February, 1985] NOTES Bull. Chem. Soc. Jpn., 58, 755—756 (1985)

NMR Spectra of Benzenes Containing Trifluoromethyl Groups

Kensuke TAKAHASHI,* Akihiro YOSHINO, Kenzo HOSOKAWA,† and Hiroshige MURAMATSU†
Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466
†*Government Industrial Research Institute, Nagoya, Hirate-machi, Kita-ku, Nagoya 462*
(Received August 20, 1984)

Synopsis. The ^1H, ^{13}C, and ^{19}F NMR spectra of the nine title compounds were measured. The substituent effect of a trifluoromethyl group were generally additive for the ^1H, ^{13}C, and ^{19}F chemical shifts. The assignment of the ^{13}C signals was assisted by the observed coupling constants between the carbon and the fluorine, which were about 275, 35, and 6 Hz for the ^1J, ^2J, and ^3J values of these compounds.

The NMR spectral data of the title compounds have not yet been systematically reported except for the ^{19}F NMR data.[1] The aim of this study was to obtain the NMR parameters of the title compounds. The values of the coupling constants between the carbon and fluorine, ^1J, ^2J, and ^3J, were also helpful for the assignment of the ^{13}C signal.

Experimental

The ^1H and ^{19}F NMR spectra were observed with a frequency-swept Hitachi R-20B spectrometer, whose center frequencies were 60 and 56.46 MHz, respectively. The ^{13}C NMR spectra were measured using a Varian XL-200 spectrometer with a frequency of 50.3 MHz. The chemical shifts were determined in a chloroform-*d* solution using a small amount of TMS and C_6F_6 as internal references.

The benzenes containing trifluoromethyl group were prepared by the fluorination of the corresponding benzene carboxylic acids by sulfur tetrafluoride in the presence of anhydrous hydrogen fluoride.[2] The compounds studied in this article are summarized (with their reference numbers) in Table 1.

Results and Discussion

Chemical Shifts. The values of the chemical shifts for ^1H, ^{19}F, and ^{13}C nuclei are given in Tables 2 and 3.

The ^1H chemical shifts fall within a range of 7.45—8.34 ppm with respect to TMS. Therefore, the hydrogen atoms in the present compounds are less shielded than those of benzene (7.31 ppm in the $CDCl_3$ solution). The substituent chemical shift (SCS) values of the trifluoromethyl group (S_o, S_m, and S_p) were evalu-

TABLE 1. COMPOUNDS STUDIED

No.	Substituents
1	1-CF_3
2	1,2-$(CF_3)_2$
3	1,3-$(CF_3)_2$
4	1,4-$(CF_3)_2$
5	1,3,5-$(CF_3)_3$
6	1-Br-2,4,6-$(CF_3)_3$
7	1,2,4-$(CF_3)_3$
8	1,2,3-$(CF_3)_3$
9	1,2,4,5-$(CF_3)_4$

TABLE 2. ^1H AND ^{19}F CHEMICAL SHIFTS OF THE COMPOUNDS STUDIED, ppm[a]

No.	δ(1)	δ(2)	δ(3)	δ(4)	δ(5)	δ(6)
1	99.25	7.61	7.45	7.52	7.45	7.61
2	102.57	102.57	7.84	7.67	7.67	7.84
3	98.94	7.89	98.94	7.73	7.59	7.73
4	98.71	7.75	7.75	98.71	7.75	7.75
5	98.76	8.10	98.76	8.10	98.76	8.10
6	—	99.17	8.13	98.61	8.13	99.17
7	102.22[b]	102.24[b]	8.11	98.42	7.98	8.03
8	104.23	107.24	104.23	8.10	7.83	8.10
9	101.95	101.95	8.34	101.95	101.95	8.34

a) ^1H and ^{19}F chemical shifts are found from 7.45 to 8.34 and from 98 to 107 ppm respectively, and referred to TMS and C_6F_6 in the $CDCl_3$ solutions. b) The assignment is tentative.

