

^{15}N , ^{13}C , AND ^1H NMR SPECTRA OF 1-SUBSTITUTED-2,4,6-TRINITRO-BENZENESAntonín LYČKA^a, Vladimír MACHÁČEK^b and Josef JIRMAN^a^a *Research Institute of Organic Syntheses, 532 18 Pardubice-Rybitví and*^b *Department of Organic Chemistry, Institute of Chemical Technology, 532 10 Pardubice*

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The ^{15}N , ^{13}C , and ^1H NMR spectra of twenty 1-substituted-2,4,6-trinitrobenzenes have been measured in hexadeuteriodimethyl sulphoxide. The $\delta(^{15}\text{N})$ chemical shifts of 2- NO_2 and 6- NO_2 groups are different from those of 4- NO_2 group. Except for 1-(4-subst. phenoxy)derivatives, the $\delta(^{15}\text{N}-4)$ are shifted upfield as compared with $\delta(^{15}\text{N}-2,6)$. The assignment of signals in the ^{15}N NMR spectra was confirmed in three cases by measurements of selectively ^{15}N -labelled compounds.

In the past few years a large number of the $\delta(^{14}\text{N})$ and $\delta(^{15}\text{N})$ chemical shifts of nitrogen atoms in various types of compounds were published^{1,2}. The ^{14}N NMR spectra are usually easily measurable but they have a substantial drawback in that the signals half-widths are large (up to 1 000 Hz). The ^{14}N NMR spectra of nitro compounds were published, too^{3,4}. Although the half-width of signals of ^{14}N atoms of nitro groups is relatively small (from 10^{-1} to 10^1 ppm) as compared with those of some other nitrogen-containing functional groups, the ^{14}N NMR spectroscopy still does not represent a suitable method to study fine structural effects in this case. A much more appropriate in this respect is the ^{15}N NMR spectroscopy, the resonance signals of the ^{15}N nuclei being very narrow. On the other hand, however, long relaxation times and low natural relative abundance of the ^{15}N isotope make the measurements of these spectra very time-consuming^{1,2}. By means of the ^{15}N NMR spectroscopy it was possible, *e.g.*, to describe⁵ the anisochronism of the nitro groups in the Meisenheimer adducts of 1,3,5-trinitrobenzene. The anisochronism found somewhat contradicts the findings^{2,4} that all the three nitro groups of 2,4,6-trinitrotoluene, 2,4,6-trinitrobenzoic acid, and other 1-X-2,4,6-trinitrobenzenes are isochronous according to the ^{14}N NMR spectra.

The aim of this communication was measurement and interpretation of ^{15}N , ^{13}C , and ^1H NMR spectra of 1-X-2,4,6-trinitrobenzenes containing relatively simple X substituents. The ^1H and ^{13}C NMR spectra of 1-X-2,4,6-trinitrobenzenes with more complex substituents are described elsewhere⁶⁻⁹.

EXPERIMENTAL

1,3,5-Trinitrobenzene¹⁰, 2,4,6-trinitrotoluene¹¹, 2,4,6-trinitrobenzoic acid¹², 2,4,6-trinitrobenzoyl chloride¹³, methyl 2,4,6-trinitrobenzoate¹⁴, 2,4,6-trinitroaniline¹⁵, N-methyl-2,4,6-trinitroaniline¹⁶, N,N-dimethyl-2,4,6-trinitroaniline¹⁷, N-cyclohexyl-2,4,6-trinitroaniline¹⁸, 2,4,6-trinitrodiphenylamine¹⁹, 2,4,6-trinitro-4'-methoxydiphenylamine²⁰, 2,4,6-trinitrophenol²¹, 1-methoxy-2,4,6-trinitrobenzene²², 1-phenoxy-2,4,6-trinitrobenzene²³, 1-(4-bromophenoxy)-2,4,6-trinitrobenzene²⁴, 1-(4-nitrophenoxy)-2,4,6-trinitrobenzene²⁵, 2,4,6-trinitrobenzenesulphonic acid²⁶, and 1-chloro-2,4,6-trinitrobenzene²⁷ were prepared by the procedures described in the literature, the melting points of the substances prepared agreed with the literature data.

