^{13}C and ^{15}N Nuclear Magnetic Resonance Spectra of Meisenheimer Complexes of 1,3,5-Trinitrobenzene

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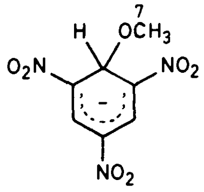
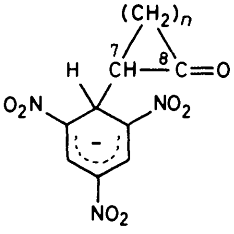
^{13}C and ^{15}N n.m.r. spectra (at the natural abundance level of ^{15}N) have been measured and interpreted for the Meisenheimer complexes (I)—(XII) of 1,3,5-trinitrobenzene (TNB) with anions of cyclopentanone, cyclohexanone, cycloheptanone, acetone, dimethyl malonate, methyl cyanoacetate, methyl acetoacetate, pentane-2,4-dione, 3-methylpentane-2,4-dione, phenol, and methanol. ^{13}C N.m.r. spectra of the corresponding carbon-acids have been measured in [$^2H_6$]DMSO. The complexes derived from ketones and esters are present in the keto-form, that of (IX) exists in the enol form. Nitrogen atoms of nitro-groups at the 2- and 6-positions of complexes derived from carbon-acids of the type CH_2XY are anisochronous as also are C(2) and C(6), C(3) and C(5), and H(3) and H(5).

^1H NUCLEAR magnetic resonance spectroscopy is the simplest method for the structural study of Meisenheimer complexes.[1] During formation of the complexes by reaction of electron-deficient aromatic compounds with nucleophiles the greatest changes in charge distribution take place at 2-, 4-, and 6-positions with respect to the sp^3-carbon atom of the cyclohexadienide anion formed. Therefore ^{13}C n.m.r. spectra have also been used for the study of Meisenheimer complexes.[2,3] Renfrow *et al.*[4] published the ^{13}C chemical shifts of sp^2-carbon atoms of the complexes of 1,3,5-trinitrobenzene (TNB) with the anions of acetone, cyclopentanone, cyclohexanone, cycloheptanone, and pentan-3-one. Further information about charge distribution in the complex molecules can be obtained from ^{15}N n.m.r. spectra.

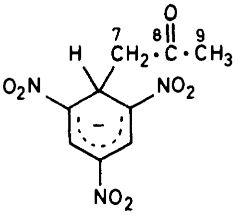
The aim of this paper is to assign all the ^{13}C chemical



(I)



(II) $n = 3$
(III) $n = 4$
(IV) $n = 5$



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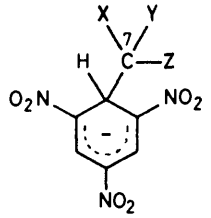
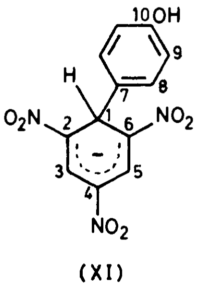
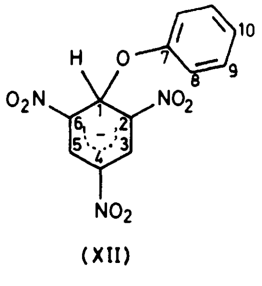


(VI) $X = Y = C(8)OOC(9)H_3, Z = H$
(VII) $X = C(8)OOC(9)H_3, Y = C(10)N, Z = H$
(VIII) $X = C(8)OOC(9)H_3, Y = C(10)OC(11)H_3, Z = H$
(IX) $X \overset{..}{=} Y = C(8)OC(9)H_3, Z = H$
(X) $X = Y = C(8)OC(9)H_3, Z = C(10)H_3$



(XI)



(XII)

shifts and to measure the ^{15}N n.m.r. spectra (at the natural abundance level of ^{15}N) of the complexes described in ref. 4 and to extend the series by examining complexes of TNB with anions of stronger acids than the ketones used so far:[4] the acids are dimethyl malonate, methyl cyanoacetate, methyl acetoacetate, pentane-2,4-dione, 3-methylpentane-2,4-dione, and phenol. The work is complemented by an interpretation of the ^{13}C and ^{15}N n.m.r. spectra of sodium 1-methoxy-2,4,6-trinitrocyclohexadienide.

