The influence of *para* substituents on the rotation of aromatic nitro groups

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The steric effect of adjacent methyl and methoxyl groups and the electronic effect of *para* substituents on the rotation of the plane of an aromatic nitro group relative to the plane of the aromatic ring has been investigated by X-ray crystallography. An electron-donating substituent in the *para* position decreases the rotation whilst an electron-withdrawing substituent increases the rotation of the plane of the nitro group relative to the aromatic ring.

The rotation of an aromatic nitro goup about the C–NO$_2$ bond is influenced by adjacent substituents. In a study directed at the development of musk odors in aromatic nitro compounds, De Ridder and Schenk examined[1] the data for compounds from the Cambridge Chrystallographic Data Base. They concluded that the out-of-plane rotation angle caused by one or two adjacent groups was affected by the steric hindrance and electronegativity of *ortho* substituents. In prior work it had been noted[2] that the plane of a nitro group with no adjacent substituents other than hydrogen is twisted by an average of 5° from the plane of the benzene ring whilst in those nitro compounds with one adjacent substituent, it is twisted by 40° and those with two by about 70°. The planes of the nitro groups in the 4- and 6- positions of 1,3-dimethyl-2,4,6-trinitrobenzene are rotated by angles of 35.7° and the one in the 2-position by an angle of 75.2° with respect to the plane of the benzene ring. In *p*-dinitrobenzene the plane of the nitro groups is rotated by an angle of 10.2° with respect to the benzene ring[3] whilst in 1,2-dinitrobenzene[4] the angles between the planes of the nitro group and the aromatic ring are 41.5 and 41.4°.

A nitro group has a powerful electron-withdrawing effect on an aromatic ring arising from the combination of a dominant inductive effect and lesser resonance effects.[5] The rotation of the nitro group has the effect of diminishing conjugation between the nitro group and the aromatic ring. However, a computational examination[6] of the effect of rotating the nitro group of nitrobenzene though 90° has led to the suggestion that there is only a small degree of conjugation between the nitro group and the aromatic ring.

With the advent of rapid X-ray crystallographic analysis, it has become possible to examine a series of substituted polynitrobenzenes to assess the effect of substituents on the rotation of nitro groups. In the crystalline state intermolecular forces and crystal packing may affect the rotation and as noted previously,[1] this caveat may affect conclusions.

As a starting point for this study, we examined the crystal structure of 3,5-dimethylnitrobenzene (Fig. 1) and calculated the one-of-plane rotation angle of the nitro group relative to the aromatic ring. This was chosen because it was one of the simplest crystalline mononitrobenzenes without a *para* substituent. The unhindered nitro group is essentially co-planar (7°) with aromatic ring and the C–N bond length is 1.474(2) Å (see Tables 1 and 2). The combined influence of an adjacent methyl group and a second nitro group on the rotation of nitro groups may be seen in the series of dinitrotoluenes: 2,3-dinitro-, 2,4-dinitro and 3,4-dinitrotoluene (Figs 2–4). The angles between the planes of the nitro groups and the aromatic ring are given in Table 1. The combined influence of methyl group and an adjacent nitro group is to produce a rotation of 85° of the 2-nitro group in 2,3-dinitrotoluene. In the case of a 3, 4-dinitrotoluene, unlike 1,2-dinitrobenzene, the two nitro groups are unequally rotated relative to the aromatic ring. In particular
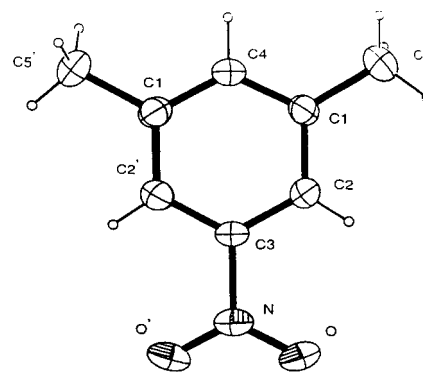

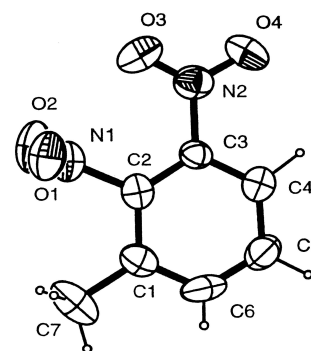**Fig. 1**   X-Ray crystal structure of 3,5-dimethylnitrobenzene.

