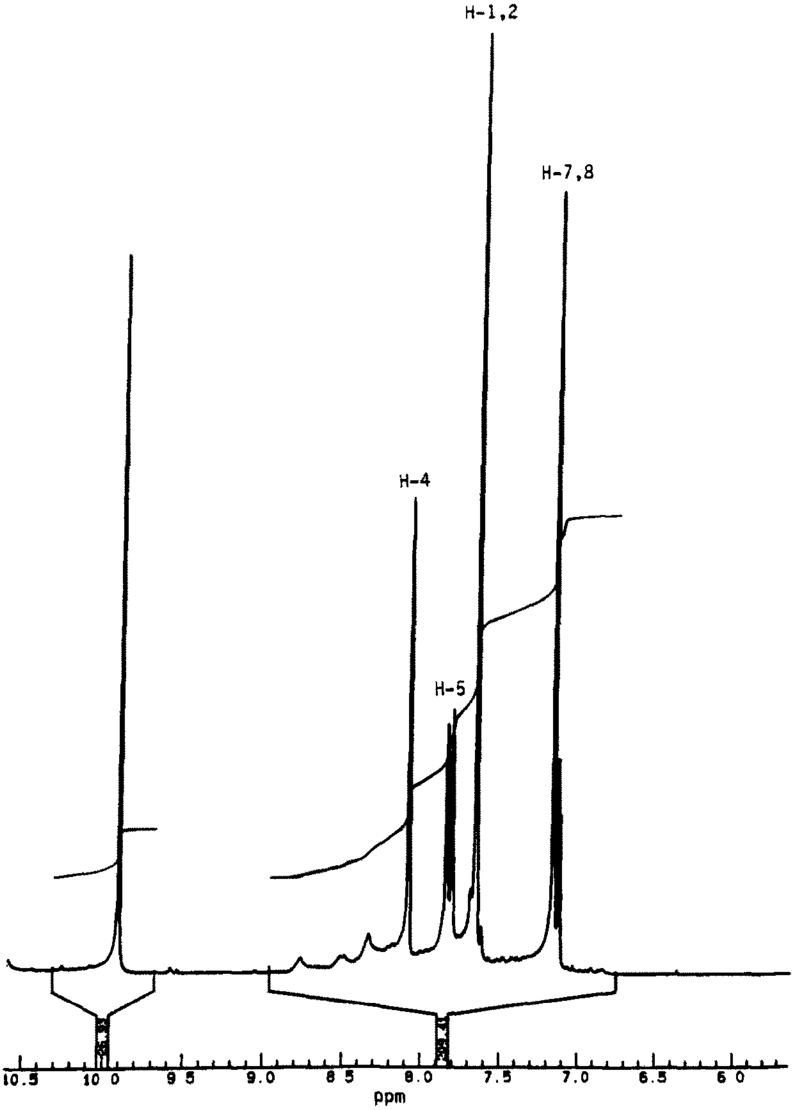

Fig. 5. ^{1}H-NMR spectrum of Schaeffer's acid.

by the results of an examination of the spectra of the hydrochlorides of α- and β-naphthylamine for which we observed a 1 ppm downfield shift in the positions of three of the four signals for the *ortho/para* protons. The exception was the signal for proton H-1 of protonated β-naphthylamine which moves downfield by only 0·62 ppm.

The results of this study indicate that although improved agreement between the calculated and observed δ values for the ring protons of naphthalenesulfonic acids under the influence of two or more substituent groups is possible when using Tables 1–4, contributions to the chemical shifts resulting from other effects (e.g. anisotropy, protonation of NH_2 groups present) also play important roles in determining the observed δ values.

REFERENCES

1. Freeman, H. S., Hsu, W. N., Esancy, J. F. & Esancy, M. K., *Dyes and Pigments*, **9** (1988) 67.
2. Emsley, J. W., Lindon, J. C. & Salman, S. R., *J. Chem. Soc., Perkin Trans 2* (1973) 611.
3. Niwa, J., *Bull. Chem. Soc. Jpn*, **50** (1977) 979.
4. Salman, S. R., *Org. Magn, Reson.*, **19** (1982) 181.
5. Salman, S. R., *Org. Magn. Reson.*, **21** (1983) 672.
6. Salman, S. R., *Org. Magn. Reson.*, **22** (1984) 385.
7. Salman, S. R., *Org. Magn. Reson.*, **23** (1985) 119.