Tableau 3. *Distances interatomiques* K–S *pour les atomes de potassium* K(1), K(2) *et* K(3)
du motif K_3AsS_4, *avec leurs écarts-type*

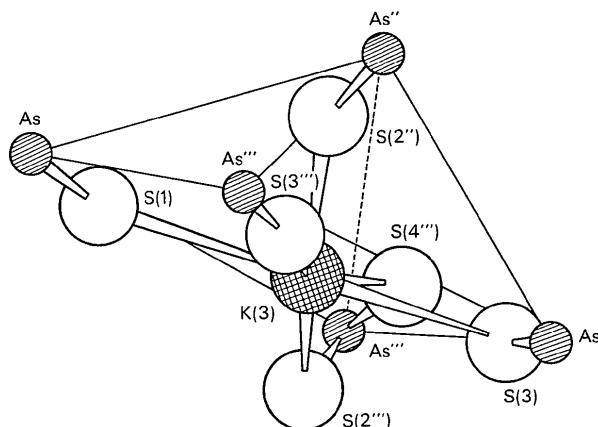| K(1)–S(1)	3,30 (2) Å	K(2)–S(1)	3,14 (2) Å	K(3)–S(1)	3,12 (1) Å
K(1)–S(1‴)	3,29 (2)	K(2)–S(1‴)	3,04 (2)	K(3)–S(2″)	3,53 (3)
K(1)–S(2)	3,23 (2)	K(2)–S(2′)	3,40 (2)	K(3)–S(2‴)	3,38 (2)
K(1)–S(3″)	3,20 (2)	K(2)–S(2″)	3,33 (3)	K(3)–S(3)	3,30 (1)
K(1)–S(4′)	3,35 (2)	K(2)–S(3″)	3,43 (2)	K(3)–S(3‴)	3,32 (1)
K(1)–S(4″)	3,21 (2)	K(2)–S(3‴)	3,38 (2)	K(3)–S(4‴)	3,24 (2)
K(1)–S(3‴)	3,63 (2)*	K(2)–S(4)	3,43 (2)		

Fig. 3. Environnement du potassium K(3).

suivant une pyramide à base quasi carrée (Fig. 3). Parmi ces tétraèdres, seul D″ fournit deux atomes de soufre S(2‴) et S(4‴), les quatre autres en fournissent chacun un.

Il existe donc trois types d'environnement pour le potassium.

Nous remercions M A. Mazurier dont le concours a été très précieux pour la partie expérimentale.

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The Crystal Structure of *N*-methyl-2-(*N*-methylamino)-3,5-dinitrobenzamide

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The crystal and molecular structure of *N*-methyl-2-(*N*-methylamino)-3,5-dinitrobenzamide, $C_9H_{10}N_4O_5$, at $-160°C$ has been determined by X-ray diffraction techniques. The crystal is orthorhombic with $a = 9.248$ (8), $b = 11.792$ (10) and $c = 9.807$ (7) Å. The space group is $Pna2_1$ with 4 molecules per unit cell. The structure was solved by direct methods and refined by least-squares methods to a final R index of 0·045 for the 1154 reflections measured by the moving-crystal moving-counter method. The benzene ring is distorted to a boat shape, probably due to overcrowding. An intramolecular N–H···O(nitro) and an intermolecular C–H(ring)···O(nitro) hydrogen bond appear to exist in the crystal.

Introduction

Structural investigation of a large number of aromatic nitro compounds (Holden & Dickinson, 1969, and the references therein) has indicated that the orientation of the nitro group is probably governed by a balance between steric interactions with *ortho* substituents and the mesomeric interaction with the aromatic nucleus.

However, formation of an intramolecular N–H$\cdots$O (nitro) hydrogen bond can bring about near planarity of the nitro group with the phenyl ring (Holden & Dickinson, 1969; Holden 1967; Cady & Larson, 1965). In *N*-methyl-2-(*N*-methylamino)-3,5-dinitrobenzamide the possibility of an intramolecular N–H$\cdots$O(nitro) or O(amido) hydrogen bond exists. We have undertaken this structural study to investigate the preferred mode of hydrogen bonding in the title compound.