EXPERIMENTAL

A solution of sodium 1-methoxy-2,4,6-trinitrocyclohexadienide (I) was prepared by addition of 3M-CH_3ONa (0.5 ml) (1.5 mmol) to a solution of TNB (320 mg, 1.5 mmol) in [$^2H_6$]DMSO (1.5 ml).

Sodium salts of complexes (II)—(V) were prepared in the following way. A solution of TNB (0.7 g, 3.3 mmol) in the respective ketone (*ca.* 2 ml) was treated with 1M-CH_3ONa (3 ml, 3 mmol). After several minutes the complex formed was precipitated by addition of dry ether (*ca.* 100 ml). The complex was collected by suction on a sintered glass, washed with dry ether several times, and dried in a vacuum desiccator. The yields are practically quantitative. The structure of the products was verified by ^1H n.m.r. spectra.[4-6]

Sodium salts of complexes (VI)—(VIII) were also prepared by the above procedure. The complex thus prepared (300 mg) was dissolved in [$^2H_6$]DMSO (2 ml), and solid TNB was added gradually until the ^1H n.m.r. spectrum contained signals for the complex only.[7] 'Solutions prepared in this way were used for the measurements of ^{13}C and ^{15}N n.m.r. spectra.

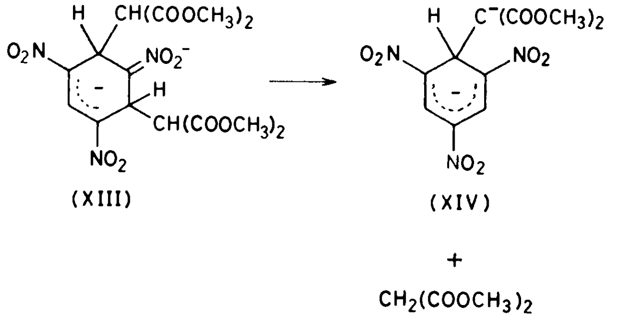
Sodium salts of complexes (VIII)—(X) and (XII) were prepared by mixing solutions of equimolar amounts of TNB and the sodium salt of the respective acid [8] or phenol in [$^2H_6$]DMSO. The structure of the complex (XII) was verified by the ^1H n.m.r. spectrum.[9] Complex (XI) was prepared by the method described in ref. 10.

^{13}C, ^{15}N, and ^1H n.m.r. spectra were measured at 25.047, 10.095, and 99.602 MHz, respectively, using a JEOL JNM-FX 100 apparatus equipped with a multinuclear tunable probe and operating in the pulse mode. For the measurements we used *ca.* 15—20% (w/v) solutions of complexes (II)—(XII) and solutions of the starting carbon-acids of comparable molar concentrations in [$^2H_6$]DMSO. The deuteriated solvent was used as an internal lock. Measurements were carried out in a 10 mm (o.d.) n.m.r. tube at room temperature; the spectra of (VIII)—(X) were also measured at 10 °C. Typical parameters of the ^{13}C n.m.r. spectra measurements were as follows; spectral width 5 000 or 6 000 Hz, 8 k, pulse width 10 μs (23 μs, *ca.* 90°), pulse repetition 3 s, proton noise decoupling. The chemical shifts were referred to the central line of the [$^2H_6$]-DMSO pattern and then transformed to the δ scale.

The samples for the ^{15}N n.m.r. spectra measurements were treated with chromium(III) trisacetylacetonate (*ca.* 10 mg ml^{-1}). Typical conditions of the ^{15}N n.m.r. measurements were as follows: spectral width 4 000 Hz, 8 k, pulse width 15 μs (30 μs, *ca.* 90°), pulse repetition 5 s, proton noise decoupling. The chemical shifts were referred to external neat [11] nitromethane (25% ^{15}N); negative δ values denote upfield shifts.

