

Multinuclear NMR Study of 1-Fluoro-2,4-Dinitrobenzene

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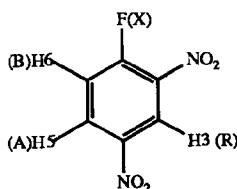
Summary: A multinuclear ^1H , ^{19}F , ^{13}C , ^{14}N and ^{17}O NMR chemical shift study of 1-Fluoro-2,4-Dinitrobenzene has been carried out in detail. The detail ^1H chemical shift study gives 9.061, 8.897, 8.033 ppm for H₃, H₅ and H₆ protons respectively while the ^{19}F chemical shift is -107.876 ppm with respect to CFCl_3 and -60.606 ppm with respect to C_6F_6 as an external standard in the neat liquid at 32°C. The ^{19}F signal is a septet. ^{13}C spectrum is analyzed on the basis of ^{13}C spin-lattice relaxation time T_1 and proton chemical shifts. Only the C5 signal is singlet and the other are doublets. The chemical shifts are 159.2, 137.3, 131.3, 144.1, 122.5 and 120.6 ppm for C₁ to C₆ respectively at 32°C with respect to TMS as an internal standard. The ^{14}N chemical shifts is -16.6 ppm (w.r.t. NO_3^- of NH_4NO_3 used as an external standard) and -18.1 ppm (w.r.t. CH_3NO_2 as an external standard). The ^{17}O Chemical shifts w.r.t. H_2O as the external standard is 607.6 ppm at 95°C.

Introduction

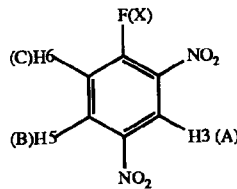
1-Fluoro-2,4-Dinitrobenzene (1) or simply FDNTB is an oily liquid with a melting point of 10-12°C and a boiling point of 296°C with a refractive index of 1.5690 at 20°C [1]. It is used in labeling terminal amino groups of polypeptides and for characterizing amines and amino acids [1]. It is also used in preparing dinitrophenyl derivatives of amino acids and related compounds [2]. This compound is usually prepared by the action the nitric acid on fluorobenzene [2]. This compound has very low solubility in most organic solvents.

NMR studies on this compound are rare because of its solubility. The first proton NMR study was done by Rao and Venkateswarlu [3]. A detailed proton magnetic resonance study of 5 mole solution in acetone and benzene has been done by Schaefer [4] at 60 MHz. Schaefer [3] showed that proton spectrum was ABR part of ABRX spectrum in benzene.

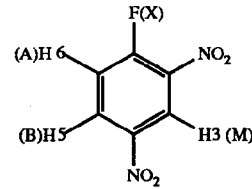
Later on the spectrum of this compound was theoretically and experimentally analyzed by Rao [5]. The convention followed by Rao was ABCX [5,6] to a first order analysis. Later on when second order perturbation method was applied, the convention of ABMX system was followed [5,7]. This compound was further studied by Rao in CDCl_3 and DMSO solution (ca 7% w/v) [8]. The chemical shifts for H₃, H₅ and H₆ were different in both solvents, because of being polar in nature [8]. Substituents effects on the H-F coupling constant was analyzed for this compound by Loemker et al [9]. A heteronuclear H-F NOE in this compound has been determined by Bell and Saunders [10]. These authors suggested that an NOE analysis can be helpful in conformational analysis and spin-rotation effects. A slightly better study on this compound has been done by Hudlicky and Bell [11]. These authors obtained 9.01 ppm, 8.72 ppm and 7.78 ppm (down field from TMS) as chemical shifts



(ABRX)
Schaefer Notation



(ABCX)
1-F-2,4-Dinitrobenzene
(1)



(ABMX)
Rao Notation

H_B or H₆ proton gave triplet, H_A (H₅) gave sextet and H_R (H₃) gave quartet [4]. In acetone the spectrum was ABC part of ABCX spectrum [4].

for H₃, H₅ and H₆ protons. The ^{19}F chemical shifts was 56.2 ppm down field from hexafluorobenzene [11]. The H-F coupling constants for this compound

have been studied by Wray and Lincoln [12]. The effect of tetra-butyl ammonium bromide addition on the chemical shifts of H3, H5 and H6 has been studied by McLaughlin and Reinheimer [13]. There is a decrease in chemical shifts of H3 and an increase in chemical shifts of H5 and H6 protons as the salt concentration increases. A comparatively recent work of Wilshire [14] shows H3 (8.98 ppm) as a quartet, H5 (8.57 ppm), as an octet and H6 (7.55 ppm) as a triplet from TMS.