Experimental

Suitable single crystals of the compound were kindly supplied by Professor R. Y. Moir. Preliminary precession photographs indicated that the crystals are orthorhombic with systematic absences of *h0l* for $h = 2n + 1$ and *0kl* for $k + l = 2n + 1$. Probable space groups are *Pna2$_1$* or *Pnam*. Intensity statistics indicated the space group to be *Pna2$_1$* which was confirmed by the structure analysis.

A small crystal approximately $0.2 \times 0.2 \times 0.2$ mm was used to measure the cell constants and the intensities at $-160\,^\circ$C on a General Electric XRD-5 spectrogoniometer and goniostat. The specimen was maintained at the working temperature of $-160\,^\circ$C by immersion in a stream of cold gaseous nitrogen which was itself surrounded by an envelope of dry nitrogen. The crystal was enclosed in a thin-walled quartz tube as a precaution against thermal shocks. Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) was used and reasonable monochromatization was achieved by means of a nickel filter and a pulse-height analyser. The cell constants were determined from a least-squares fit of 2θ values for 9 reflections measured by scanning α_1 and α_2 peaks with a narrow beam. The density was measured by the flotation method using degassed potassium iodide solution. Crystal data are given in Table 1. The moving-crystal moving-counter technique was used to measure the intensities. The required goniostat settings were precomputed and set manually. One standard reflection was measured after every 10 reflections to check the variation in intensity with time or temperature change. A linear interpolation was used to scale the intensities. Of the 1253 unique reflections measured (those for which $2\theta \le 164^\circ$ for Cu $K\alpha$) 1154 reflections which had intensities 1.3 times the appropriate background counts were used in the structure analysis. The remaining reflections were given a value of half the local background and flagged with a minus sign. Absorption corrections were considered to be unnecessary and were not made. The intensity data were reduced to a set of structure amplitudes in the usual manner.

Structure determination and refinement

The structure was solved by direct methods using the program *MULTAN* (Main, Woolfson & Germain, 1971). All reflections with $|E| \ge 1.4$ were used. A set of 6 starting reflections was chosen manually, since initial

Table 1. *Crystal data*

Orthorhombic
Formula $C_9H_{10}N_4O_5$, F.W. 254.2
$a = 9.248\,(8)$ Å
$b = 11.792\,(10)$
$c = 9.807\,(7)$
$U = 1069.5$ Å^3
$Z = 4$
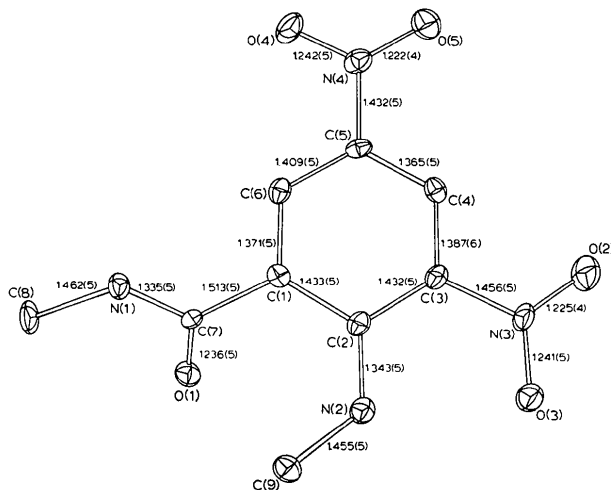$D_x = 1.578$ g cm^{-3}
$D_m = 1.56$ g cm^{-3}

