|  |  |  |  |  |
|---|---|---|---|---|
| N3 | 0.3527 (2) | 0.7722 (2) | 0.51237 (11) | 0.0366 (3) |
| O | 0.4814 (2) | 0.7164 (2) | 0.84870 (9) | 0.0507 (4) |
| C15 | 0.2781 (3) | 0.7524 (4) | 0.8981 (2) | 0.0516 (5) |
| N4 | 0.0938 (2) | 0.8444 (3) | 0.39842 (13) | 0.0481 (4) |

Table 2. *Selected geometric parameters (Å, °)*

|  |  |  |  |
|---|---|---|---|
| S—C3 | 1.738 (2) | C2—C3 | 1.401 (2) |
| S C1 | 1.759 (2) | C8—N2 | 1.308 (2) |
| C1—N4 | 1.269 (2) | C8—N3 | 1.359 (2) |
| C1—N1 | 1.404 (2) | N2—C9 | 1.400 (2) |
| N1—C8 | 1.403 (2) | C9—C10 | 1.392 (2) |
| N1—C2 | 1.413 (2) | C10—N3 | 1.378 (2) |
| C3—S—C1 | 92.26 (8) | N2—C8—N3 | 114.56 (15) |
| N4—C1—N1 | 123.9 (2) | N2—C8—N1 | 124.82 (15) |
| N4—C1—S | 126.55 (14) | N3—C8—N1 | 120.62 (14) |
| N1—C1—S | 109.54 (13) | C8—N2—C9 | 103.36 (14) |
| C8—N1—C1 | 122.32 (14) | C10—C9—N2 | 110.54 (14) |
| C8—N1—C2 | 123.39 (13) | C14—C9—N2 | 130.0 (2) |
| C1—N1—C2 | 114.29 (14) | N3—C10—C9 | 105.17 (14) |
| C7—C2—N1 | 128.3 (2) | N3—C10—C11 | 131.2 (2) |
| C3—C2—N1 | 112.19 (15) | C8—N3—C10 | 106.37 (14) |

Table 3. *Hydrogen-bonding geometry (Å, °)*

| *D*—H···*A* | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|
| C7—H7···N2 | 2.30 (2) | 2.880 (2) | 120 (2) |
| N3—H3···N4 | 2.02 (3) | 2.617 (3) | 129 (2) |
| C4—H4···O$^{i}$ | 2.64 (3) | 3.523 (3) | 157 (2) |
| C14—H14···N4$^{ii}$ | 2.76 (2) | 3.473 (3) | 132 (2) |
| N4—H4···N2$^{iii}$ | 2.78 (3) | 3.472 (3) | 138 (2) |

Symmetry codes: (i) $x, y, z-1$; (ii) $1+x, y, z$; (iii) $x-1, y, z$.

The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and difference Fourier techniques, and refined using *SHELXL*93 (Sheldrick, 1993). Final full-matrix least-squares refinement was based on $F^2$ with anisotropic displacement parameters for all non-H atoms and isotropic displacement parameters for H atoms.

Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1188). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# *N*,*N*-Dimethyl-2,4-dinitroaniline

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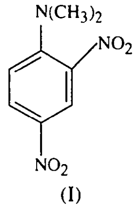
## Abstract

The title compound, $C_8H_9N_3O_4$, has both the *o*-nitro group and the 1-dimethylamino group twisted out of the plane of the benzene ring, whereas the *p*-nitro group is almost coplanar with the ring.

## Comment

In the absence of any specific electrostatic interaction, the *o*-nitro group in an *o*-nitrobenzene derivative, *e.g.* 2,4-$(O_2N)_2C_6H_3X$, (II), is twisted out of the plane of the aryl ring (Table 3). This is well illustrated by the amino compounds with $X$ = (cyclohexyl)$_2$N (Punte & Rivero, 1991), $X$ = ($^{i}$Pr)$_2$N (Punte, Rivero, Socolovsky & Nudelman, 1989) and $X$ = (cyclohexyl)($^{i}$Pr)N (Punte, Rivero, Socolovsky & Nudelman, 1991), in which not only are the *o*-nitro groups twisted out of the plane of the aryl rings [between 37.3 (2) and 46.3 (2)°], but so are the bulky amino groups [by 28.5 (5) to 37.7 (2)°].