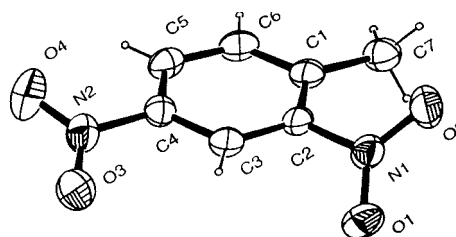**Fig. 2**   X-Ray crystal structure of 2,3-dinitrotoluene.

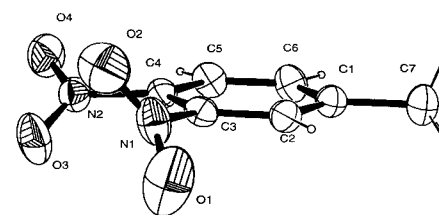**Fig. 3**   X-Ray crystal structure of 2,4-dinitrotoluene.

Fig. 4   X-Ray crystal structure of 3,4-dinitrotoluene.

* Correspondence.

Table 1 The angle (°)(ESD *ca.* 0.2°) between the plane of the nitro group and the phenyl ring

		A	B
3,5-Dimethylnitrobenzene		7	
2,3-Dinitrotoluene	2-Nitro group	85	85
	3-Nitro group	4	5
2,4-Dinitrotoluene	2-Nitro group	45	28
	4-Nitro group	16	4
3,4-Dinitrotoluene	3-Nitro group	52	55
	4-Nitro group	30	28
2,3,4-Trinitrotoluene	2-Nitro group	58	
	3-Nitro group	64	
	4-Nitro group	27	
2,3-Dinitroanisole	2-Nitro group	74	
	3-Nitro group	28	
3-Methyl-4-nitroanisole	4-Nitro group	11	10
1,2-Dimethoxy-4,5-dinitrobenzene	4-Nitro group	2	
	5-Nitro group	31	
Methyl 3,4-dinitrobenzoate	3-Nitro group	31	
	4-Nitro group	68	

In some crystals there were two independent molecules in the unit cell. A = molecule 1, B = molecule 2.

Table 2 C–N Bond lengths (Å) to the nitro groups

		A	B
3,5-Dimethylnitrobenzene		1.474(2)	
2,3-Dinitrotoluene	2-Nitro group	1.480(6)	1.482(6)
	3-Nitro group	1.466(6)	1.461(7)
2,4-Dinitrotoluene	2-Nitro group	1.471(3)	1.474(3)
	4-Nitro group	1.469(2)	1.469(3)
3,4-Dinitrotoluene	3-Nitro group	1.466(3)	1.475(3)
	4-Nitro group	1.459(3)	1.464(3)
2,3,4-Trinitrotoluene	2-Nitro group	1.473(3)	
	3-Nitro group	1.482(3)	
	4-Nitro group	1.469(3)	
2,3-Dinitroanisole	2-Nitro group	1.4690(19)	
	3-Nitro group	1.464(2)	
3-Methyl-4-nitroanisole	4-Nitro group	1.459(4)	1.462(5)
1,2-Dimethoxy-4,5-dinitrobenzene	4-Nitro group	1.460(4)	
	5-Nitro group	1.475(3)	
Methyl 3,4-dinitrobenzoate	3-Nitro group	1.470(2)	
	4-Nitro group	1.470(2)	

the nitro group that is *para* to the methyl group has rotated less than that of the 3-nitro group. This effect is also noticeable in 2,3,4-trinitrotoluene (Fig. 5) in which the 4-nitro group is rotated less than the 41° of 1,2-dinitrobenzene.

A methoxyl group can have a similar steric effect. Comparison of 2,3-dinitroanisole (Fig. 6) with 2,3-dinitrotoluene (Fig. 2) reveals the steric effect of the methoxyl group on the rotation of the 2-nitro group.