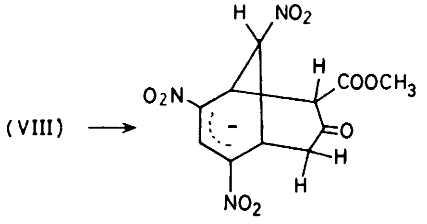
RESULTS AND DISCUSSION

Preparation of the sodium salts of complexes (II)—(V) by reaction of TNB with ketones catalysed by methoxide ion produces pure complexes in almost quantitative yield. Application of the same procedure for preparation of sodium salts of complexes (VI)—(VIII) produces diadducts of type (XIII) on precipitation with ether, and excess of TNB is extracted in ether.[7] The diadduct decomposes into dianion (XIV) and starting acid on dissolution in DMSO.[7]



(XIII) (XIV)

This mixture can be transformed into a monoadduct of type (VI) upon addition of TNB. Besides the reactions described complex (VIII) undergoes slow cyclization to give (XV).[7]



(XV)

Complex (IX) is cyclized so rapidly that it cannot be isolated in the manner described. However, reaction of the sodium salt of pentane-2,4-dione with TNB in DMSO produces complex (IX) as the only product, and its solution is stable even at room temperature for several days, δ_H ([$^2H_6$]DMSO; 10 °C) *ca.* 15 (OH), 8.29 (3- and 5-H), 5.73 (1-H), and 2.12br and 1.86br (CH_3).

Complex (VIII) prepared in both ways had identical ^1H and ^{13}C n.m.r. spectra; however, preparation from the sodium salt of methyl acetoacetate is simpler in this case, δ_H ([$^2H_6$]DMSO; 10 °C) 8.26br (3- and 5-H), 5.41 (1-H), 3.50br (7-H), 3.50 (OCH_3), and 2.28 ($COCH_3$).

Complex (X) was prepared by reaction of the sodium salt of 3-methylpentane-2,4-dione with TNB, δ_H ([$^2H_6$]-DMSO; 10 °C) 8.30 (3- and 5-H), 6.15 (1-H), 2.19 [$(CH_3)_2$], and 0.99 (CH_3). In the ^{13}C n.m.r. spectra of complexes (VIII)—(X) we could identify weak carbon signals of the starting carbon-acids formed probably by hydrolysis of the sodium salts due to the presence of water in [$^2H_6$]DMSO. The assignment of these signals was confirmed by addition of authentic carbon-acids to solutions of the complexes.

TABLE 1

^{13}C Chemical shifts (p.p.m.) for Meisenheimer complexes of 1,3,5-trinitrobenzene with carbanions, CH_3O^-, and $C_6H_5O^-$ in [$^2H_6$]DMSO at 25 °C

Complex	C(1)	C(2) or C(6)	C(3) or C(5)	C(4)	C(7)	C(8)	C(9)	C(10)	C(11)
(I) [a]	69.14	132.40	126.35	121.72	56.66				
(II)	37.44	134.78; 131.98	128.47; 127.30	121.39	53.06	215.05	δ(CH_2)	37.08; 25.97; 20.53	
(III)	35.33	133.85; 131.68	127.88; 127.00	121.56	55.34	207.50	δ(CH_2)	40.42; 28.31; 26.02; 23.10	
(IV)	40.48	132.85; 130.69	128.70; 127.94	121.91	57.91	211.89	δ(CH_2)	42.23; 30.24; 27.55; 25.97; 25.33	
(V)	34.03	133.50	127.71	121.02	47.03	205.81	29.83		
(VI)	38.43	130.30	128.89	122.36	52.17	167.00	52.52		
(VII)	39.83	129.46; 128.82	129.46; 128.82	122.21	42.76	165.15	53.64	116.30	
(VIII) [b]	38.25	131.2; 131.0	128.8; 128.6	122.3	60.43	168.20	52.18	200.32	29.07
(IX) [b]	36.91	134.37	127.71	120.22	112.67	200.31 183.98	25.56 21.11		
(X) [b]	*c*	135.19	125.01	120.98	69.26	206.33	28.19	17.90	
(XI)	41.79	136.34	125.82	120.31	130.50	128.18	115.48	158.62	
(XII)	59.58	135.22	125.04	120.99	158.28	115.78	129.67	118.65	

[a] In 75% [$^2H_6$]DMSO–25% CH_3OH (v/v). [b] At 10 °C. [c] Signal for C(1) probably overlapped by solvent.