2,4,6-Trinitro-4'-cyanodiphenylamine was prepared in the same way as 2,4,6-trinitro-4'-methoxydiphenylamine²⁰ from 1-chloro-2,4,6-trinitrobenzene and 4-cyanoaniline. M.p. 137 to 139°C. For C₁₃H₇N₅O₆ (329.2) calculated: 47.43% C, 2.14% H, 21.27% N; found: 47.70% C, 2.28% H, 21.02% N. 1-(4'-Tert-butylphenoxy)-2,4,6-trinitrobenzene was prepared by the same way as 1-phenoxy-2,4,6-trinitrobenzene²³ from 4-tert-butylphenol and 1-chloro-2,4,6-trinitrobenzene. M.p. 126–128°C. For C₁₆H₁₅N₃O₇ (361.3) calculated: 53.19% C, 4.18% H, 11.63% N; found: 53.39% C, 4.05% H, 11.30% N. 2-(¹⁵N-Nitro)-4,6-dinitrophenol was prepared by nitration of 2,4-dinitrophenol with H¹⁵NO₃ (10% ¹⁵N; Isocommerz, Berlin), ref.²⁸. 1-Chloro-(2-¹⁵N-nitro)-4,6-dinitrobenzene and 1-phenoxy-(2-¹⁵N-nitro)-4,6-dinitrobenzene were prepared by the procedures described for the non-labelled compounds.

The ¹⁵N, ¹³C, and ¹H NMR spectra were measured with a JNM FX-100 (JEOL) apparatus at 10.095, 25.047, and 99.602 MHz, respectively, in the pulse mode with the Fourier transformation at 300 K. For the measurements, 10–20% solutions of the substances in hexadeuteriodimethyl sulphoxide were used. The ¹H and ¹³C NMR spectra were measured in the standard way with the digital resolution of 0.24 Hz/point (for ¹H) and 0.61 Hz/point (for ¹³C). The chemical shifts $\delta(^1\text{H})$ and $\delta(^{13}\text{C})$ are related to the solvent signal ($\delta(^1\text{H})$ 2.55 and $\delta(^{13}\text{C})$ 39.6). After the measurements of ¹H and ¹³C NMR spectra, the sample solutions in hexadeuteriodimethyl sulphoxide were treated with c. 10 mg/ml chromium(III) tris-acetylacetonate (Cr(acac)₃), and the ¹⁵N NMR spectra were measured: the spectral width 5 000 Hz, 8 k, 30° pulse, 4 s repetition time, the proton noise decoupling. The chemical shifts were related to external neat nitromethane (25% ¹⁵N, δ 0.0), the negative values denoting the upfield shifts. The $\delta(^{15}\text{N})$ chemical shifts are not corrected for bulk-susceptibility effects.

RESULTS AND DISCUSSION

Table I summarizes the $\delta(^1\text{H})$ chemical shifts of the protons in compounds I–XX. The protons of 2,4,6-trinitrophenyl group form a sharp singlet with the chemical shift from 8.64 (for 2,4,6-trinitrophenol or 2,4,6-trinitrophenoxide ion) to 9.38 (for 1-(4'-nitrophenoxy)-2,4,6-trinitrobenzene). For a series of ten 1-X-2,4,6-trinitrobenzenes containing X substituents with known substituent constants²⁹ σ_{I} , σ_{R} (X = H, CH₃, OCH₃, OC₆H₅, NH₂, NHCH₃, N(CH₃)₂, Cl, COOH, COOCH₃) we found a rough correlation with $\delta(^1\text{H})$ in the form of Eq. (1)

$$\delta(^1\text{H}) = -(1.14 \pm 0.65) \cdot 10^{-1} + (5.4 \pm 2.2) \cdot 10^{-1}\sigma_{\text{I}} + (3.5 \pm 1.3) \cdot 10^{-1}\sigma_{\text{R}}$$

$$(s = 0.1008, r = 0.780, n = 10). \quad (1)$$

The chemical shifts of the other protons (beside the 2,4,6-trinitrophenyl group) were assigned on the basis of the substitution shifts of substituents³⁰.