Fig. 1. An *ORTEP* drawing of the *N*-methyl-2-(*N*-methylamino)-3,5-dinitrobenzamide molecule showing the atomic numbering, bond lengths and thermal ellipsoids (50% probability).
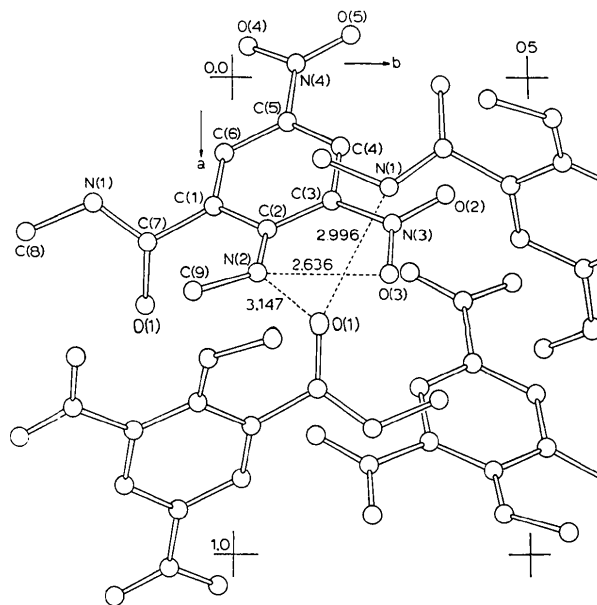

Fig. 2. Molecular packing as seen along the *c* axis. The hydrogen bonds are shown by broken lines.

attempts with the program selecting the starting set were unsuccessful. Although the correct combination had a significantly lower R index, the values of ABSFOM, usually considered to be a powerful discriminator, did not give any indications of the correct combination. An E map revealed the positions of all non-hydrogen atoms except the two methyl carbon atoms. Their positions were located from a difference Fourier synthesis. The usual R index was 0·14 at this stage.

The refinement was carried out by least-squares methods. Three cycles of full-matrix least-squares calculations using individual isotropic temperature factors reduced R to 0·085. The thermal parameters were converted to their anisotropic equivalent form and an additional 3 least-squares cycles reduced R to 0·063. A difference Fourier synthesis at this point clearly revealed the positions of all the hydrogen atoms. The parameters of the hydrogen atoms were also refined in 2 subsequent cycles of least-squares calculations using a block-diagonal approximation. The shifts in

parameters for all non-hydrogen atoms were less than $\frac{1}{5}$ of the corresponding estimated standard deviation and thus the refinement was considered complete. The final R index for all observed reflections is 0·045.

The quantity minimized by the least-squares calculations was $\sum w(|F_o| - |F_c|)^2$ and the weighting scheme was $\sqrt{w} = |F_o|/16\cdot0$ if $|F_o| < 16\cdot0$, $\sqrt{w} = 1$ if $16\cdot0 \le |F_o| \le 24\cdot0$ and $\sqrt{w} = 24\cdot0/|F_o|$ if $|F_o| > 24\cdot0$. The atomic scattering factors used throughout this study were those of Hanson, Herman, Lea & Skillman (1964) for O, N and C and those of Stewart, Davidson & Simpson (1965) for hydrogen.

The data-reduction program of Ahmed, Hall, Pippy & Huber (1966) was used. All other calculations were carried out on an IBM 370/165 computer using programs written or modified by one of us (G.J.P.).

Results and discussion

An *ORTEP* diagram of the molecule along with the atomic numbering scheme and the bond distances is

Table 2. *Final parameters of non-hydrogen atoms*

All values are $\times 10^4$. The estimated standard deviations are given in parentheses. The form of the temperature factor is