In contrast, in the title compound ($X$ = $H_2N$), (I), the *o*-nitro group and the $NH_2$ group are almost coplanar with the benzene ring (Prasad, Gabe & Le Page, 1982). This is the consequence of a hydrogen bond between the nitro and amino groups. The *o*-nitro and attached aryl ring are also nearly coplanar in *o*-nitroaryl sulfides, *e.g.* for $X$ = SPh (Korp, Bernal & Martin, 1981), as a result of S—O interactions.



(I)

In order to investigate more closely the effect of the size of a non-electrostatically interacting $X$ group on the planarity of the *o*-nitro group and its attached aryl ring, the structure determination of the title compound, (I) ($X$ = $NMe_2$), was undertaken. Despite the amino group of

(I) having a much smaller bulk than $X$ = N($^i$Pr)$_2$, both compounds exhibit similar distortions from planarity (Table 3). Clearly, there is no simple correlation between the size of the $X$ group and the deviation from planarity.

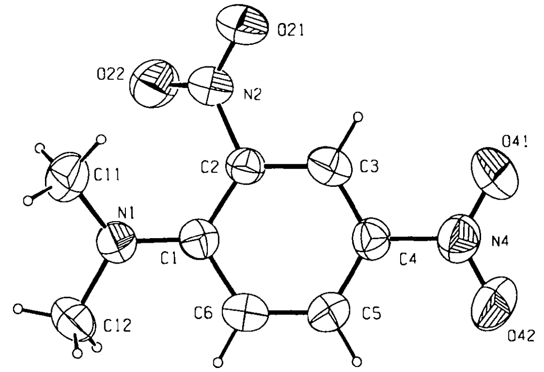


Fig. 1. A view of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The range of deviations from coplanarity of a non-hindered nitro group and its attached aryl ring can be judged from the data for the *p*-nitro groups in compounds of type (II) (Table 3).

The bond distances and angles are within expected ranges. The internal angles of the benzene ring are listed in Table 2 since variation in these angles is seen due to the presence of the substituents (Domenicano & Hargittai, 1992). The torsion angles for the substituent groups are also listed in Table 2.

## Experimental

The title compound was prepared from 2,4-$(O_2N)_2C_6H_3X$ [(II), $X$ = Cl] and dimethylamine, and recrystallized from ethanol; m.p. 349 K.

*Crystal data*

$C_8H_9N_3O_4$
$M_r$ = 211.18
Orthorhombic
*Pcab*
$a$ = 7.1330 (10) Å
$b$ = 13.2060 (10) Å
$c$ = 20.355 (5) Å
$V$ = 1917.4 (6) Å$^3$
$Z$ = 8
$D_x$ = 1.463 Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda$ = 0.7107 Å
Cell parameters from 250 reflections
$\theta$ = 0.06–24.96°
$\mu$ = 0.120 mm$^{-1}$
$T$ = 294 (1) K
Block
0.28 × 0.24 × 0.22 mm
Yellow

*Data collection*

Enraf–Nonius with FAST area-detector diffractometer
*MADNES* scans (Pflugrath & Messerschmidt, 1989)
Absorption correction: none
6340 measured reflections

1520 independent reflections
673 observed reflections [$I > 2\sigma(I)$]
$R_{int}$ = 0.071
$\theta_{max}$ = 24.91°
$h = -6 \rightarrow 7$
$k = -13 \rightarrow 14$
$l = -22 \rightarrow 21$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.0464
$wR(F^2)$ = 0.1099
$S$ = 0.799
1520 reflections
138 parameters
H atoms riding [*SHELXL*93 (Sheldrick, 1993) defaults, C—H 0.93–0.98 Å]

