N-Methyl-2,6-dinitro-4-trifluoromethylaniline

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Abstract. $C_8H_6N_3O_4F_3$, $M_r = 265 \cdot 15$, monoclinic, $P2_1/c$, $a = 8 \cdot 929$ (1), $b = 17 \cdot 672$ (2), $c = 15 \cdot 566$ (2) Å, $\beta = 123 \cdot 17$ (1)°, $Z = 8$, $D_c = 1 \cdot 71$ g cm^{-3}, $R = 0 \cdot 067$ for 1807 observed reflections. The two independent molecules are similar in conformation, each having one nitro group essentially planar with the aromatic ring (dihedral angles of 2 and 6°) and the other considerably out of the aromatic plane (dihedral angles of approximately 50°).

Introduction. Because of the current need to understand more fully the action of many herbicides and insecticides in terms of both environmental and biological effects, and since diverse variations of activity for related series of compounds cannot be satisfactorily explained by the usual stereo-electronic arguments, more complete knowledge of the molecular structures is necessary. Falling into this category of compounds are N-aliphatic derivatives of 2,6-dinitroaniline in which the correlation between the type and extent of N-substitution with the electron-withdrawing ability of the substituents does not follow traditional lines (Giam, 1970). We have undertaken single-crystal X-ray diffraction studies of some of these compounds (Towns, Brown & Giam, 1974, 1975) and report in this paper the third such structure (Fig. 1a).

A yellow wedge-shaped crystal, $0 \cdot 50 \times 0 \cdot 40 \times 0 \cdot 25$ mm, was mounted with the reciprocal-lattice point $10\bar{1}$ on the φ axis of a Picker FACS-1 fully automated four-circle diffractometer. The reciprocal lattice revealed $2/m$ symmetry with systematic extinctions $k = 2n + 1$ for $0k0$ and $l = 2n + 1$ for $h0l$, uniquely characterizing the space group as $P2_1/c$. Cell constants were determined by measuring the $K\alpha_1 - K\alpha_2$ doublet of Cu radiation for 12 reflections with

$2\theta > 60°$. Intensity data were collected to $2\theta = 125°$ (Ni-filtered, Cu $K\bar{\alpha}$ radiation) with a fixed $\theta : 2\theta$ rate of $2°$ min^{-1}. A variable scan width, $2 \cdot 0 + 0 \cdot 3 \tan \theta$, and 10 s background measurements at the extremities of the scan were used to measure 3642 independent reflections. Reference reflections, measured periodically, showed a random variation of approximately 2% and no systematic decay. The intensities were corrected for absorption as a function of φ (maximum transmission ratio $1 \cdot 11 : 1 \cdot 10$, linear $\mu = 15 \cdot 7$ cm^{-1} for Cu $K\bar{\alpha}$), for Lorentz and polarization in the usual manner, and then converted to structure amplitudes. 1807 reflections for which $|F| > 6\sigma(F)$ (chosen to eliminate all systematic extinctions) were considered statistically significant and were used for the structure determination and refinement.

Normalized structure magnitudes, E's, were calculated with a K curve, and the phases of 196 of these with $E > 1 \cdot 7$ were determined with multiple tangent refinement. One of the several E maps calculated contained structural fragments of the two molecules which were used as a partial trial structure to locate the remaining atoms. Once all 36 non-hydrogen atoms were located, the structure was refined by block-diagonal least squares [using $1/\sigma^2$ weights and minimizing $\Sigma w(|F_o| - |F_c|)^2$]. Scattering factors for all non-hydrogen atoms are from Cromer & Waber (1965) and those for H are from Stewart, Davidson & Simpson (1965). A difference electron density map showed peaks of approximately $0 \cdot 3$ e Å^{-3} which corresponded to the expected positions of the 12 H atoms. These were then included in structure factor calculations with fixed isotropic temperature factors of $4 \cdot 0$ Å^2 but not refined. The final R values ($\Sigma w |F_o| - |F_c| / \Sigma w |F_o|$) are $R = 0 \cdot 067$ ($w = 1 \cdot 0$) and $R_w = 0 \cdot 081$ ($w = 1/\sigma^2$). The final fractional coordinates and anisotropic thermal parameters for the non-hydrogen atoms are given in Table 1 and the coordinates of the H atoms in Table 2.*
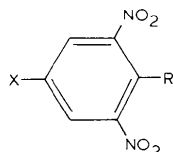

Fig. 1. Molecular formula. (a) R = NHCH$_3$, X = CF$_3$, this study; (b) R = N(C$_3$H$_7$)$_2$, X = Cl, Towns, Brown & Giam (1974); (c) R = NHC(CH$_3$)$_3$, X = CF$_3$, Towns, Brown & Giam (1975).