$$\exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\right].$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	4820 (3)	−1466 (2)	6308 (0)*	29 (3)	22 (2)	43 (3)	3 (4)	7 (5)	−5 (5)
O(2)	2478 (4)	3605 (2)	7697 (4)	112 (5)	14 (2)	89 (4)	21 (5)	−84 (8)	−26 (5)
O(3)	4157 (3)	2650 (2)	8695 (3)	64 (3)	20 (2)	39 (3)	−6 (5)	−33 (6)	−2 (4)
O(4)	−645 (3)	274 (2)	4011 (3)	70 (4)	29 (2)	54 (3)	−19 (5)	−62 (7)	−1 (5)
O(5)	−872 (3)	2013 (2)	4686 (4)	57 (3)	19 (2)	81 (3)	13 (5)	−42 (7)	15 (5)
N(1)	2672 (3)	−2351 (2)	6584 (4)	26 (3)	12 (2)	46 (3)	1 (4)	10 (7)	−9 (5)
N(2)	4142 (4)	421 (2)	8527 (4)	37 (3)	17 (2)	32 (3)	0 (5)	−16 (7)	5 (5)
N(3)	3100 (4)	2707 (2)	7918 (4)	47 (4)	12 (2)	34 (3)	−9 (5)	−13 (7)	−10 (4)
N(4)	−262 (4)	1094 (3)	4720 (4)	41 (3)	23 (2)	33 (3)	−11 (5)	−21 (7)	13 (5)
C(1)	2725 (4)	−300 (3)	6614 (4)	27 (4)	17 (2)	15 (3)	0 (5)	11 (7)	7 (5)
C(2)	3221 (4)	592 (3)	7489 (4)	27 (4)	15 (2)	25 (4)	−9 (5)	4 (7)	1 (5)
C(3)	2610 (4)	1686 (3)	7223 (4)	32 (4)	15 (3)	29 (3)	−14 (6)	−3 (8)	−8 (5)
C(4)	1466 (4)	1845 (3)	6329 (5)	38 (4)	18 (2)	27 (4)	7 (6)	7 (8)	3 (6)
C(5)	948 (4)	941 (3)	5612 (4)	23 (4)	21 (3)	22 (3)	−13 (5)	−2 (8)	8 (5)
C(6)	1609 (4)	−133 (3)	5715 (4)	31 (4)	16 (2)	27 (3)	−8 (6)	11 (8)	0 (6)
C(7)	3501 (4)	−1426 (3)	6507 (4)	37 (4)	16 (2)	15 (3)	10 (6)	−19 (8)	−9 (5)
C(8)	3278 (4)	−3480 (3)	6351 (6)	43 (4)	10 (2)	81 (5)	8 (6)	9 (10)	−7 (7)
C(9)	4537 (5)	−665 (3)	9123 (4)	64 (5)	18 (2)	34 (4)	−4 (6)	−42 (8)	12 (6)

* Value chosen to fix the origin.

Table 3. *Final parameters of the hydrogen atoms*

The positional parameters are $\times 10^3$. The estimated standard deviations are given in parentheses. The distance of the hydrogen atom to the atom to which it is bonded is given in the last column.

Atom	Bonded to	x	y	z	$B(\text{Å}^2)$	Distance (Å)
H(1)	C(4)	103 (5)	251 (3)	622 (5)	1·1 (0·9)	0·89 (4)
H(2)	C(6)	141 (6)	−84 (4)	503 (6)	3·3 (1·4)	1·08 (5)
H(3)	N(1)	170 (5)	−225 (4)	677 (5)	1·8 (1·1)	0·92 (5)
H(4)	N(2)	452 (6)	91 (4)	905 (7)	3·9 (1·3)	0·85 (6)
H(5)	C(8)	365 (5)	−354 (4)	533 (6)	2·2 (1·2)	1·07 (6)
H(6)	C(8)	253 (5)	−399 (4)	630 (6)	2·5 (1·1)	0·91 (5)
H(7)	C(8)	406 (7)	−361 (5)	725 (9)	6·3 (1·8)	1·15 (8)
H(8)	C(9)	465 (5)	−50 (3)	1011 (4)	0·8 (0·9)	0·99 (4)
H(9)	C(9)	375 (5)	−122 (4)	894 (5)	1·5 (1·0)	0·99 (4)
H(10)	C(9)	547 (5)	−95 (4)	867 (6)	2·3 (1·1)	1·03 (5)

illustrated in Fig. 1 and the molecular packing in Fig. 2. The final atomic parameters are listed in Tables 2 and 3* and the bond angles in Table 4.