$w = 1/[\sigma^2(F_o^2) + (0.0327P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.193 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.195 e Å$^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.8318 (4) | 0.9936 (2) | 0.1135 (2) | 0.0438 (8) |
| N1 | 0.8971 (3) | 1.0217 (2) | 0.17329 (13) | 0.0511 (7) |
| C11 | 1.0141 (5) | 0.9571 (3) | 0.2143 (2) | 0.0651 (10) |
| C12 | 0.8914 (5) | 1.1281 (2) | 0.1937 (2) | 0.0665 (10) |
| C2 | 0.7997 (4) | 0.8922 (2) | 0.0942 (2) | 0.0414 (8) |
| N2 | 0.7862 (4) | 0.8086 (2) | 0.1410 (2) | 0.0581 (8) |
| O21 | 0.8310 (4) | 0.7240 (2) | 0.12241 (14) | 0.0849 (9) |
| O22 | 0.7189 (3) | 0.8254 (2) | 0.19531 (13) | 0.0731 (8) |
| C3 | 0.7527 (4) | 0.8673 (2) | 0.0308 (2) | 0.0507 (9) |
| C4 | 0.7286 (4) | 0.9414 (2) | −0.0159 (2) | 0.0467 (9) |
| N4 | 0.6731 (4) | 0.9146 (3) | −0.0817 (2) | 0.0621 (8) |
| O41 | 0.6603 (4) | 0.8259 (2) | −0.09652 (15) | 0.1055 (11) |
| O42 | 0.6406 (3) | 0.9819 (2) | −0.12051 (13) | 0.0842 (8) |
| C5 | 0.7475 (4) | 1.0423 (2) | 0.0019 (2) | 0.0493 (9) |
| C6 | 0.7971 (4) | 1.0673 (2) | 0.0644 (2) | 0.0518 (9) |

Table 2. *Selected bond and torsion angles (°)*

| | | | |
|---|---|---|---|
| C2—C1—C6 | 115.2 (3) | C3—C4—C5 | 119.4 (3) |
| C3—C2—C1 | 121.8 (3) | C6—C5—C4 | 120.2 (3) |
| C2—C3—C4 | 120.7 (3) | C5—C6—C1 | 122.5 (3) |
| C2—C1—N1—C11 | 27.0 (4) | C3—C2—N2—O22 | −138.4 (3) |
| C6—C1—N1—C11 | −150.7 (3) | C1—C2—N2—O22 | 32.9 (4) |
| C2—C1—N1—C12 | −167.9 (3) | C3—C4—N4—O42 | 175.1 (3) |
| C6—C1—N1—C12 | 14.4 (4) | C5—C4—N4—O42 | −1.2 (4) |
| C3—C2—N2—O21 | 36.8 (4) | C3—C4—N4—O41 | −4.9 (5) |
| C1—C2—N2—O21 | −151.9 (3) | C5—C4—N4—O41 | 178.9 (3) |

Table 3. *Angles (°) between the least-square-planes of benzene rings and substituents in 1-X-2,4-$(O_2N)_2C_6H_3$*

| | Substituents | | | |
|---|---|---|---|---|
| $X$ | 2-$O_2N$ | 4-$O_2N$ | $X$ | References |
| F | 16.0 (7) | 8.4 (7) | – | (*a*) |
| Clα | 41.8 (4) | 11.1 (4) | – | (*b*) |
| Clβ | 68.8 (6) | 13.1 (6) | – | (*b*) |
| MeO | 33 | 8 | 13 | (*c*) |
| | 35 | 2 | 5 | |
| $C_3H_2N_2$* | 69.0 (1) | 9.1 (2) | 26.2 (1) | (*d*) |
| $(C_6H_{11})^i$PrN† | 54.3 (5) | 6.5 (2) | 34.6 (5) | (*e*) |
| $(C_6H_{11})_2$N† | 37.3 (2) | 3 (3) | 37.7 (2) | (*f*) |
| | 46.3 (2) | 1 (5) | 29.8 (3) | |
| $Pri_2N$ | 40.5 (4) | 5.5 (2) | 28.5 (5) | (*g*) |
| $Me_2N$ | 38.2 (3) | 3.5 (3) | 26.2 (3) | (*h*) |
| $F_2N$ | 27.0 | 5.2 | – | (*i*) |
| $H_2N$ | 4.3 (4) | 6.6 (4) | 2.7 (5) | (*j*) |
| PhS | 7.1 | 5.4 | – | (*k*) |