The $\delta(^{13}\text{C})$ chemical shifts were assigned on the basis of comparison of relative intensities in the decoupled spectra and shape of the multiplets in the proton-coupled spectra or with application of the selective decoupling. The coupling constants $J(^{13}\text{C}, \text{H})$ in the 2,4,6-trinitrophenyl group have the following values: $^2J(\text{C-4}, \text{H-3}) \sim \sim 5 \text{ Hz}$, $^2J(\text{C-2}, \text{H-5}) \doteq ^4J(\text{C-2}, \text{H-5}) \sim 2.5 \text{ Hz}$, $^1J(\text{C-3}, \text{H-3}) > 173 \text{ Hz}$ (e.g., in 2,4,6-trinitroaniline it is $^1J = 174.5 \text{ Hz}$, in 2,4,6-trinitrobenzoyl chloride $^1J = 179.5$). The knowledge of the coupling constants was utilized in analyses of the ^{13}C NMR spectra in such cases when the molecules contained another aromatic ring beside the trinitrophenyl group. The application of the substituent chemical shifts³¹ of the 1-substituent to the assignment of the signals of carbon atoms of trinitrophenyl group was unsuccessful due probably to sterical interactions between the X substituent and nitro groups at positions 2 and 6.

TABLE I

The ^1H chemical shifts of 1-X-2,4,6-trinitrobenzenes measured in hexadeuteriodimethyl sulphoxide at 300 K

X	$\delta(3, 5)$	The other protons (δ)
H	9.22	—
CH ₃	9.05	2.60
OH	8.64	—
OCH ₃	9.11	4.09
OC ₆ H ₅	9.31	7.04—7.57
4-OC ₆ H ₄ NO ₂	9.38	7.41 and 8.34
4-OC ₆ H ₄ Br	9.31	7.13 and 7.62
4-OC ₆ H ₄ C(CH ₃) ₃	9.28	(Ar) 7.01 and 7.41; (CH ₃) 1.30
NH ₂	9.08	—
NHCH ₃	8.96	2.86
N(CH ₃) ₂	8.87	2.94
NHC ₆ H ₁₁	8.94	(CH) 3.17; (CH ₂) 1.1—2.0; (NH) 8.62
NHC ₆ H ₅	8.98	(Ar) 7.11—7.50; (NH) 10.27
4-NHC ₆ H ₄ CN	9.06	(Ar) 7.33 and 7.80; (NH) 10.32
4-NHC ₆ H ₄ OCH ₃	8.95	(Ar) 6.93 and 7.16; (NH) 10.26
COOH	9.19	—
COOCH ₃	9.27	4.06
COCl	9.18	—
Cl	9.24	—
SO ₃ ⁻	8.82	—

TABLE II
The ^{13}C chemical shifts of 1-X-2,4,6-trinitrobenzenes measured in hexadeuteriodimethyl sulphoxide at 300 K

