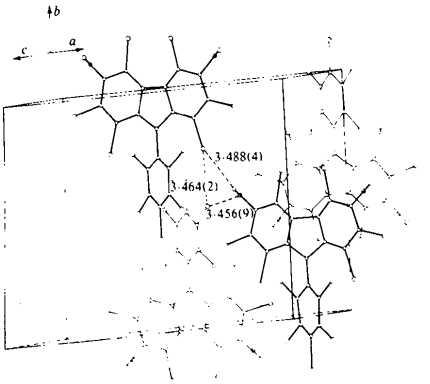

Fg. 4. Perspective view of the unit-cell contents, showing shortest intermolecular distances (Å).

The PPF molecules are stacked in layers parallel to the (103) planes in the crystal (Fig. 4).

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Crystallographic Studies of High-Density Organic Crystals, 3,5-Diamino-2,4,6-trinitrophenol

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(*Received* 22 *January* 1981; *accepted* 29 *April* 1981)

Abstract. $C_6H_5N_5O_7$, M_r = 259·1, orthorhombic, $P2_12_12_1$, a = 4·9653 (5), b = 8·8984 (5), c = 20·607 (3) Å, D_{calc} = 1·89 Mg m^{-3} for Z = 4; Cu $K\alpha$ (λ = 1·5418 Å) diffractometer data; 909 intensities; 860 I's > 3σ above background; final R = 0·044. The effects of both nitro and amino substitution are exhibited by the aromatic ring. All H atoms are involved in strong intramolecular and weaker intermolecular H···O contacts. The C–N and N–O distances, O–N–O angles and C–N torsion angles of the nitro groups show trends which could be related to different degrees of negative-charge delocalization by the groups.

Introduction. The densities of organic crystals containing atoms no heavier than O are typically 1·1–1·3 Mg m^{-3}. Nitro-group substitution can produce a dramatic increase in crystal density, with some polynitro compounds approaching 2·0 Mg m^{-3}. We are in the process of investigating the crystal structures of

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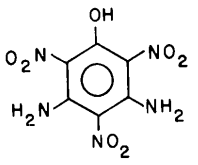
several high-density nitro-organics to understand better the various aspects of crystal packing which are responsible for exceptional densities. Herein, we report the first compound in this series, *viz* 3,5-diamino-2,4,6-trinitrophenol (I).



(I)

The compound was obtained from Dr H. Adolph, Naval Surface Weapons Center, White Oak, Maryland. Numerous crystallization trials were required to provide adequate crystal sizes for diffraction studies. The best specimens were obtained from glacial acetic acid as yellow rods with 'squashed' hexagonal cross sections. The space group and approximate cell parameters were obtained from oscillation and Weissenberg photographs with Ni-filtered Cu radiation. Accurate cell parameters were determined, and intensity measurements made with a Picker FACS-I diffractometer and graphite-monochromatized Cu radiation. A crystal 0·08 × 0·15 × 0·43 mm was mounted parallel to the long axis [100], and aligned to place this direction along the instrument's φ axis. The unit-cell parameters were determined by least squares from the 2θ values of nine reflections manually centered at $\pm 2\theta$ (average $|2\theta_o - 2\theta_c| = 0{\cdot}003°$).

Intensities were measured with the θ–2θ scan technique with a scan rate of 2° min^{-1} and 10 s backgrounds. The 2θ scan width was calculated from $1{\cdot}5° + 0{\cdot}3° \tan\theta$. 969 reflections were measured to a 2θ maximum of 127° giving 909 unique reflections. 860 were 3σ above background. The *MULTAN* 80 system (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) was used for structure solution, revealing all of the C, N, and O atoms. The structure was refined by the method of full-matrix least squares with anisotropic temperature factors applied to C, N, and O, and isotropic terms for H. The quantity minimized was $\sum w(F_o - F_c)^2$, $w = [1/\sigma(F)]^2$. Those reflections for which $I_c < 3\sigma(I)$ were not included in the refinement. The final R ($\sum ||F_o| - |F_c|| / \sum |F_o|$) and weighted R $\{[\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}\}$ factors were 0·044 and 0·042 respectively. Atomic coordinates and thermal parameters are listed in Table 1.* All calculations were performed on a Univac 1108 computer at the University of Maryland's Computer Science Center with the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) of crystallographic programs.