References: (*a*) Wilkins & Small (1991); (*b*) Wilkins, Small & Gleghorn (1990); (*c*) Nyburg, Faerman, Prasad, Palleros & Nudelman (1987); (*d*) Fronczek, Parodi, Fischer, Hsieh & Chang (1989); (*e*) Punte, Rivero, Socolovsky & Nudelman (1991); (*f*) Punte & Rivero (1991); (*g*) Punte, Rivero, Socolovsky & Nudelman (1989); (*h*) this study; (*i*) Batail, Louer, Grandjean, Dudragne & Michaud (1976); (*j*) Prasad, Gabe & Le Page (1982); (*k*) Korp, Bernal & Martin (1981). * 1-pyrazole. † $C_6H_{11}$ = cyclohexyl.

Examination of the structure with *PLATON* (Spek, 1994*a*) showed that there were no solvent accessible voids in the crystal lattice.

Data collection: *CAD*-4/*PC* (Enraf–Nonius, 1992); *MADNES* (Pflugrath & Messerschmidt, 1989). Cell refinement: *CAD*-4/*PC*; *MADNES*. Data reduction: *CAD*-4/*PC*; *MADNES*; *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SOLVER* in *NRCVAX*. Program(s) used to refine structure: *NRCVAX*94; *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*94; *ORTEP*II (Johnson, 1976) in *PLATON* (Spek, 1994*a*); *PLUTON* (Spek, 1994*b*). Software used to prepare material for publication: *NRCVAX*94; *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1321). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Energetic Materials: the Biguanidium Nitrates

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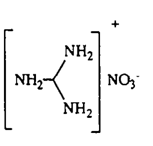
## Abstract

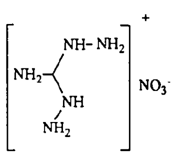
The structures of two new potentially energetic biguanidium salts, biguanidium nitrate, $C_2H_8N_5^+.NO_3^-$ [(BIGH)$NO_3$], and biguanidium dinitrate, $C_2H_9N_5^{2+}$.-2$NO_3^-$ [($BIGH_2$)$(NO_3)_2$], have been determined from X-ray data collected at 193 K. The mono- and diprotonated biguanidium nitrates are dense organic materials with efficient packing of planar anions and biplanar (twisted) cations connected by multiple hydrogen bonds. The experimental densities are compared with those obtained from empirical calculations.

## Comment

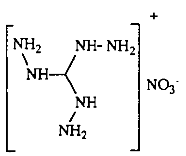
There is current interest (Borman, 1994) in the development of new energetic materials (such as explosives or propellants) and in understanding the properties of these materials, particularly with respect to their structures (Olah & Squire, 1991). One class of compounds that have solicited interest are derived from guanidinium nitrate (GN) and include, for example, diaminoguanidinium nitrate (DAGN) (Ritchie, Lee, Cromer, Kober & Lee, 1990) and triaminoguanidinium nitrate (TAGN) (Bracuti, 1979; Choi & Prince, 1979; Oyumi & Brill, 1985).



GN



DAGN



TAGN

The utility of these compounds in the field of energetic materials is derived from their rapid thermal decomposition into all-gaseous products (Oyumi & Brill, 1985, and references therein). The effectiveness of materials as either explosives or propellants is related to the density of the solid, the gas volume produced and the heat of combustion (Gilardi & Karle, 1991). DAGN and TAGN have useful properties as propellants, their densities being fairly high for organic materials (1.61 and 1.59 Mg m$^{-3}$ for DAGN and TAGN, respectively). Our

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