Discussion. The overall conformations of the two unique molecules (Fig. 2) are identical. For each molecule one of the two nitro groups is very nearly coplanar with the aromatic ring (dihedral angles of 6 and 2°, respectively, for molecules 1 and 2) and the other group is twisted 50 and 51° from this same plane. A similar conformation is observed in the *tert*-butyl derivative,

Fig. 1(*b*) (Towns *et al.*, 1975), and, as is observed in this study, the twisted nitro group is on the same side of the ring as the aliphatic moiety and bent away from this chain to reduce steric interaction. In contrast to the *tert*-butyl derivatives, in which the CF_3-group is skewed with respect to the ring, both molecules in this study show a preferential orientation of one C—F bond to be

Table 1. *Final fractional coordinates and anisotropic temperature factors*

Estimated standard deviations are in parentheses. Temperature factors are of the form:
$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \times 10^{-4}].\ \text{Coordinates are} \times 10^4.$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(11)	3020 (8)	1281 (3)	2828 (5)	134 (13)	21 (2)	44 (4)	5 (8)	50 (13)	1 (5)
C(12)	3175 (8)	1637 (3)	2044 (4)	145 (14)	25 (2)	33 (4)	0 (9)	37 (12)	−8 (5)
C(13)	3324 (8)	2404 (3)	1989 (4)	156 (14)	26 (2)	38 (4)	−9 (9)	44 (13)	2 (5)
C(14)	3294 (9)	2893 (3)	2676 (5)	168 (15)	21 (2)	40 (4)	−1 (9)	36 (13)	0 (5)
C(15)	3223 (8)	2582 (3)	3473 (5)	142 (14)	24 (2)	45 (4)	10 (9)	38 (13)	−5 (5)
C(16)	3166 (8)	1808 (3)	3569 (4)	107 (12)	23 (2)	29 (3)	−2 (8)	26 (11)	−1 (5)
N(11)	3235 (8)	1196 (3)	1290 (4)	219 (14)	26 (2)	50 (4)	−8 (8)	67 (13)	−6 (4)
O(11)	3152 (8)	1511 (3)	568 (4)	399 (16)	36 (2)	70 (4)	−13 (9)	139 (14)	−2 (4)
O(12)	3255 (8)	493 (3)	1349 (4)	428 (17)	26 (2)	74 (4)	−7 (9)	129 (14)	−10 (4)
C(17)	3354 (11)	3721 (4)	2568 (6)	308 (21)	23 (2)	60 (5)	1 (12)	75 (19)	−2 (6)
F(11)	3704 (10)	4091 (3)	3364 (4)	887 (27)	25 (2)	108 (5)	−5 (11)	203 (20)	−11 (4)