There has been no work on carbon-13, Nitrogen-14, Nitrogen-15 and Oxygen-17 on this compound. We report here some revised work on ^1H , ^{19}F and new results on ^{13}C , ^{14}N and ^{17}O resonances.

Results and Discussion

The parameters obtained from the multi-nuclear ^1H , ^{13}C , ^{19}F , ^{14}N and ^{17}O are listed in the Table 1 along with the values reported in the previous analysis for ^1H and ^{19}F nuclei. All the three protons show less shielding towards TMS than previous work by Hudlicky and Bell [11] and Wilshire [14] in which both authors used solvents. The similar coupling constant obtained in this study is found to be slightly high which is in good agreement with those obtained by using solvents. The chemical shifts and coupling constant decreased simultaneously with the use of solvent. Well resolved protons spectrum is shown in Fig. 1. The quartet for proton H3 between the nitro groups is well resolved from the octet of proton H5. It is interesting to note that the ranges of the H-F coupling for FDNTB is significantly greater than those for the H-H couplings, especially those for which long range effects are observed. The ^{19}F coupling constants has been found to be consistent with literature values in different solvents, and the chemical shifts reported in table are slightly different from that of Hudlicky and Bell [11]. The difference is about 4.4 ppm. This may be due to the deuterated chloroform which was used as solvents by Hudlicky and Bell [11]. In the present work CFCl_3 and C_6F_6 are used as external references. The reason for CFCl_3 used as internal standard is that it reacts with FDNTB and makes a solid compound. The ^{19}F signal of the compounds is clearly resolved into a septet.

The peak assignment for ^{13}C is shown in Fig. 2. The ppm values are given in Table 1. For help in

Table 1

Nuclei	Chemical Shifts in ppm		Coupling constant	
	Present (neat)	Previous (solutions)	Present	Previous
Proton				
H3	9.061	8.98(a) 9.01(b)	$J_{6,F}$ 9.39 $J_{3,5}$ 2.85	9.2 (a) 2.82(a)
H5	8.897	8.57 (a) 8.72 (b)	$J_{3,6}$ $J_{5,6}$	<0.3(a) 9.2(a)
H6	8.033	7.55 (a) 7.78 (b)		
Carbon-13				
			Relaxation Time (T_1) in sec	
C1	159.246 (Doublet)	3.0	J_{C1-F} - 273.4	
C2	137.293 (Doublet)	14.0		
C3	131.286 (Doublet)	0.9		
C4	144.141 (Doublet)	15.0		
C5	122.530 (Doublet)	1.0		
C6	120.582 (Doublet)	1.1		
Fluorine-19				
	-107.876 (f)		$J_{1,5}$ 3.75 $J_{1,3}$ 6.38	3.72(e) 6.49(e)
	-60.622(d)	56.2(b)	$J_{1,6}$ 10.18	10.19(e)
Nitrogen-14				
	-16.607 (f)			
	-18.111(g)			
Oxygen-17				
	607.638(h)			

a. Ref. 14 sample was used in 0.4M solution in CDCl_3

b. Ref. 11 in CDCl_3

c. CFCl_3 as external standard with external 5 mm tube

d. C_6F_6 as external standard with external 5 mm tube.

Ref. 12.

f. Ammonium nitrate as external standard with external 5 mm tube

g. CH_3NO_2 as external standard with external 5 mm tube

h. H_2O as external standard with external 5 mm tube.

the assignments spin lattice relaxation times were measured using the $(180 - t - 90)_n$ pulse sequence [15]. The C1 peak was assigned on the basis of the relaxation time and J_{CF} reported for fluorobenzene. J_{CF} for fluorobenzene is reported as -245.07 [16] and -244.7 [17]. The T_1 for doublet peaks with $J_{CF} = -273.4$ Hz is nearly same. Hence the C1 assignment is satisfactory. In the off-resonance mode ^{13}C spectrum the C4 and C2 peaks are not split up into doublets. Therefore C4 and C2 belong to carbon at-