Table 4. *The bond angles (°) and their estimated standard deviations*

C(6)–C(1)–C(2)	121·3 (3)	C(6)–C(1)–C(7)	116·0 (3)
C(1)–C(2)–C(3)	115·2 (3)	C(2)–C(1)–C(7)	122·3 (3)
C(2)–C(3)–C(4)	122·5 (4)	C(1)–C(7)–O(1)	120·8 (3)
C(3)–C(4)–C(5)	119·2 (4)	C(1)–C(7)–N(1)	116·1 (3)
C(4)–C(5)–C(6)	120·9 (4)	N(1)–C(7)–O(1)	123·0 (3)
C(5)–C(6)–C(1)	120·1 (4)	C(7)–N(1)–C(8)	120·9 (3)
C(1)–C(2)–N(2)	123·1 (3)	C(2)–N(2)–C(9)	126·6 (3)
C(3)–C(2)–N(2)	121·6 (3)	C(2)–C(3)–N(3)	122·5 (3)
C(4)–C(5)–N(4)	119·4 (4)	C(4)–C(3)–N(3)	115·0 (3)
C(6)–C(5)–N(4)	119·7 (3)	C(3)–N(3)–O(2)	119·1 (3)
C(5)–N(4)–O(4)	117·8 (3)	C(3)–N(3)–O(3)	119·2 (3)
C(5)–N(4)–O(5)	119·2 (3)	O(2)–N(3)–O(3)	121·7 (3)
O(4)–N(4)–O(5)	122·9 (4)		

The C–C distances in the benzene ring vary from 1·365 to 1·433 Å, with a mean value of 1·403 Å. The C–C distances on either side of the crowded position, C(2), [C(1)–C(2)=1·433(5), C(2)–C(3)=1·432(5) Å] are significantly longer than the value of 1·392 Å found in benzene (Cox, Cruickshank & Smith, 1958). Similar increases in C–C bond lengths have been observed in 1,3-diamino-2,4,6-trinitrobenzene (Holden, 1967). The steric effects of overcrowding are also reflected in the nonplanarity of the benzene ring (See Table 5). The benzene ring is distorted to a boat shape with C(2) and C(5) significantly out of the plane, with the two ends making dihedral angles of 7·4 and 3·4° respectively with the 4 coplanar central atoms. The substituent atoms N(3) and C(7) are also displaced from the plane of the central atoms in directions opposite to C(2) and C(5), probably to avoid close contacts. The strain in the molecule is somewhat relieved by the distortion of the bond lengths and angles within the molecular plane.

The bond lengths and angles in the nitro group are normal compared to values found in other aromatic nitrocompounds. Holden & Dickinson (1969) list a large number of such structures. Some of the more recent work includes 4-hydroxy-5,7-dinitrobenzfurazan (Mathew & Palenik, 1971), potassium picrate (Maart-

Table 5. *Least-squares planes*

Deviations (Å × 10³) in bold-face type indicate atoms which were used to define the plane.

	I	II	III
C(1)	27	**−6**	**−4**
C(2)	**−54**	−99	
C(3)	39	6	
C(4)	7	**−6**	
C(5)	**−37**	−40	
C(6)	18	6	
C(7)	289	247	**14**
N(2)	−264	−328	
N(3)	113	70	
N(4)	−112	−94	
N(1)			**−5**
O(1)			**−5**
C(8)			−130
C(9)	−718	−795	
O(2)	120	87	
O(3)	205	143	

Parameters of the planes*

$l \times 10^4$	6623	6513	1422
$m \times 10^4$	2178	2195	−149
$n \times 10^4$	−7169	−7264	9897
p(Å)	−3·085	−3·143	6·787

* Equation of the plane in the form: deviation $(Å) = lX + mY + nZ − p$ where X, Y, Z are the orthogonal coordinates (in Å) and p is the distance of the plane from the origin.

mann-Moe, 1969; Palenik, 1972), s-trinitrobenzene (Choi & Abel, 1972), picryl chloride (Willis, Stewart, Ammon, Preston, Gluyas & Harris, 1971), N-methyl-2,4,6-trinitroacetanilide (Christoph & Fleischer, 1973). A common structural feature of aromatic nitro compounds is the increased internal angle at the carbon atom to which the nitro group is attached. In the present study, the angles at the nitro-substituted carbon atoms are larger than 120° while the angle at the amino carbon is only 115·2°, in agreement with the observation by Bailey & Prout (1965) and Carter, McPhail & Sim (1966). Carter *et al.* attribute this phenomenon to small changes in the hybridization at the carbon atom.