TABLE 3. ^{13}C CHEMICAL SHIFTS OF THE COMPOUNDS STUDIED, ppm

No.	1-C	2-C	3-C	4-C	5-C	6-C	CF_3	
1	131.28 (32)[a]	125.57	129.16	132.17	129.16	125.57	125.03 (272)	
2	b)	b)	128.46	132.79	132.79	128.46	123.82 (275)	
3	132.63 (34)	123.15	132.63 (34)	129.30	130.26	129.30	124.37 (272)	
4	134.99 (33)	126.58	126.58	134.99 (33)	126.58	126.58	124.36 (272)	
5	134.00 (35)	126.24	134.00 (35)	126.24	134.00 (35)	126.24	123.43 (272)	
6	124.28	135.18 (32)	128.60	131.52 (35)	128.60	135.18 (32)	122.77 (274)(2,6)	123.35 (273)(4)
7	b)	b)	125.83	135.51 (34)	129.77	129.56	122.88 (275)(1,2)	123.41 (273)(4)
8	130.80 (38)	128.28 (38)	130.80 (38)	131.96 (6)	132.70	131.96 (6)	123.12 (274)(1,3)	122.21 (275)(2)
9	132.78 (38)	132.78 (38)	128.32 (4)	132.78 (38)	132.78 (38)	128.32 (4)	121.63 (276)	

a) The values in parentheses are the coupling constants between the carbon and the fluorine in Hz. b) Signals are not confirmed yet.

ated from a comparison of the chemical shifts of **1** with that of benzene. They are 0.30, 0.14, and 0.21 ppm, respectively. An ortho-effect, which is an interaction effect of two adjacent substituents, was also taken into consideration. Thus, S_{abc} is used to express the ortho-effect of the a- and b-positioned substituents to the c-positioned nucleus. Then S_{123} and S_{124} can be estimated to be 0.09 and 0.01 ppm from a comparison of the observed chemical shifts of 1,2-disubstituted compounds (**2**) with its calculated ones based on the additivity. The S_{123}, which is 0.09 ppm, gives an appreciable effect to the chemical shifts while the S_{124} can be neglected. By using these SCS values, the chemical shifts of the tri- and tetra-substituted compounds can be evaluated from the additivity rule to obtain values which are in agreement with the experimental ones within 0.1 ppm. The ^{1}H NMR spectrum of **1** was previously analyzed by Kostelnik *et al.*[3] The chemical shifts of **1** in a $CDCl_3$ solution were evaluated by visual fittings of the observed spectrum to the simulated one where the calculation was performed by changing the chemical-shift values and keeping the spin couplings constant.

The ^{19}F chemical shifts of the trifluoromethyl group were similarly treated. The SCS values (S_o, S_m, and S_p) of the ^{19}F chemical shifts of the substituent CF_3 groups are 3.32, −0.31, and −0.54 ppm, respectively. These were derived from a comparison of the chemical shifts of disubstituted compounds (**2**, **3**, and **4**) with that of **1**. Typical examples of the calculated chemical shifts are given for **7** as follows:

$$\delta(\text{F-1}) = 99.25 + S_0 + S_p = 102.03 \text{ (Exp. 102.22)}$$

$$\delta(\text{F-2}) = 99.25 + S_0 + S_m = 102.26 \text{ (Exp. 102.24)}$$

$$\delta(\text{F-4}) = 99.25 + S_m + S_p = 98.40 \text{ (Exp. 98.42)}$$

The SCS values of the ^{13}C chemical shifts of the trifluoromethyl group were obtained from the ^{13}C chemical shifts of **1** as compared with that of benzene (128.33 ppm in $CDCl_3$). The values are 2.95, −2.76, 0.83, and 3.84 ppm, respectively, for the ipso-, ortho-, meta-, and para-carbons. The observed ^{13}C chemical shifts for tri- and tetrasubstituted compounds are consistent with the calculated ones, which were derived by using the above-mentioned SCS values, within 2 ppm with two exceptions. The large deviations are found to be 4 and 2 ppm for the C_3 of **9** and the C_3 of **2**. When an ortho-effect of S_{123}, which is assumed to be 2.0 ppm, is introduced, the observed ^{13}C chemical shifts become consistent with the calculated ones within 1 ppm.