The electronic contribution of a substituent on the rotation of a nitro group is revealed by an examination of 3-methyl-4-nitroanisole (Fig. 7). Although the 3-methyl group would be expected to produce a rotation of *ca* 30–40°, the rotation in the presence of the *p*-methoxyl group is only 11°. However, the C(1)–O(1) distance [1.365(4) Å] is only marginally shorter than the average (1.378 Å) for this bond length. The effect is more pronounced with 1,2-dimethoxy-4,5-dinitrobenzene (Fig. 8) when compared to 1,2-dinitrobenzene and 3,4-dinitrotoluene. The 4-nitro group is almost in the plane (2°) of the aromatic ring and the other is at an angle of 30°. The carbon–oxygen bond lengths are also shorter [1.349(3) and 1.354(3) Å] An electron-donating substituent reduces the tendency of a nitro group to rotate. On the other hand an electron-withdrawing substituent has the reverse effect. The 4-nitro group of methyl 3,4-dinitrobenzoate (Fig. 9) is rotated to a greater extent (*ca* 30°) than the 4-nitro group of 3,4-dinitrotoluene.

In most cases, the C–N bond lengths between the aromatic ring and the nitro groups are close to 1.47 Å (see Table 2). There is a slight tendency for those nitro groups that are closer to co-planarity with the aromatic ring to have a slighty shorter C-N bond length and slightly longer N–O bond lengths compared to those that are rotated. As has been observed previously,[1] the C–C(N)–C bond angles involving the nitro group are also on average slightly greater that 120° whilst those bearing the methyl or methoxyl substituent are slightly less (Table 3) possibly reflecting a difference in the 's' character of the bonding.

Experimental
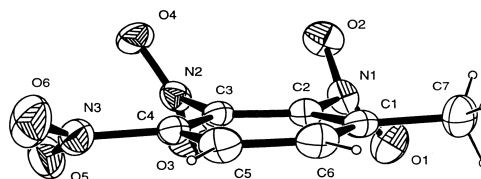
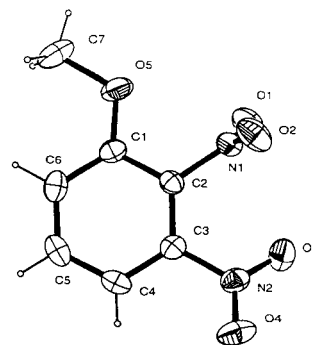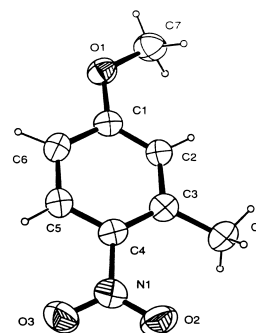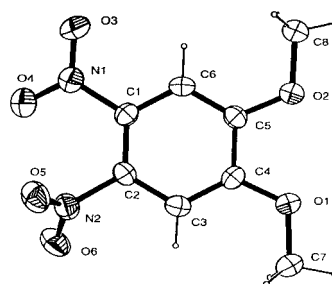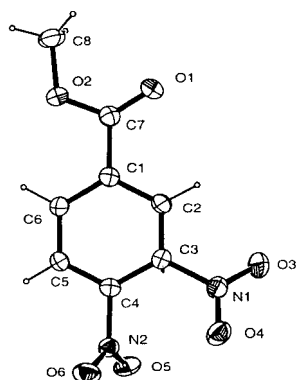**Fig. 5**   X-Ray crystal structure of 2,3,4-trinitrotoluene.

Fig. 6   X-Ray crystal structure of 2,3-dinitroanisole.

Fig. 7   X-Ray crystal structure 3-methyl-4-nitroanisole.

Fig. 8   X-Ray crystal structure 1,2-dimethoxy-3,4-dinitrobenzene.