Table 1. *Fractional coordinates and isotropic temperature factors, with e.s.d.'s in parentheses*

For non-hydrogen atoms $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}\, a_i^*\, a_j^*\, \mathbf{a}_i.\mathbf{a}_j$

	x	y	z	U_{eq}/U (Å^2)
C(1)	0·769 (1)	0·1723 (5)	0·4158 (2)	0·018 (7)
C(2)	0·614 (1)	0·2493 (5)	0·3688 (2)	0·018 (7)
C(3)	0·408 (1)	0·1714 (6)	0·3327 (2)	0·022 (8)
C(4)	0·394 (1)	0·0112 (5)	0·3398 (2)	0·015 (9)
C(5)	0·573 (1)	−0·0697 (5)	0·3820 (2)	0·023 (5)
C(6)	0·738 (1)	0·0199 (5)	0·4229 (2)	0·025 (6)
O(7)	0·9562 (8)	0·2391 (4)	0·4520 (2)	0·017 (4)
N(8)	0·6562 (9)	0·4042 (5)	0·3590 (2)	0·03 (1)
N(9)	0·242 (1)	0·2432 (5)	0·2934 (2)	0·03 (1)
N(10)	0·2000 (9)	−0·0712 (4)	0·3035 (2)	0·02 (1)
N(11)	0·585 (1)	−0·2170 (5)	0·3849 (3)	0·029 (3)
N(12)	0·8894 (9)	−0·0518 (5)	0·4753 (2)	0·028 (9)
O(8*A*)	0·8529 (8)	0·4683 (4)	0·3877 (2)	0·02 (1)
O(8*B*)	0·5142 (8)	0·4816 (4)	0·3225 (2)	0·03 (1)
O(10*A*)	0·0129 (7)	−0·0040 (4)	0·2754 (2)	0·02 (1)
O(10*B*)	0·2169 (9)	−0·2108 (4)	0·2997 (2)	0·02 (1)
O(12*A*)	1·0285 (8)	−0·1625 (5)	0·4614 (2)	0·07 (1)
O(12*B*)	0·8635 (9)	−0·0031 (5)	0·5297 (2)	0·04 (1)
H(7)	0·92 (2)	0·350 (7)	0·444 (3)	0·09 (2)
H(9*A*)	0·28 (1)	0·334 (6)	0·281 (3)	0·07 (2)
H(9*B*)	0·13 (2)	0·178 (8)	0·257 (3)	0·12 (3)
H(11*A*)	0·52 (2)	−0·284 (8)	0·359 (3)	0·09 (3)
H(11*B*)	0·65 (2)	−0·258 (8)	0·414 (3)	0·08 (3)

Discussion. An *ORTEP* drawing (Johnson, 1971) is given in Fig. 1 and bond lengths and angles are listed in Table 2. The deviations of the six ring atoms from their least-squares plane are larger than those generally observed in aromatic systems, the maximum and r.m.s. values being 0·069 and 0·052 Å respectively. With the exception of the phenolic OH, the most in-plane of the six ring substituents, the out-of-plane deviation of each substitutent atom directly linked to the ring is of the

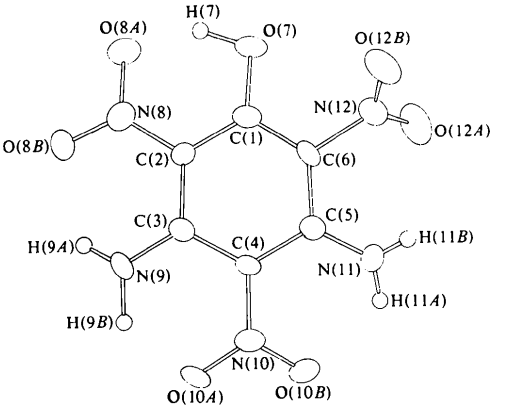


Fig. 1. An *ORTEP* drawing of (I) with the C, N and O atoms depicted as 50% probability boundary ellipses. H atoms are shown as circles of radius 0·1 Å.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36144 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°), *with e.s.d.'s in parentheses*

