Carbon-13 NMR assignments for 2,4,7-trinitro-9-fluorenone and 2,4,5,7-tetranitro-9-fluorenone*

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Summary
    Two-dimensional pulse sequences (COSY, HETCOR) are used to
assign the carbon-13 spectra of 2,4,7-trinitro-9-fluorenone and
of 2,4,5,7-tetranitro-9-fluorenone.

Introduction
    One method to investigate charge transfer complexation in
various polymer systems is based on measuring chemical shift
differences in complexed and uncomplexed states. The chemical
shift changes for two main reasons. The first is partial
electron transfer from the highest occupied molecular orbital
of the donor to the lowest unoccupied molecular orbital of the
acceptor. This changes the electron density around the two
groups involved, consequently modifying the shielding of the
magnetic nuclei observed. In one case that does not involve
polymers, this kind of shift has been observed in solid-state
high-resolution carbon-13 NMR (1). The second reason for
chemical shift changes could be the appearance of aromatic
shielding effects due to the spatial proximity of aromatic
donor and acceptor groups. This has been noted for proton
resonances (2) and carbon resonances (3) in some polymer
systems. A combination of both reasons is probably present in
all aromatic charge transfer complexes.
    In the course of investigating charge transfer complexes by
NMR spectroscopy, we started a study of the "classical"
photoconductive complex of poly(N-vinylcarbazole) with 2,4,7-
trinitro-9-fluorenone (2,4,7-TNF) (4). This involved
measurements of chemical shifts in complexed and uncomplexed
states both in solution and in film for the two components of
the complex. At the beginning of our study we noted that there
were no definite assignments for the proton or carbon NMR
spectra of poly(V-vinylcarbazole) and 2,4,7-TNF. In a separate
paper we presented the assignments for poly(N-vinylcarbazole)
(5). Analysis of the NMR spectra of 2,4,7-TNF is the subject of
this paper. Another good acceptor molecule: 2,4,5,7-tetranitro-
9-fluorenone (2,4,5,7-TENF) is also investigated here.

Experimental
    2,4,7-TNF (Polysciences) and 2,4,5,7-TENF (Aldrich) were
separately dissolved in DMSO-d_6 (Merck, Sharp & Dhome) and
their spectra were run on a Bruker AM-400 spectrometer. Edited
carbon spectra and COSY and HETCOR two-dimensional spectra were
obtained using pulse sequences available in the Bruker library.

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*Dedicated to Prof. Dr. H.-J. Cantow on the occasion of his 65th birthday

Results and discussion

The ^{1}H-NMR spectrum of 2,4,7-TNF is presented in Figure 1, together with the two-dimensional COSY spectrum. A COSY spectrum (6) will give the projection of the one-dimensional proton spectrum on the diagonal, while the cross-peaks will indicate scalar coupling between the protons that generate them. The cutoff in Figure 1 was chosen to show only ortho and meta coupled protons. There are three cross-peaks in the figure: one indicates ortho coupling between protons 5 and 6, and the two others show meta couplings (1 and 3; 6 and 8). The final assignments for the proton resonances are given on the one-dimensional spectrum in Figure 1.

The carbon-13 spectrum of 2,4,7-TNF, however, is very complicated, as shown in Figure 2. There are 13 signals corresponding to the 13 carbon atoms in the molecule. The only signal that can be assigned directly, based on its chemical shift, is the carbonyl, at 186.2 ppm. A first help in assigning the carbon spectrum comes from employing a sequence called SEFT (6). Under the conditions of SEFT, methine and methyl carbons present positive peaks, while unprotonated and methylene carbons give negative peaks. The result of the SEFT sequence is that the first five signals (at 118.9; 122.2; 126.0; 127.9 and 130.8 ppm) belong to protonated carbons, while the other 7 at lower field are non-protonated carbons. The effect of aromatic nitro groups on carbon chemical shifts is not additive, thus preventing calculations and predictions of chemical shifts.