TABLE 2

^{13}C Chemical shifts (p.p.m.) for parent carbon-acids, phenol, and 1,3,5-trinitrobenzene in [$^2H_6$]DMSO at 25 °C [a]

Carbon acids	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)	C(13)
Cyclopentanone	38.02	219.85	38.02	22.93	22.93		
Cyclohexanone	41.53	211.25	41.53	26.73	24.51	26.73	
Cycloheptanone	43.52	214.23	43.52	30.12	23.92	23.92	30.12
Acetone	30.83	206.98	30.83				
Dimethyl malonate	40.96	167.29	52.37				
Methyl cyanoacetate	24.50	165.05	53.20	115.29			
Methyl acetoacetate	49.50	168.01	52.00	201.95	30.24		
Pentane-2,4-dione ketone	57.80	203.82	30.88				
Pentane-2,4-dione enol	100.74	191.01	24.68				
3-Methylpentane-2,4-dione ketone	60.31	206.04	29.25	12.28			
3-Methylpentane-2,4-dione enol	104.95	190.65 189.89	23.40	21.06			
Phenol [b]	119.14	129.67	115.44	157.45			
1,3,5-Trinitrobenzene		δ[C(1)] 148.67		δ[C(2)] 124.16			

[a] The numbering of carbon-acids corresponds to that in the complexes. [b] The numbering refers to that in complex (XI).

Complexes (I), (V), (VI), and (IX)—(XII) had ^{13}C n.m.r. spectra containing only three signals for the cyclohexadienide ring, C(2) + C(6), C(3) + C(5), and C(4). These signals were assigned by comparison of the proton decoupled and proton coupled spectra. The two signals for quaternary carbon atoms in the intensity ratio 2 : 1 were assigned to C(2)+C(6) and C(4). C(3) and C(5) and C(2) and C(6) have different chemical shifts in complexes (II)—(IV), (VII), and (VIII) [see ref. 4 for the complexes (II)—(IV)]. C(1) was assigned with the help of selective decoupling from 1-H [δ (1-H) 5.0—6.2; see ref. 1 for the complexes (I)—(V), ref. 7 for (VI) and (VIII), ref. 10 for (XI), ref. 9 for (XII)] and, in the case of complexes (I) and (V) on the basis of its multiplicity in the proton coupled spectrum, also. In complexes (XI) and (XII) the C(1) is the only *sp*^{3} carbon. C(7) in compounds (II)—(IV) and (VI)—(VIII), which exhibit broadened doublets in the proton coupled spectra, were also assigned on the basis of selective decoupling from 7-H. For the assignment of C(7) it was important to find that after transformation of the carbon-acid into the complex δ [C(7)] is shifted by 8.9—18.3 p.p.m. downfield compared with δ [C(7)] in the starting substance (Tables 1—3). The other signals were assigned on the basis of their multiplicities in the proton coupled spectra. Some signals in the spectrum of compound (XI) were assigned on the basis of selective decoupling, δ_C 115.48 [C(9)], [δ_H 6.6 (9-H)], 128.18 [C(8)] [δ_H 7.0 (8-H)], and 125.82 p.p.m. [C(3) and C(5)] [δ_H 8.3 (3- and 5-H)]. The integral intensities of the signals at 136.34 and 130.50 p.p.m. were 2 : 1. The signals for C(8)—C(10) in compound (XII) were

TABLE 3

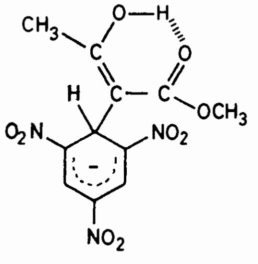
Differences (p.p.m.) in ^{13}C chemical shifts $\Delta_{2,6}$, $\Delta_{3,5}$, Δ_{CO}, and Δ_7 [a]

Complex	$\|\Delta_{2,6}\|$	$\|\Delta_{3,5}\|$	Δ_{CO}	Δ_7
(II)	2.80	1.17	+4.80	15.04
(III)	2.17	0.88	+3.75	13.81
(IV)	2.16	0.76	+2.34	14.39
(V)	0	0	+1.17	16.20
(VI)	0	0	+0.29	11.21
(VII)	0.64	0.64	−0.10	18.26
(VIII)	0.2	0.2	−0.19 [b] +1.63 [c]	10.93
(IX)	0	0	−9.30 +7.03	11.93 [d]
(X)	0	0	−0.29	8.95
(XI)	0	0		11.36

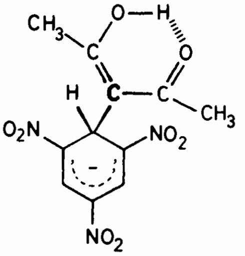
[a] Δ_7 is the difference in δ (^{13}C) of C(7) in the parent carbon-acid and complex. [b] For ester carbonyl. [c] For ketone carbonyl. [d] With respect to the enol form of pentane-2,4-dione.

assigned according to the typical pattern for the proton coupled spectra of monosubstituted benzene derivatives and by comparison with the ^{13}C chemical shifts of phenol. The ^{13}C chemical shifts are given in Table 1.