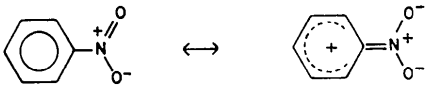
C(1)–C(2)	1·416 (7)	N(8)–O(8*A*)	1·277 (6)
C(1)–C(6)	1·373 (7)	N(8)–O(8*B*)	1·240 (6)
C(1)–O(7)	1·332 (7)	N(10)–O(10*A*)	1·247 (6)
C(2)–C(3)	1·441 (7)	N(10)–O(10*B*)	1·248 (5)
C(2)–N(8)	1·409 (6)	N(12)–O(12*A*)	1·237 (6)
C(3)–C(4)	1·435 (7)	N(12)–O(12*B*)	1·208 (5)
C(3)–N(9)	1·320 (7)	O(7)–H(7)	1·02 (6)
C(4)–C(5)	1·434 (7)	N(9)–H(9*A*)	0·87 (6)
C(4)–N(10)	1·424 (6)	N(9)–H(9*B*)	1·11 (7)
C(5)–N(11)	1·314 (7)	N(11)–H(11*A*)	0·88 (7)
C(5)–C(6)	1·421 (7)	N(11)–H(11*B*)	0·78 (7)
C(6)–N(12)	1·463 (6)		

C(2)–C(1)–C(6)	119·3 (5)	C(1)–C(6)–N(12)	116·9 (4)
C(2)–C(1)–O(7)	123·2 (4)	C(2)–N(8)–O(8*A*)	119·1 (4)
C(6)–C(1)–O(7)	117·4 (4)	C(2)–N(8)–O(8*B*)	123·0 (4)
C(1)–C(2)–C(3)	120·5 (4)	C(4)–N(10)–O(10*A*)	120·1 (4)
C(1)–C(2)–N(8)	119·3 (4)	C(4)–N(10)–O(10*B*)	120·0 (4)
C(3)–C(2)–N(8)	120·2 (4)	C(6)–N(12)–O(12*A*)	117·6 (4)
C(2)–C(3)–C(4)	117·2 (4)	C(6)–N(12)–O(12*B*)	118·2 (4)
C(2)–C(3)–N(9)	121·8 (5)	O(8*A*)–N(8)–O(8*B*)	117·9 (4)
C(4)–C(3)–N(9)	121·0 (5)	O(10*A*)–N(10)–O(10*B*)	119·9 (4)
C(3)–C(4)–C(5)	122·1 (4)	O(12*A*)–N(12)–O(12*B*)	124·1 (4)
C(3)–C(4)–N(10)	119·3 (4)	C(1)–O(7)–H(7)	103 (4)
C(5)–C(4)–N(10)	118·6 (4)	C(3)–N(9)–H(9*A*)	120 (4)
C(4)–C(5)–C(6)	115·8 (4)	C(3)–N(9)–H(9*B*)	119 (4)
C(4)–C(5)–N(11)	123·9 (5)	C(5)–N(11)–H(11*A*)	129 (5)
C(6)–C(5)–N(11)	120·3 (5)	C(5)–N(11)–H(11*B*)	121 (5)
C(5)–C(6)–C(1)	123·7 (4)	H(9*A*)–N(9)–H(9*B*)	113 (5)
C(5)–C(6)–N(12)	119·4 (4)	H(11*A*)–N(11)–H(11*B*)	109 (7)

same sign but greater magnitude than the associated ring atom. Deviations of this magnitude are often observed in nitro-amino-substituted aromatics: for example, 2,3,4,6-tetranitroaniline (Dickinson, Stewart & Holden, 1966) and 1,3,5-triamino-2,4,6-trinitrobenzene (Cady & Larson, 1965). The N(8), N(10) and N(12) nitro groups make angles of 8·3, 15·5 and 54·5°, respectively, with the benzene ring. Large deviations of nitro groups from the benzene plane for similar structures have been reported. Examples are, ammonium picrate (Maartmann-Moe, 1969), 2,4,6-trinitroaniline (Holden, Dickinson & Bock, 1972) and 2,3,4,6-tetranitroaniline.