The next step in assigning the carbon spectrum is to use a two-dimensional pulse sequence called HETCOR (6). It generates a spectrum having carbon frequency on one dimension and proton frequency on the other. This spectrum is not symmetrical, unlike COSY, and every cross-peak correlates one carbon signal with one proton signal. Figure 3 presents the HETCOR spectrum of the protonated carbons. To obtain all correlations between directly bonded carbons and protons, an average value for C-H one-bond coupling constant of 142 Hz was used as an input in the pulse sequence. The assignment of the protonated carbon signals is obvious in Figure 3, as written on the carbon one-dimensional spectrum. To assign the remaining 7 carbon signals, another HETCOR sequence was employed in which a typical two-bond C-C-H coupling constant was used as an input (7.5 Hz). The result of this HETCOR sequence is presented in Figure 4. The assignments are not so straightforward in this spectrum, because in an extended aromatic system one can find such a value of the coupling constant over more that two bonds sometimes. Starting with the signal at 137.8 ppm, which has no correlation with the proton spectrum, one can assign it to carbon 4a, with no protons over two bonds. The higher field signal (136.0 ppm) is correlated with only one proton (5), which means it has to belong to carbon 5a. The signal at 144.7 has also only one correlation (proton 3), therefore it can be assigned to carbon 4. Carbon 7 (143.2 ppm) can be assigned due to the existence of two correlating protons (8 and 6). Also, carbon 2 (148.9 ppm) is correlated with protons 1 and 3. There are two signals left at this stage, belonging to carbons 8a and 9a, both having three cross-signal with protons. At 149.6 ppm,
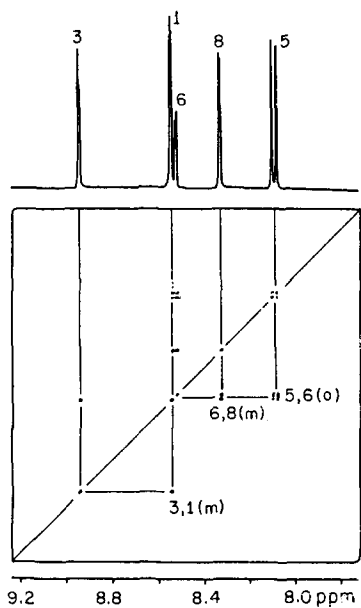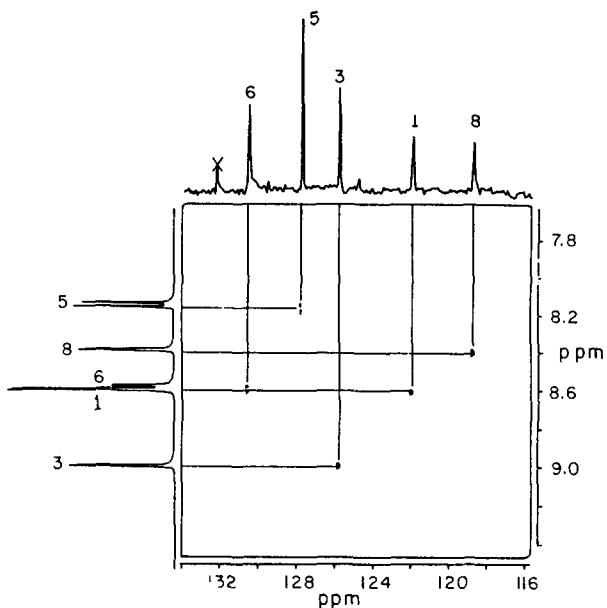
Figure 1: COSY spectrum of 2,4,7-TNF

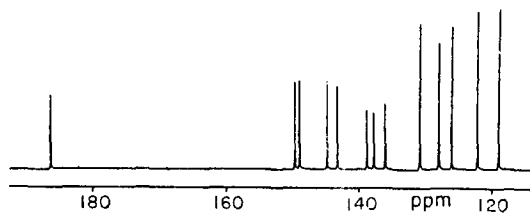Figure 3: HETCOR spectrum of 2,4,7-TNF (J_{C-H} = 142 Hz)
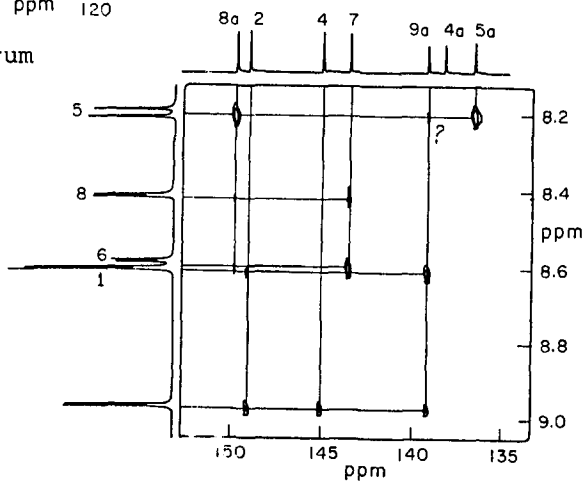
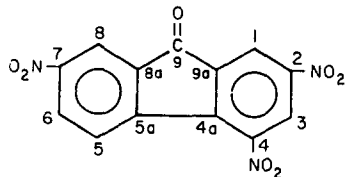Figure 2: Carbon-13 spectrum of 2,4,7-TNF

Figure 4: HETCOR spectrum of 2,4,7-TNF (J_{C-H} = 7.5 Hz)

the carbon correlated with protons 5,6 and 8 has to be 8a, and this leaves 9a at 138.7 ppm correlated with protons 1,3 and 5. It is very difficult, if not impossible, to explain why there seems to be a correlation between 9a and 5, but the presence of this cross-peak which we believe to be an artifact, doesn't seem to interfere with the whole asssignment.

Using the same spectral methods, or even comparing the spectra of 2,4,7-TNF and of 2,4,5,7-TENF, a complete assignment is now possible. Table 1 summarizes the chemical shift data for the proton and carbon spectra of the two compounds presented in this paper.

Table 1
Chemical shifts of 2,4,7-TNF and 2,4,5,7-TENF

Carbon	Proton	2,4,7-TNF		2,4,5,7-TENF	
		C	H	C	H
1	1	122.9	8.59	122.5	8.78
2		148.9		149.7	
3	3	126.0	8.98	125.8	8.97
4		144.7		145.4	
5	5	127.9	8.18		
6	6	130.8	8.61		
7		143.2			
8	8	118.9	8.42		
9		186.2		183.8	
4a		137.8		136.3	
5a		136.0			
8a		149.6			
9a		138.7		139.1	

References
1. W. G. Blann, C. A. Fyfe, J. R. Lyerla and C. S. Yannoni, J. Am. Chem. Soc., 103, 4030 (1981).
2. A. Natansohn, Polymer Bulletin, 9, 67 (1983).
3. A. Natansohn, J. Polym. Sci., Polym. Chem. Ed., 22, 3161 (1984).
4. J. M. Pearson and M. Stolka, "Poly(N-vinylcarbazole)", Gordon and Breach Science Publishers, New York, 85 (1981).
5. A. Natansohn, Polymer Preprints (ACS), 29(1), 162 (1988).
6. R. Benn and H. Gunther, Angew. Chem., Int. Ed. Engl., 22, 350 (1983).