Table 3   Comparison of aromatic C–C–C bond angles(°)(ESD)

	C–C(N)–C		C–C(Me)–C	
	A	B	A	B
2,3-Dinitrotoluene				
2-Nitro group	122.3(5)	122.5(4)	115.5(5)	116.3(5)
3-Nitro group	120.2(5)	120.9(4)		
2,4-Dinitrotoluene				
2-Nitro group	124.35(18)	123.65(18)	115.54(18)	115.48(18)
4-Nitro group	122.08(19)	122.00(19)		
3,4-Dinitrotoluene				
3-Nitro group	120.78(19)	120.8(2)	118.4(2)	118.1(2)
4-Nitro group	119.39(19)	119.9(2)		
2,3,4-Trinitrotoluene				
2-Nitro group	122.9(2)		115.9(2)	
3-Nitro group	118.9(2)			
2-Nitro group	119.9(2)			

Fig. 9   X-Ray crystal structure of methyl 3,4-dinitrotoluene.

5-dinitrobenzene which was prepared by the nitration of 1,2-dimethoxybenzene.[7] All samples were recrystallised prior to the X-ray structure determination.

X-Ray crystallographical data and structure determination
(a) 3,5-dimethylnitrobenzene $C_8H_9NO_2$, M_r 151.16, trigonal, space group P3(1)21 (No. 152), $a = 8.2069(2)$, $b = 8.2069(2)$, $c = 10.0112(3)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 583.95(3)$ Å^3, $Z = 3$, $D_{calc} = 1.29$ g cm^{-3}, $\mu = 0.09$ mm^{-1}, $F(000) = 240$. Data were collected using a crystal of size $0.3 \times 0.3 \times 0.3$ mm^3 on a KappaCCD diffractometer. A total of 7011 reflections were collected for $4.97 < \theta < 27.48°$ and $-10 \leq h \leq 10$, $-8 \leq k \leq 10$, $-12 \leq l \leq 12$. There were 885 independent reflections and 850 reflections with $I > 2\sigma(I)$ were used in the refinement. No absorption correction was applied. The structure was solved by direct methods and refined by SHELXL-97. The drawings used ORTEP-3 for Windows. The final R indices were $[I>2\sigma\ (I)]$ $R_1 = 0.045$, $wR_2 = 0.130$ and (all data) $R_1 = 0.046$ and $wR_2 = 0.132$. The largest difference peak and hole was 0.29 and -0.33 e Å^{-3}.
(b) 2,3-dinitrotoluene $C_7H_6N_2O_4$, M_r 182.14, monoclinic, space group Pc (No.7), $a = 7.6169(17)$, $b = 14.669(3)$, $c = 7.8126(13)$ Å, $\alpha = \gamma = 90°$, $\beta = 108.094(16)°$, $V = 829.8(3)$ Å^3, $Z = 4$, $D_{calc} = 1.46$ g cm^{-3}, $\mu = 0.12$ mm^{-1}, $F(000) = 376$. Data were collected using a crystal of size $0.3 \times 0.3 \times 0.3$ mm^3 on a KappaCCD diffractmeter. A total of 3843 reflections were collected for $3.90 < \theta < 22.10°$ and $-8 \leq h \leq 8$, $-15 \leq k \leq 15$, $-8 \leq l \leq 8$. There were 1980 independent reflections and 1628 reflections with $I > 2\sigma(I)$ were used in the refinement. No absorption correction was applied. The structure was solved by direct methods and refined by SHELXL-97. The drawings used ORTEP-3 for Wndows. The final R indices were $[I>2\sigma(I)]$ $R_1 = 0.059$, $wR_2 = 0.130$ and (all data) $R_1 = 0.076$ and $wR_2 = 0.140$. The largest difference peak hole was 0.19 and -0.19 e Å^{-3}. There were two independent molecules of essentially the same geometry.
(c) 3,4-dinitrotoluene $C_7H_6N_2O_4$, M_r 182.14, monoclinic, space group P2$_1$/c (No.14), $a = 7.7258(2)$, $b = 5.8211(5)$, $c = 13.1097(5)$ Å, $\alpha = \gamma = 90°$, $\beta = 92.83°$, $V = 1600.45(9)$ Å^3, $Z = 8$, $D_{calc} = 1.51$ g cm^{-3}, $\mu = 0.13$ mm^{-1}, $F(000) = 752$. Data were collected using a crystal of size $0.2 \times 0.15 \times 0.10$ mm^3 on a KappaCCD diffractometer. A total of 11573 reflections were collected for $3.95 < \theta < 25.00°$ and $-8 \leq h \leq 8$, $-18 \leq k \leq 18$, $-15 \leq l \leq 15$. There were 2735 independent