X	$\delta(\text{C-1})$	$\delta(\text{C-2})$	$\delta(\text{C-3})$	$\delta(\text{C-4})$	The other carbon atoms (δ)
H ^a	124.16	148.67	124.16	148.67	—
CH ₃	133.27	151.06	122.70	145.80	(CH ₃) 15.09
OH	159.35	141.85	125.77	127.86	—
OCH ₃	151.01	144.04	124.84	141.65	(OCH ₃) 64.99
OC ₆ H ₅	145.32	144.04	125.62	143.41	(C-1) 156.47; (C-2) 115.87; (C-3) 130.38; (C-4) 124.79
4-OC ₆ H ₄ NO ₂	144.34	144.00	126.11	143.80	(C-1') 161.10; (C-2') 116.61; (C-3') 126.20; (C-4') 144.00
4-OC ₆ H ₄ Br	144.87	143.94	125.81	143.65	(C-1') 156.56; (C-2') 118.02; (C-3') 132.97; (C-4') 116.65
4-OC ₆ H ₄ C. (CH ₃) ₃	145.55	144.09	125.57	143.27	(C-1') 154.33; (C-2') 115.29; (C-3') 126.99; (C-4') 147.16 (CCH ₃) 34.24; (CH ₃) 31.22
NH ₂	143.78	134.34	128.26	132.78	—
NHCH ₃	143.36	136.05	127.08	132.35	(CH ₃) 33.26
N(CH ₃) ₂	142.48	141.22	126.06	135.76	(CH ₃) 42.48
NHC ₆ H ₁₁	140.88	136.73	126.94	133.37	(CH) 55.34; (CH ₂) 32.29(2C); 24.74(1C); 24.00(2C)
NHC ₆ H ₅	138.25	139.07	126.91	135.66	(C-1') 139.22; (C-2') 121.24; (C-3') 129.37; (C-4') 126.21
4-NHC ₆ H ₄ CN	136.10	141.22	126.69	138.25	(C-1') 144.48; (C-2') 119.82; (C-3') 133.71; (C-4') 106.66; (CN) 118.80
4-NHC ₆ H ₄ . .OCH ₃	139.22	138.34	127.04	134.74	(C-1') 131.91; (C-2') 123.62; (C-3') 114.42; (C-4') 157.79; (CH ₃) 55.39
COOH	130.20	147.02	125.18	147.80	(CO) 162.66
COOCH ₃	127.88	146.72	125.65	148.24	(CO) 161.81; (CH ₃) 54.69
COCl	130.11	146.97	125.23	147.80	(CO) 162.47
Cl	125.33	149.31	123.82	146.43	—
SO ₃ ⁻	137.76	149.75	121.63	148.38	—

^a Ref. 5.

The $\delta(\text{C-1})$ chemical shifts (Table II) vary according to the X substituent within the limits from δ 124.16 (for 1,3,5-trinitrobenzene) to δ 159.35 (for 2,4,6-trinitrophenoxide anion), the $\delta(\text{C-2})$ chemical shifts are found in the region δ 134.34–151.06. The $\delta(\text{C-3})$ chemical shift depends relatively little on the nature of the X substituent and has the value of δ 125.76 \pm 3. The lowest $\delta(\text{C-3})$ value was found with 2,4,6-trinitrobenzenesulphonic acid due probably to the strong interactions of bulky $-\text{SO}_3^-$ group with nitro groups. For the series of 1-X-2,4,6-trinitrobenzenes (X = H, CH₃, OCH₃, OC₆H₅, NH₂, NHCH₃, N(CH₃)₂, Cl, COOH, COOCH₃, and SO₃⁻) an only rough correlation was found between $\delta(\text{C-4})$ and σ_I and σ_R constants²⁹ expressed by Eq. (2)

$$\Delta\delta(^{13}\text{C-4}) = -(2.6 \pm 1.9) + (12.2 \pm 7.0)\sigma_I + (22.4 \pm 4.1)\sigma_R$$

$$(s = 3.268, r = 0.888, n = 11).$$
 (2)

TABLE III

The ¹⁵N chemical shifts of 1-X-2,4,6-trinitrobenzenes measured in hexadeuteriodimethyl sulphoxide at 300 K

X	$\delta(\text{N-2,6})$	$\delta(\text{N-4})$	The other nitrogen atoms (δ)
H	-18.7	-18.7	—
CH ₃	-12.7	-18.3	—
OH	-11.8	-14.6	—
OCH ₃	-18.0	-18.9	—
OC ₆ H ₅	-20.2	-19.6	—
4-OC ₆ H ₄ NO ₂	-21.3	-19.8	—
4-OC ₆ H ₄ Br	-20.4	-19.4	—
4-OC ₆ H ₄ C(CH ₃) ₃	-19.8	-19.2	—
NH ₂	-14.4	-16.8	-286.4 (NH ₂)
NHCH ₃	-13.2	-16.7	-287.3 (NH)
N(CH ₃) ₂	-12.6	-17.7	—
NHC ₆ H ₁₁	-12.8	-17.4	-269.7 ^a (NH)
NHC ₆ H ₅	-15.7	-17.7	-276.1 ^a (NH)
4-NHC ₆ H ₄ CN	-15.8	-17.9	-123.3 (CN); -279.7 ^a (NH)
4-NHC ₆ H ₄ OCH ₃	-15.3	-17.4	-274.7 (NH)
COOH	-18.3	-20.0	—
COOCH ₃	-20.4	-20.8	—
COCl	-18.6	-20.1	—
Cl	-19.2	-20.4	—
SO ₃ ⁻	-12.2	-18.9	—

^a The measurement without addition of Cr(acac)₃.