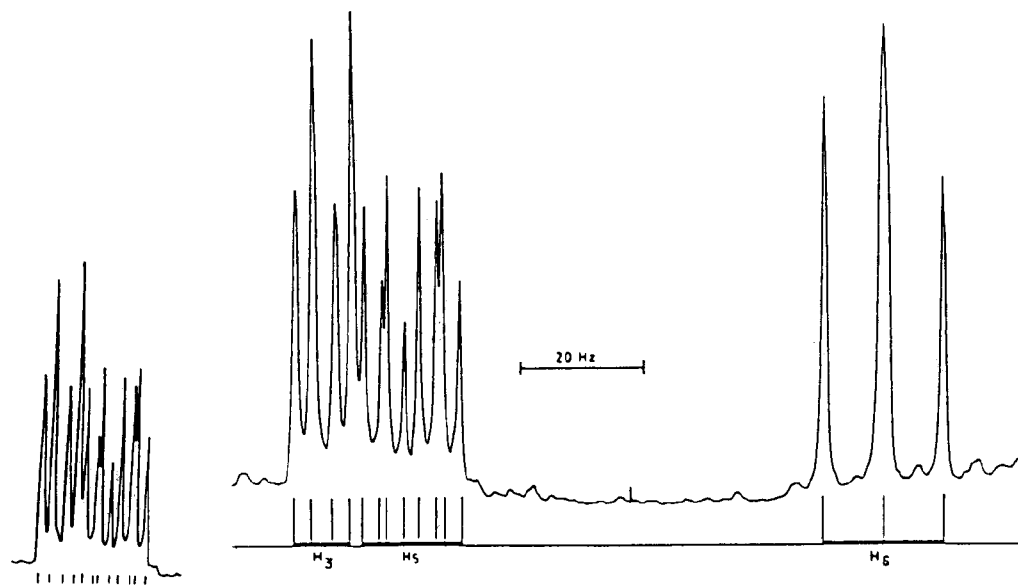


Fig.1: Well resolved proton spectrum of 1-Fluoro-2,4- Dinitrobenzene at 32°C (expanded portion only). The spectrum is ABMX type.

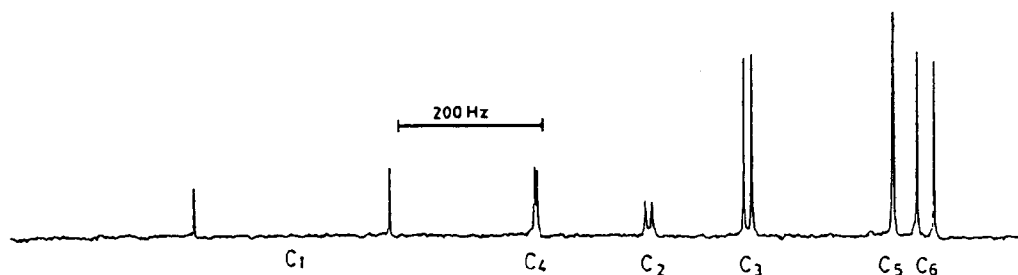


Fig.2: Carbon-13 spectrum of 1-Fluoro-2,4-Dinitrobenzene at 32°C. (Only expanded portion of spectrum is shown).

tached to NO₂ groups. On account of interaction with NO₂ groups the relaxation time of C2 should be less compared to C4 which is true here with C2 carbon. The assignment of C3, C5 and C6 is based on the peak positions of protons. A detailed 2D NMR may resolve the assignment of C3, C5 and C6 carbons.

The ¹⁴N chemical shift lies between - 16.61 (w.r.t. NO₃⁻ of NH₄NO₃ as external standard. The two nitro peaks are not resolvable. Literature values on similar compounds give these values around - 14 ppm w.r.t. CH₃NO₂ [18]. The ¹⁴N spectrum with NH₄NO₃ used as external standard is shown in Fig. 3.

The oxygen-17 spectrum of FDNTB is shown in Fig. 4. The chemical shift is temperature dependent and was not clearly resolvable into two separate

peaks for the oxygen of two nitro groups. The chemical shift is 604.4 ppm at 95°C. Resolution into two peaks may be possible at high temperatures. The reported chemical shift for nitrobenzene is 569 ppm [19]. The present value is near that value and difference is due to the second nitro and fluorine groups attached to this compound. A detailed study on this compound is under way in these laboratories and this may show some more interesting results.

Experimental

All spectra have been recorded on the neat compound with a JEOL FX-90Q FT NMR using external lock. The compound shows poor solubility, hence internal lock has not been used. The resonance frequencies for ¹H, ¹⁹F, ¹³C, ¹⁴N and ¹⁷O were 89.55 MHz, 84.25 MHz, 22.49 MHz, 6.43