The Meisenheimer complexes derived from ketones (II)—(V), dimethyl malonate (VI), and methyl cyanoacetate (VII) are present only in the keto-form. This finding agrees with the fact that the starting carbon-acids in DMSO contain such small amounts of the enol form that it cannot be detected by n.m.r. The keto-form of complex (X) is reinforced by the presence of methyl group 10-CH_3. Complex (VIII) derived from methyl acetoacetate also exists in the keto-form, δ_C 60.49 p.p.m. [C(7), ^1J(C–H) 131 Hz], but in the ^{13}C spectrum there are reproducible signals which could be assigned to the enol form (XVI) of complex (VIII) which is present in *ca.* 10% amount. These signals are found in the spectra of the complex (VIII) prepared by the both procedures and also in the presence of excess of TNB or methyl acetoacetate with respect to the complex. The presence of enol form (XVI) in complex (VIII) can be inferred from the results of kinetic studies of the reaction of TNB with methyl acetoacetate.[7] The amount of the enol form of the complex (VIII) is low compared with that of methyl 2-(2,4,6-trinitrophenyl)acetoacetate, which exists exclusively in the enol form.[12]



(XVI)



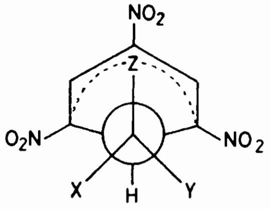
(XVII)

Complex (IX) exists only in enol form (XVII), δ_C 112.67 p.p.m. [C(7), ^1J(C–H) 0 Hz]. Pairs of considerably broadened signals were observed for the carbonyl and methyl groups of this complex at 200.31 and 183.98 and 25.56 and 21.11 p.p.m., respectively.

The complexes of TNB derived from the carbon-acids of the type CHXYZ had a prochiral centre at C(1) and a chiral centre at C(7) (ref. 13). These complexes lack a plane of symmetry which crosses the prochiral centre [13] at C(1), and, therefore, the pairs C(2) and C(6), C(3) and C(5), H(3) and H(5), and N(2) and N(6) are diastereotopic and, hence, potentially anisochronous due to symmetry irrespective of the rotation about the C(1)–C(7) bond being fast or slow on the n.m.r. time scale. The chemical shift non-equivalence was really observed both in the ^1H and ^{13}C n.m.r. spectra of complexes (II)—(IV) (refs. 4 and 6), (VII) (ref. 7), and (VIII) (Table 1). Its formation was explained [4,6] by hindered rotation about the C(1)–C(7) bond.

The magnitude of the chemical shift non-equivalence $\Delta_{2,6}$ and $\Delta_{3,5}$ depends on the different character of the substituents X and Y (Z = H). The greatest differences were found for complexes with cyclic ketones where X is CH_2 and Y is C=O ($\Delta_{2,6} > 2$ p.p.m.), the smallest one for complex (VIII) with methyl acetoacetate (X = $COOCH_3$, Y = $COCH_3$, Z = H, $\Delta_{2,6} < 0.2$ p.p.m.).

The complexes of TNB with anions of carbon-acids of the type CH_2X_2 have prochiral centres at C(1) and C(7) and have a plane of symmetry in one conformation, which plane crosses both the prochiral centres and bisects the angles X–C(7)–X and C(2)–C(1)–C(6). If rotation about the bond C(1)–C(7) is free or if the complexes exist in conformations having a plane of symmetry [(XVIII) and (XIX)], then the respective pairs of protons, carbon atoms, and nitrogen atoms will be enantiotopic.[13]



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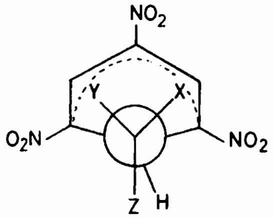
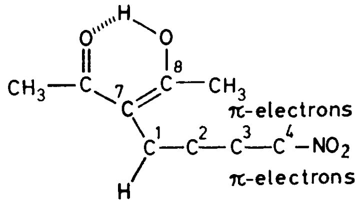


(XIX)

Free rotation about the C(1)–C(7) bond is improbable. From inspection of models it follows that conformation (XIX) is the most probable. The conformation of complex (V) must be different. This complex exists either in conformation (XIX) with X = Y = H and Z = $COCH_3$ [the others have Z = H except for complex (X)] or in conformation (XVIII). The difference in the conformations is obviously due to the relative magnitudes of the protons to the other substituents.