F(12)	1926 (9)	3991 (3)	1800 (5)	533 (21)	29 (2)	159 (7)	19 (10)	−51 (19)	23 (6)
F(13)	4599 (9)	3934 (3)	2425 (6)	651 (25)	33 (2)	250 (8)	−28 (11)	299 (26)	0 (6)
N(12)	3405 (7)	1558 (3)	4527 (4)	198 (13)	28 (2)	43 (3)	−21 (8)	57 (12)	−7 (4)
O(13)	4561 (7)	1077 (3)	5015 (3)	229 (12)	37 (2)	49 (3)	8 (8)	57 (11)	11 (4)
O(14)	2501 (7)	1871 (3)	4794 (4)	257 (12)	41 (2)	70 (4)	−3 (8)	107 (12)	−10 (4)
N(13)	2654 (8)	554 (3)	2808 (4)	237 (14)	20 (2)	66 (4)	2 (8)	87 (14)	0 (4)
C(18)	2037 (10)	162 (4)	3366 (5)	269 (19)	27 (3)	69 (5)	−12 (11)	99 (18)	−3 (6)
C(21)	1678 (8)	8374 (3)	−33 (4)	128 (13)	23 (2)	36 (4)	−2 (8)	33 (12)	0 (5)
C(22)	1261 (8)	8131 (3)	712 (4)	169 (14)	20 (2)	41 (4)	−9 (9)	55 (13)	−6 (5)
C(23)	1335 (8)	7381 (3)	982 (4)	136 (13)	23 (2)	41 (4)	−7 (9)	40 (13)	−2 (5)
C(24)	1799 (8)	6824 (3)	536 (5)	143 (14)	18 (2)	46 (4)	−3 (8)	45 (13)	−3 (5)
C(25)	2136 (8)	7018 (3)	−190 (4)	116 (13)	23 (2)	44 (4)	−6 (8)	46 (13)	−6 (5)
C(26)	2010 (8)	7760 (3)	−484 (4)	127 (13)	25 (2)	34 (4)	−3 (9)	44 (12)	−4 (5)
N(21)	798 (8)	8655 (3)	1226 (4)	237 (14)	24 (2)	61 (4)	−8 (8)	86 (14)	−11 (4)
O(21)	509 (8)	8420 (3)	1856 (4)	468 (19)	33 (2)	94 (5)	9 (9)	183 (17)	0 (5)
O(22)	641 (7)	9334 (2)	998 (4)	351 (15)	22 (2)	102 (4)	3 (8)	145 (15)	−5 (4)
C(27)	1865 (11)	6016 (4)	852 (6)	285 (20)	24 (2)	85 (6)	−10 (11)	120 (20)	−4 (6)
F(21)	2540 (8)	5559 (2)	491 (5)	748 (23)	23 (2)	238 (7)	37 (10)	376 (24)	14 (6)
F(22)	333 (6)	5749 (2)	598 (4)	264 (12)	31 (2)	171 (6)	−13 (7)	134 (14)	15 (5)
F(23)	2869 (7)	5929 (3)	1878 (4)	465 (17)	38 (2)	77 (4)	−12 (9)	60 (13)	15 (4)
N(22)	2143 (7)	7886 (3)	−1365 (4)	167 (12)	30 (2)	44 (3)	0 (8)	61 (11)	−5 (4)
O(23)	3383 (7)	7596 (3)	−1357 (4)	231 (12)	55 (2)	69 (4)	24 (9)	96 (12)	14 (5)
O(24)	931 (6)	8239 (3)	−2091 (3)	210 (11)	40 (2)	43 (3)	18 (8)	57 (10)	1 (4)
N(23)	1711 (7)	9105 (3)	−249 (4)	219 (13)	20 (2)	53 (4)	−10 (8)	73 (12)	0 (4)
C(28)	2674 (11)	9428 (4)	−677 (5)	302 (21)	23 (2)	67 (5)	−5 (11)	94 (19)	5 (6)