Both nitro groups are very close to being coplanar with the benzene ring. The dihedral angle between the best plane through the benzene ring and the N(3) nitro group is 4·8°; the corresponding value for the N(4) nitro group is 5·4°. The average value of the dihedral angle between unhindered nitro groups and the benzene ring is 6° (Holden & Dickinson, 1969) and in the case of a nitro group with an *ortho* sub-

Table 6. *Contacts involving the probable hydrogen bonds*

D–H$\cdots A$*	Position of A	D–H (Å)	H$\cdots A$ (Å)	$D\cdots A$ (Å)	D–H$\cdots A$ (°)
N(1)–H(3)$\cdots$O(1)	$x - \frac{1}{2}, -y - \frac{1}{2}, z$	0·92 (5)	2·35 (5)	2·996 (4)	127 (4)
N(2)–H(4)$\cdots$O(1)	$1 - x, -y, \frac{1}{2} + z$	0·85 (6)	2·38 (6)	3·143 (4)	149 (5)
N(2)–H(4)$\cdots$O(3)	x, y, z	0·85 (6)	2·11 (5)	2·634 (4)	120 (5)
C(6)–H(2)$\cdots$O(3)	$\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$	1·08 (5)	2·27 (5)	3·356 (5)	176 (4)

* Donor–Hydrogen$\cdots$Acceptor.

stituent, the average value is 40°. The near coplanarity of the N(3) nitro group in the presence of an *ortho* substituent (methylamino group) is indicative of an intramolecular hydrogen bond. Similar intramolecular hydrogen bonding has been found in *o*-nitroanilines (*e.g.* Holden, 1967; Cady & Larson, 1965; Dyall, 1961).

The dimensions of the amide group are in excellent agreement with those in benzamide (Blake & Small, 1972) and *o*-nitrobenzamide (Fujimori, Tsukihara, Katsube & Yamamoto, 1972). The amide group is planar within the accuracy of the present analysis. However, the amide plane is rotated by 51° from the mean plane of the benzene ring. Intramolecular steric repulsion due to an *ortho* hydrogen atom is known to cause rotation of the amide group by as much as 24·6° in benzamide (Blake & Small). The formation of an intramolecular N–H···O bond involving a nitro, rather than an amido, oxygen atom may be due to this steric interaction.

The dimensions for the possible hydrogen bonds are tabulated in Table 6 and shown in Fig. 2. The intramolecular hydrogen bond N(2)–H(4)···O(3) has a relatively small N–H–O angle, but otherwise appears normal. However, N(2)–H(4) is also involved in another hydrogen bond, N(2)–H(4)···O(1), thus forming a bifurcated hydrogen bond.

The hydrogen atom H(2) bonded to C(6) of the ring has a relatively short C–H···O contact, very suggestive of a hydrogen bond. The angle C–H···O is very close to being linear and the O(3)···H(2) contact of 2·27 Å is 0·2 Å less than the expected van der Waals contact of 2·5 Å. Similar C–H···O hydrogen bonds have been found in several polynitro aromatic compounds, *e.g.* *N*-methyl-*N*,2,4,6-tetranitroaniline (Cady, 1967); 4-hydroxy-5,7-dinitrobenzfurazan (Mathew & Palenik, 1971); potassium picrate (Palenik, 1972); *N*-methyl-2,4,6-trinitroacetanilide (Christoph & Fleischer, 1973) and *s*-trinitrobenzene (Choi & Abel, 1972).

There are 10 intermolecular contacts less than 3·3 Å between the nonhydrogen atoms. All these distances involve the oxygen atoms, occupying the periphery of the molecule. The closest approach is 2·991 Å [between C(2) and O(4)] and even this is within the limits of van der Waals contacts.

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