Renfrow *et al.*[4] discussed the Δ_{CO} differences in the chemical shifts of carbonyl carbon of the starting ketone and the complex. However, the chemical shifts δ (CO) of the carbon-acids were not measured in the same solvent as the spectra of complexes. Therefore, we have measured the ^{13}C n.m.r. spectra of the starting acids in [$^2H_6$]DMSO at the same molar concentration as the complexes (Table 2). The values of δ (CO) found by us are considerably different from the values given in the literature.[4] The Δ_{CO} differences (Table 3) found in this way are more significant, and their dependence on the size of the ketone ring is regular in contrast to ref. 4. The value of Δ_{CO} for complex (V) is considerably different from those of complexes (II)—(IV), which supports the suggested different conformation of complex (V). Complex (X) has a still lower Δ_{CO} value of opposite sign to that of the other complexes derived from ketones and an unusual δ (1-H) value (see earlier). This finding indicates that the conformation of this complex is different from the other ketone-derived complexes (Z = CH_3). Renfrow *et al.*[4] supposed that changes in the chemical shifts Δ_{CO} are due to an interaction between the carbonyl and 2-NO_2 groups. If this presumption is correct, then the interaction between the NO_2 and ester carbonyl groups in complexes (VI)—(VIII) is substantially weaker than that in complexes (II)—(IV) because the Δ_{CO} values are smaller by one order of magnitude (Table 3).

The spectrum of complex (IX) (which is present in the enol form) exhibits pairs of broadened signals for carbonyl (δ 200.31 and 183.98) and methyl groups (δ 25.56 and 21.11 p.p.m.) but only three sharp signals in the aromatic region for C(2) + C(6), C(3) + C(5), and C(4). The enol form of pentane-2,4-dione in [$^2H_6$]DMSO has one sharp signal for CH_3 (δ 24.68) and C=O (δ 191.01 p.p.m.). The presence of pairs of signals can be explained in two ways. (i) One of the C=O groups and one of the CH_3 groups is exposed to shielding by the π electrons of cyclohexadienide anion (XX). (ii) The enolic section of the complex (IX) is unsymmetrical, one of the C=O groups having greater C=O character and the other greater C–O character than in the pentane-2,4-dione enol form itself. The same conclusion holds for methyl groups also. The signals are considerably broadened, which means that the rate constant of the proton transfer between the oxygen atoms is substantially smaller than 100 s^{-1}.



(XX)

As the enolic section of complex (IX) is unsymmetrical, the aromatic region of the spectrum should exhibit pairs of signals for C(2) + C(6) and C(3) + C(5). In fact two signals only were found for these carbon atoms, which can be explained in three ways. (i) Complex (IX) in its enol form exists in a conformation with a plane of symmetry [planar enolic section of the complex in a plane perpendicular to that of the cyclohexadienide ring (XX)]. The pairs C(2) + C(6) and C(3) + C(5), therefore, lose their diastereotopic character and are isochronous in the same way as *e.g.* in complex (XI). (ii) The difference in character of the groups $-C(=O)-CH_3$ and $=C(OH)-CH_3$ is too small for chemical shift non-equivalence to be observed. (iii) The rate of proton transfer between –OH and =O is sufficient for the pairs C(2) + C(6) and C(3) + C(5) to collapse, because their chemical shift differences would probably not be greater than in the case of complex (VIII) ($|\Delta_{2,6}| < 0.2$ p.p.m.)

Preparation of the Meisenheimer complexes from TNB and carbon-acids catalysed with sodium methoxide involves sodium 1-methoxy-2,4,6-trinitrocyclohexadienide (I) as an intermediate. Therefore, its ^{13}C n.m.r. spectrum was submitted to analysis and the following coupling constants were found: ^1J[C(1)–H] 128.1, ^1J[C(3)–H] 166.0, ^1J[C(7)–H] 141.6, ^2J[C(4)–H] 3.4, ^3J[C(1)–H(3)] 4.9, ^3J[C(1)–H(7)] 4.9, ^3J[C(3)–H] 3.1 and 4.3, and ^3J[C(7)–H] 5.5 Hz. Values of ^{13}C chemical shifts of complex (I) are given in Table 1.