reflections and 1942 reflections with $I > 2\sigma(I)$ were used in the refinement. No absorption correction was applied. The structure was solved by direct methods and refined by SHELXL-97. The drawings used ORTEP-3 for Windows. The final R indices were $[I>2\sigma(I)]$ $R_1 = 0.049$, $wR_2 = 0.119$ and (all data) $R_1 = 0.076$ and $wR_2 = 0.134$. The largest difference peak and hole was 0.26 and -0.28 e Å^{-3}.
(d) 2,3,4-trinitrotoluene $C_7H_5N_3O_6$, M_r 227.14, triclinic space group P$\bar{1}$ (No.2), $a = 7.7097(4)$, $b = 8.2267(6)$, $c = 8.6514(7)$ Å, $\alpha = 87.143(3)°$, $\beta = 64.730(3)°$, $\gamma = 66.439(3)°$, $V = 449.99(5)$ Å^3, $Z = 2$, $D_{calc} = 1.68$ g cm^{-3}, $\mu = 0.15$ mm^{-1}, $F(000) = 232$. Data were collected using a crystal of size $0.20 \times 0.10 \times 0.05$ mm^3 on a KappaCCD diffractometer. A total of 3505 reflections were collected for $4.06 < \theta < 22.96°$ and $-8 \leq h \leq 8$, $-8 \leq k \leq 9$, $-9 \leq l \leq 9$. There were 1238 independent reflections and 891 reflections with $I > 2\sigma(I)$ were used in the refinement. No absorption correction was applied. The structure was solved by direct methods and refined using SHELXL-97. The drawings used ORTEP-3 for Windows. The final R indices were $[I>2\sigma(I)]$ $R_1 = 0.038$, $wR_2 = 0.085$ and (all data) $R_1 = 0.063$ and $wR_2 = 0.095$. The largest difference peak and hole was 0.19 and -0.22 e Å^{-3}.
(e) 2,3-dinitroanisole $C_7H_6N_2O_5$, M_r 198.14, triclinic space group P$\bar{1}$ (No.2), $a = 7.4114(3)$, $b = 7.8862(3)$, $c = 8.1835(3)$ Å, $\alpha = 114.543(2)°$, $\beta = 101.604(2)°$, $\gamma = 94.008(2)°$, $V = 419.83(3)$ Å^3, $Z = 2$, $D_{calc} = 1.57$ g cm^{-3}, $\mu = 0.14$ mm^{-1}, $F(000) = 204$. Data were collected using a crystal of size $0.20 \times 0.20 \times 0.15$ mm^3 on a KappaCCD diffractometer. A total of 4272 reflections were collected for $4.00 < \theta < 24.82°$ and $-8 \leq h \leq 8$, $-8 \leq k \leq 9$, $-8 \leq l \leq 9$. There were 1414 independent reflections and 1162 reflections with $I > 2\sigma(I)$ were used in the refinement. No absorption correction was applied. The structure was solved by direct methods and refined using SHELXL-97. The drawings used ORTEP-3 for Windows. The final R indices were $[I>2\sigma(I)]$ $R_1 = 0.035$, $wR_2 = 0.086$ and (all data) $R_1 = 0.046$ and $wR_2 = 0.092$. The largest difference peak and hole was 0.17 and -0.16 e Å^{-3}.
(f) 3-methyl-4-nitroanisole $C_8H_9NO_3$, M_r 167.16, triclinic space group P$\bar{1}$ (No.2), $a = 7.1047(9)$, $b = 10.3834(14)$, $c = 10.8386(16)$ Å, $\alpha = 95.878(7)°$, $\beta = 92.896(7)°$, $\gamma = 95.312(5)°$, $V = 790.50(19)$ Å^3, $Z = 4$, $D_{calc} = 1.41$ g cm^{-3}, $\mu = 0.11$ mm^{-1}, $F(000) = 352$. Data were collected using a crystal of size $0.20 \times 0.10 \times 0.10$ mm^3 on a KappaCCD diffractometer. A total of 5640 reflections were collected for $3.82 < \theta < 23.00°$ and $-7 \leq h \leq 7$, $-11 \leq k \leq 10$, $-11 \leq l \leq 11$. There were 2162 independent reflections and 1569 reflections with $I > 2\sigma(I)$ were used in the refinement. No absorption correction was applied. The structure was solved by direct methods and refined using SHELXL-97. The drawings used ORTEP-3 for Windows. The final R indices were $[I>2\sigma(I)]$ $R_1 = 0.063$, $wR_2 = 0.158$ and (all data) $R_1 = 0.090$ and $wR_2 = 0.175$. The largest differencee peak and hole was 0.28 and -0.23 e Å^{-3}.
(g) 1,2-dimethoxy-4,5-dinitrobenzene $C_8H_8N_2O_6$, M_r 228.16, monoclinic space group P2$_1$/n (No.14), $a = 4.4627(5)$, $b = 26.082(3)$, $c = 8.4270(8)$ Å, $\alpha = \gamma = 90°$, $\beta = 101.670(6)°$, $V = 960.6(2)$ Å^3, $Z = 4$, $D_{calc} = 1.58$ g cm^{-3}, $\mu = 0.14$ mm^{-1}, $F(000) = 472$. Data were collected using a crystal of size $0.30 \times 0.10 \times 0.05$ mm^3 on a KappaCCD diffractometer. A total of 3795 reflections were collected for $3.88 < \theta < 21.93°$ and $-4 \leq h \leq 4$, $-27 \leq k \leq 27$, $-8 \leq l \leq 8$. There were 1161 independent reflections and 928 reflections with $I > 2\sigma(I)$ were used in the refinement. Absorption correction was applied using MULTISCAN. The structure was solved by direct methods and refined using SHELXL-97. The drawings used ORTEP-3 for Windows. The final R indices were $[I>2\sigma(I)]$ $R_1 = 0.044$, $wR_2 = 0.095$ and (all data) $R_1 = 0.060$ and $wR_2 = 0.102$. The largest differencee peak and hole was 0.14 and -0.21 e Å^{-3}.