Coupling Constants. The observed values of the coupling constants between the carbon and fluorine were about 275, 35, and 6 Hz for the ^1J, ^2J, and ^3J (Table 3). The values for **1** were previously reported.[4] These values were useful for the assignment of the ^{13}C signals of the compounds studied. However, the splitting of the ^{13}C signals was disadvantageous for finding the signals. Several signals of **2** and **7** have not yet been confirmed.

The long-range coupling constants between the hydrogen and fluorine are generally small and change in magnitude from compound to compound. An example of the ^{1}H spectra is given in Fig. 1 for **2**. This was analyzed as an AA′BB′ spin system. The analysis shows that the chemical shift between the H_3 and the H_4 is 10.1 Hz at 60 MHz and the J_{34}, J_{35}, J_{36}, and J_{45} values are 8.0, 1.3, 0.5, and 7.6 Hz, respectively. The upfield spectrum is broader than the other half by about 0.2 Hz, as shown in Fig. 1. The origin of the broadening is considered to be the couplings between the hydrogens and fluorines. Therefore it is concluded that $|^5J_{HF}|>|^4J_{HF}|$. This is consistent with the analyzed values of **1**.[3] However, $|^4J_{HH}|>|^5J_{HH}|$ has been found in a similar system of toluene.[6] The ^{1}H signal of **6** appeared as a sextet whose splitting was about 0.7 Hz. The situation is also the same with the ^{1}H signals of **5**. The splitting of about 0.7 Hz is consistent with the couplings reported for **1** and **5**.[3,5]

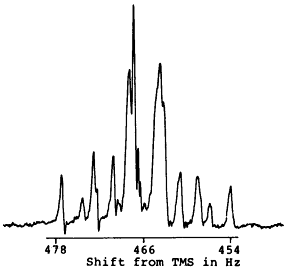

Fig. 1. An observed ^{1}H NMR spectrum of **2** at 60 MHz.

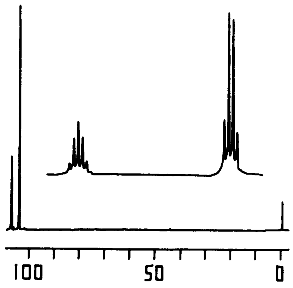

Fig. 2. An observed ^{19}F[^{1}H] NMR spectrum of **8** at 188.22 MHz with an expanded one.

The fluorine–fluorine couplings may be observed for the compounds (**6**, **7**, and **8**), which have unequivalent CF_3 groups. The line breadth of the ^{19}F signal of **6** is about 1.1 Hz. Therefore, the ^6J(F–F) is smaller than 1 Hz. On the other hand, the ^5J(F–F) observed for **8** is about 16 Hz. This is shown in the ^{19}F[^{1}H] spectrum as given in Fig. 2 and consistent with the reported values.[1]

References

1) G. P. Vdovin, Yu. P. Egorov, E. V. Konovalov, A. P. Krasnoshchek, V. G. Lukmanov, E. P. Saenko, L. M. Yagunol'skii, *Teoret. i Eksperim. Khimi.*, **11**, 44 (1975).

2) K. Hosokawa, T. Ueda, and H. Muramatsu, Preprint presented at the 49th National Meeting of the Chemical Society of Japan, Tokyo, April 1984, Vol. **2**, p. 917 (1H16).

3) R. J. Kostelnik, M. P. Williamson, D. E. Wisnosky, and S. M. Castellano, *Can. J. Chem.*, **47**, 3313 (1969).

4) D. Doddrell, M. Barfield, W. Adcock, M. Aurangzeb, and D. Jordan, *J. Chem. Soc., Perkin Trans. 2*, **1976**, 402.

5) J. V. Acrivos, *Mol. Phys.*, **5**, 1 (1962).

6) M. P. Williamson, R. J. Kostelnik, and S. M. Castellano, *J. Chem. Phys.*, **49**, 2218 (1968).