The samples were treated with chromium(III) trisacetylacetonate (*ca.* 10 mg ml^{-1}) and the ^{15}N n.m.r. spectra were measured at the natural abundance level of ^{15}N. Chromium(III) trisacetylacetonate was added to shorten the relaxation times of ^{15}N which can reach up to several tens of seconds in the case of nitro-compounds.[14] By repeated measurement of the ^{13}C n.m.r. spectrum after measurement of the ^{15}N n.m.r. spectrum it was proved that the studied complexes did not react with chromium(III) trisacetylacetonate. The relaxation reagent influences only slightly the δ (^{15}N) values. The ^{15}N chemical shifts are given in Table 4.

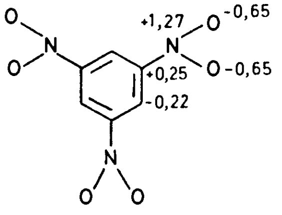
TABLE 4

^{15}N Chemical shifts (p.p.m.) for nitro-groups[a] of Meisenheimer complexes [measured in the presence of chromium(III) trisacetylacetonate, *ca.* 10 mg ml^{-1}] in [$^2H_6$]DMSO at 25 °C and referred to external neat nitromethane

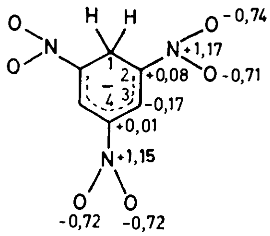
Complex	δ[N(2) or N(6)]	δ[N(4)]
(I) [b]	−7.0	−13.6
(I) [b,c]	−6.8	−13.3
(II)	−7.3; −8.7	−16.1
(III)	−6.1; −7.9	−15.7
(IV)	−7.2; −8.5	−15.6
(V)	−8.9	−16.2
(VI)	−8.8	−15.6

[a] Negative values denote upfield shift. [b] In 75% [$^2H_6$]-DMSO–25% CH_3OH (v/v). [c] Measured without chromium(III) trisacetylacetonate.

The spectra of ' symmetrical ' complexes (I), (V), and (VI) contain only two signals with relative intensity 2 : 1 which were assigned to nitrogen atoms N(2) + N(6) and N(4). The spectra of the ' non-symmetrical ' complexes (II)—(IV) each contain three signals with relative intensity 1 : 1 : 1, which means that the nitrogen atoms N(2) and N(6) are as anisochronous as the carbons and protons in the cyclohexadianide ring in this type of complex. To our knowledge this chemical shift non-equivalence of the nitrogen atoms has been observed for the first time.



(TNB)



(XXI)

The SCF MO method was used [15] for calculations of the π-electron densities at individual atoms of the anion (XXI) formed by addition of hydride anion to 1,3,5-trinitrobenzene. The calculated π-electron densities at the nitrogen atoms of the anion are *ca.* 0.1 higher than in TNB. The calculated difference between electron densities at nitrogen atoms in TNB and anion (XXI) are somewhat higher for N(4) than for N(2). At the same time the measured δ (^{15}N) difference related to TNB is, on the contrary, much greater for N(2) and N(6) than for N(4)-{δ (^{15}N) −18.3 for TNB in [$^2H_6$]DMSO and −18.7 (p.p.m.) for TNB in [$^2H_6$]DMSO in the presence of chromium(III) trisacetylacetonate}. The nitro-groups at the 2- and 6-

positions can be presumed to deviate from coplanarity, which causes a lowering of conjugation with the nucleus and, hence, a shift of δ (^{15}N) to lower field [for aliphatic nitro-compounds it is δ (^{15}N) $>$ 0 p.p.m.[16]]. However, this reason is obviously not responsible for differences between δ [$^{15}N(2,6)$] and δ [$^{15}N(4)$], because in complex (I) which contains coplanar nitro-groups (analogous to 1,1-dimethoxy-2,4,6-trinitrocyclohexadienide[17]) the chemical shift δ [$^{15}N(2,6)$] is still somewhat greater than in complexes with bulky anions of carbon-acids.

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