(h) methyl 3,4-dinitrobenzoate $C_8H_6N_2O_6$, M_r 226.15, triclinic space group $P\bar{1}$ (No.2), $a = 7.8023(3)$, $b = 7.9080(3)$, $c = 8.3277(3)$ Å, $\alpha = 63.015(2)°$, $\beta = 87.666(2)°$, $\gamma = 88.142(2)°$ $V = 457.45(3)$ Å^3, $Z = 2$, D_{calc}=1.64 g cm^{-3}, $\mu = 0.14$ mm^{-1}, $F(000)$= 232. Data were collected using a crystal of size $0.4 \times 0.4 \times 0.3$ mm^3 on a KappaCCD diffractometer. A total of 4708 reflections were collected for $3.74 < \theta < 24.96°$ and $-7 \leq h \leq 9$, $-9 \leq k \leq 9$, $-9 \leq l \leq 9$. There were 1563 independent reflections and 1404 reflections with $I > 2\sigma(I)$ were used in the refinement. No absorption correction was applied. The structure was solved by direct methods and refined using SHELXL-97. The drawings used ORTEP-3 for Windows. The final R indices were [$I>2\sigma(I)$] $R_1 =$ 0.039, $wR_2 = 0.100$ and (all data) $R_1 = 0.044$ and $wR_2 = 0.103$. The largest differencee peak and hole was 0.199 and -0.217 e Å^{-3}.

The crystallographic data and the structure determination for 2,4-dinitrotoluene have been described elsewhere.[8]

The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 255845 – 225852)

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