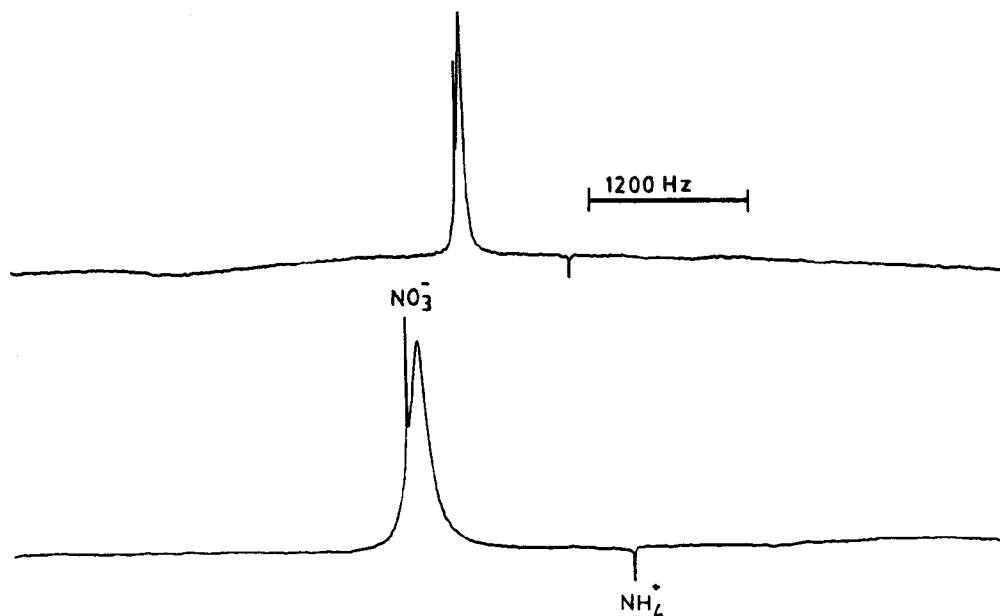


Fig.3: Nitrogen-14 spectrum of 1-Fluoro-2,4-Dinitrobenzene at 32°C using NH_4NO_3 as external standard.

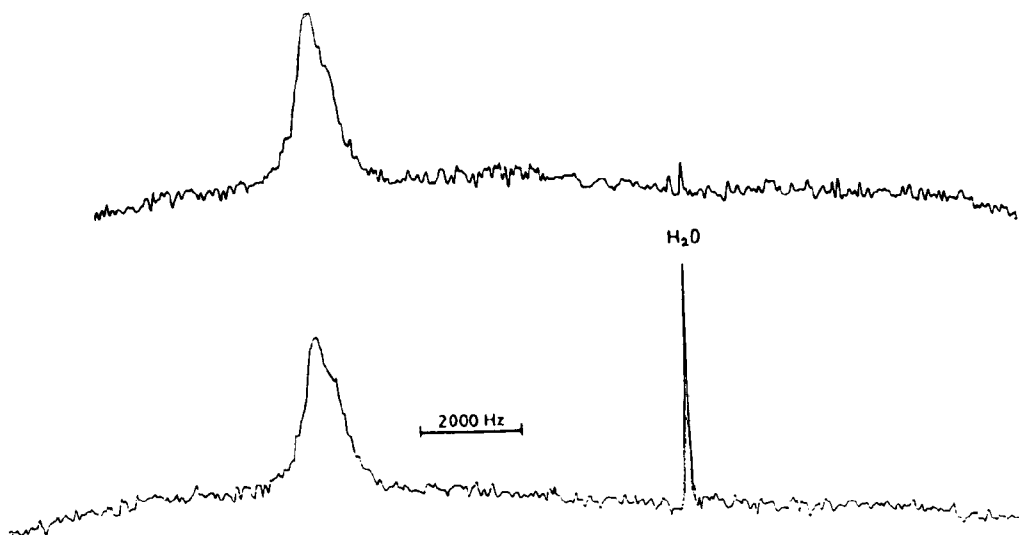


Fig.4: Oxygen-17 spectrum of 1-Fluoro-2,4-Dinitrobenzene at 95°C using H_2O as external standard.

MHz, 12.11 MHz respectively. For ^1H and ^{13}C , TMS was used as internal standard, for ^{19}F , CFCl_3 was used as external standard. For ^{14}N and ^{17}O , CH_3NO_2 and H_2O were used as external standards in 5 mm o.d. tube respectively. The 90° pulse for ^1H , ^{19}F , ^{13}C , ^{14}N and ^{17}O were 30 μs , 25 μs , 47 μs and 23 μs respectively. The spectra for ^{13}C , ^{14}N and ^{17}O were completely proton noise decoupled at 1 kHz. The proton decoupling frequency was 89.55 MHz.

FDNTB was obtained from Merck having purity greater than 99% and was used without further purification. The sample was prepared in 10 mm o.d. NMR tube. All our measurements were made at 32°C. ^{17}O chemical shifts were done at 95°C for getting better results. An extra delay time was used for ^{14}N and ^{17}O to avoid the base line rolling.

Four measurements of chemical shifts were performed for each nuclei. Average value are given

in Table 1. The spin rate of the sample tube was always 15 rps.

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