The σ_I parameter is less significant for the correlation than the σ_R parameter.

The ^{15}N NMR spectra of compounds *I*–*XX* (Table III) exhibit always two signals for 2,4,6-trinitrophenyl group. Their relative intensities were approximately 2 : 1 and were assigned to nitrogen atoms of 2- and 6- NO_2 and 4- NO_2 , respectively. The assignment of signals to the nitro groups is based on the presumption that the relaxation times of the two types of nitro groups are not much differing. If this presumption were markedly broken, the assignment could be incorrect. Therefore, we prepared three compounds selectively enriched in the ^{15}N isotope at the position 2, *viz.* 2,4,6-trinitrophenol, 1-chloro-2,4,6-trinitrobenzene, and 1-phenoxy-2,4,6-trinitrobenzene. The measurements of ^{15}N NMR spectra of these compounds confirmed that the relative signal intensities of nitro groups (under the measurement conditions given in Experimental) reflect their abundance.

The difference between ^{15}N chemical shifts of the nitro groups at positions 2 (and/or 6) and position 4 is c. 1–7 ppm. Hence, the ^{14}N NMR spectra could hardly exhibit two separated absorptions with respect to the large half-widths of signals. In all the cases except the 1-phenoxy derivatives the chemical shift of 4- NO_2 group is shifted upfield as compared with 2- NO_2 and 6- NO_2 . The opposite is true of 1-(4'-substituted phenoxy)-2,4,6-trinitrobenzenes, but the difference $\delta(^{15}\text{N-4}) - \delta(^{15}\text{N-2,6})$ is decreased from the value $\Delta\delta = 1.5$ ppm (for the 1-(4-nitrophenoxy)-derivative) to 0.6 ppm (for 1-(4-*tert*-butylphenoxy) derivative). In the case of 1-(4-substituted phenylamino) derivatives the difference $\delta(\text{N-4}) - \delta(\text{N-2,6})$ is independent of the substituent.

The chemical shifts of nitrogen atoms of 4- NO_2 group correlate (in the series with $\text{X} = \text{H}, \text{CH}_3, \text{OCH}_3, \text{OC}_6\text{H}_5, \text{NH}_2, \text{NHCH}_3, \text{N}(\text{CH}_3)_2, \text{Cl}, \text{COOH}, \text{COOCH}_3, \text{and SO}_3^-$) with the substituent constants σ_I and σ_R according to Eq. (3)

$$\Delta\delta(^{15}\text{N}) = (0.37 \pm 0.33) - (6.8 \pm 1.2) \sigma_I - (3.9 \pm 0.7) \sigma_R$$

$$(s = 0.555, r = 0.931, n = 11). \quad (3)$$

Craik *et al.* studied³² chemical shifts $\delta(^{15}\text{N})$ and $\delta(^{17}\text{O})$ of *meta* and *para* substituted nitrobenzenes. For a series of twelve *para* substituted nitrobenzenes they found a correlation between $\delta(^{15}\text{N})$ and σ_I, σ_R in the form of Eq. (4)

$$\Delta\delta(^{15}\text{N}) = -6.0\sigma_I - 1.0\sigma_R^0. \quad (4)$$

In the reaction series of substituted nitrobenzenes³² as well as 1-*X*-2,4,6-trinitrobenzenes, both σ_I and σ_R have negative values. The sensitivity of $\delta(^{15}\text{N})$ to polar effects of the *X* substituent in the series of 1-*X*-2,4,6-trinitrobenzenes is somewhat greater, the resonance contribution of the substituents being especially larger. The greater resonance contribution of the substituents in the series of 1-*X*-2,4,6-trinitro-

benzenes is unexpected, as the 2-NO₂ and 6-NO₂ groups should cause deviation of the X substituent out of the plane of the benzene ring and, hence, lowering of the resonance therewith.

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