Table 2. *Hydrogen coordinates* ($\times 10^4$)

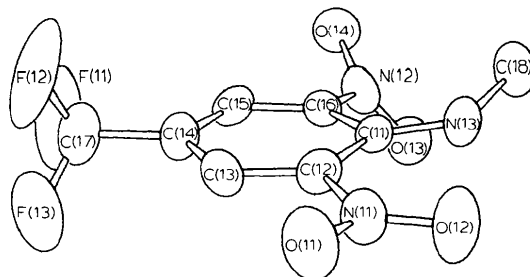|	x	y	z
H(C13)	3381	2627	1410
H(C15)	3171	2932	3976
H(N13)	3845	296	3038
H(C18)	1220	−265	2948
H(C18)′	1350	524	3531
H(C18)″	3061	−41	4028
H(C23)	1049	7252	2502
H(C25)	2458	6610	−523
H(N23)	2262	9372	431
H(C28)	1766	9588	−1406
H(C28)′	3458	9026	−694
H(C28)″	3407	9864	−267

Fig. 2. Conformation of the molecule with the atom-numbering scheme for molecule 1 indicated. Note that one nitro group is twisted out of the aromatic ring plane and away from the methyl substituent at N(13).

Table 3. *Bond distances and angles*

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
C(j1)-C(j2)	1·446 (9)Å	1·464 (10)Å	C(j2)-C(j1)-C(j6)	112·8 (5)°	112·6 (5)°
C(j1)-C(j6)	1·433 (9)	1·409 (9)	C(j1)-C(j2)-C(j3)	122·8 (6)	122·1 (6)
C(j2)-C(j3)	1·370 (9)	1·382 (8)	C(j1)-C(j6)-C(j5)	123·4 (6)	124·7 (6)
C(j5)-C(j6)	1·381 (8)	1·375 (8)	C(j2)-C(j3)-C(j4)	121·7 (6)	120·3 (6)
C(j3)-C(j4)	1·385 (9)	1·392 (9)	C(j6)-C(j5)-C(j4)	120·7 (6)	120·1 (6)
C(j4)-C(j5)	1·391 (10)	1·363 (10)	C(j3)-C(j4)-C(j5)	118·2 (6)	119·9 (5)
C(j4)-C(j7)	1·479 (9)	1·502 (9)	C(j2)-C(j1)-N(j3)	122·7 (6)	122·1 (6)
C(j1)-N(j3)	1·322 (8)	1·340 (8)	C(j6)-C(j1)-N(j3)	124·3 (6)	125·3 (6)
C(j2)-N(j1)	1·436 (9)	1·425 (9)	C(j1)-C(j2)-N(j1)	121·1 (5)	122·2 (5)
C(j6)-N(j2)	1·455 (9)	1·456 (9)	C(j3)-C(j2)-N(j1)	116·0 (6)	115·7 (6)
N(j3)-C(j8)	1·438 (10)	1·462 (11)	C(j1)-C(j6)-N(j2)	121·7 (5)	120·0 (5)
N(j1)-O(j1)	1·221 (8)	1·216 (9)	C(j5)-C(j6)-N(j2)	114·7 (5)	115·2 (5)
N(j1)-O(j2)	1·244 (7)	1·238 (7)	C(j3)-C(j4)-C(j7)	120·8 (7)	118·5 (6)
N(j2)-O(j3)	1·228 (7)	1·215 (8)	C(j5)-C(j4)-C(j7)	121·0 (6)	121·6 (6)
N(j2)-O(j4)	1·223 (8)	1·226 (7)	C(j1)-N(j3)-C(j8)	128·8 (6)	126·2 (6)
C(j7)-F(j1)	1·280 (10)	1·305 (10)	C(j2)-N(j1)-O(j1)	119·6 (5)	119·1 (5)
C(j7)-F(j2)	1·271 (11)	1·288 (10)	C(j2)-N(j1)-O(j2)	119·2 (6)	119·4 (6)
C(j7)-F(j3)	1·303 (12)	1·346 (10)	C(j6)-N(j2)-O(j3)	116·5 (6)	118·0 (5)
C(j4)-C(j7)-F(j1)	113·6 (7)°	113·0 (7)°	C(j6)-N(j2)-O(j4)	117·2 (5)	117·4 (6)
C(j4)-C(j7)-F(j2)	113·5 (7)	113·8 (6)	F(j1)-C(j7)-F(j2)	107·9 (7)	107·7 (6)
C(j4)-C(j7)-F(j3)	113·1 (7)	112·3 (6)	F(j1)-C(j7)-F(j3)	103·8 (7)	106·0 (7)
O(j1)-N(j1)-O(j2)	121·0 (6)	121·5 (6)	F(j2)-C(j7)-F(j3)	104·0 (7)	103·2 (7)
O(j3)-N(j2)-O(j4)	126·2 (6)	124·4 (6)			

nearly coplanar with the ring [dihedral angles of 13·3 and 9·9° about the C(j4)—C(j7) bonds] and on the same side as the twisted nitro group.

The intramolecular bond distances and angles (Table 3) are internally consistent within two estimated standard deviations and agree with the two previous studies, Fig. 1(b) and (c). The seemingly large angles C(j1)—N(j3)—C(j8), 128·8 and 126·2°, are slightly smaller than that found in the *tert*-butyl derivative, 129·6°, but significantly larger than those observed in the diethyl derivative, 121·1 and 120·0°.

By comparing the three structures of this series studied to date, one can conclude that the addition of a single aliphatic chain to the N will cause one nitro group to twist out of plane, but leave the other group in plane, and that the addition of a second chain will cause both groups to twist out of plane. This twisting will disrupt the electron-withdrawing ability of the nitro groups and therefore change the net charge of the *meta* carbons [C(j3) and C(j5)] which will in turn effect the herbicidal activity at these sites. The effect of the aliphatic substituent is not a direct one, in terms of electron-withdrawing ability at C(j1), but is indirect on the nitro groups.

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