The benzene ring exhibits the characteristic effects of both nitro- and amino-group substitution (Holden & Dickinson, 1977). Thus, the bond-distance pairs C(2)–C(3), C(3)–C(4) and C(4)–C(5), C(5)–C(6) are longer (1·433 Å average) than the 1·392 Å C–C distance in benzene (Cox, Cruickshank & Smith, 1958) because of amino-group substitutions at C(3) and C(5). The average values of the internal C–C–C angles at the benzene atoms bearing the amino and nitro substituents are 116·5 and 122·1° respectively. These features, and others, have been categorized by Holden & Dickinson (1977) as typical of amino- and nitro-substituted aromatics. Other compounds which show these characteristics are 1,3,5-triamino-2,4,6-trinitrobenzene (Cady & Larson, 1965), 2,4,6-trinitroaniline (Holden, Dickinson & Bock, 1972) and 2,3,4,6-tetranitroaniline (Dickinson, Stewart & Holden, 1966).

π-electron delocalization from an aromatic ring to a nitro group can be envisaged as increasing the contribution of canonical form (II*b*) to the resonance hybrid.



(II*a*) (II*b*)

Several structural features of the three nitro groups in (I) are listed in Table 3, and all of these characteristics show trends that would be expected for the order of increasing π-delocalization of C(6)–NO_2 < C(4)–NO_2 < C(2)–NO_2. The most obvious relationship is that between C–N distance and C–NO_2 out-of-plane rotation, the larger amounts of C=N character corresponding to the smaller torsion angles. Additionally, the decrease in the C–N bonds accompanies an increase in the N–O distances (N=O → N–O), and there is a decrease in the O–N–O angles. This last characteristic is exemplified in numerous alkene structures [$R_1R_2C{=}C$] in that the $\angle R_1{-}C{-}R_2$ becomes smaller as the C=C bond shortens (Ammon & Plastas, 1971). The exceptionally long N(8)–O(8*A*) distance of 1·277 Å can be attributed to the strong hydrogen bond between O(8*A*) and the adjacent hydroxyl H.

The C–O distance of 1·332 Å and the external angles at C(1) are similar to the values in other nitrophenols (Iwasaki & Kawano, 1977).

The packing arrangement of the molecule projected down **a** is shown in Fig. 2. There are two O–H···O contacts in the structure while all the others are of the N–H···O type. The O(7)···O(8*A*) intramolecular distance of 2·48 Å (H···O = 1·60 Å) indicates a strong hydrogen bond between the hydroxyl and the adjacent nitro group. This is less than the average value of 2·58 Å for similar contacts observed in other nitrophenols (Iwasaki & Kawano, 1977). The four amino H atoms form strong intramolecular contacts to the O atoms of adjacent nitro groups. Three of these H atoms are also involved in somewhat weaker intermolecular O···H interactions. Both H(11*B*) and

Table 3. *Structure features of the nitro groups*

E.s.d.'s for bond lengths are 0·006–0·008 Å, for bond angles 0·4° and for torsion angles 0·5–0·6°.

	C–N length	C–N* torsion angle	⟨N–O⟩ length	∠O–N–O
C(2)–NO_2	1·409 Å	5·6°	1·258 Å	117·9°
C(4)–NO_2	1·424	12·9	1·247	119·9
C(6)–NO_2	1·463	52·5	1·222	124·1

* Each torsion angle is an average of the four C–C–N–O dihedral angles associated with each nitro group.

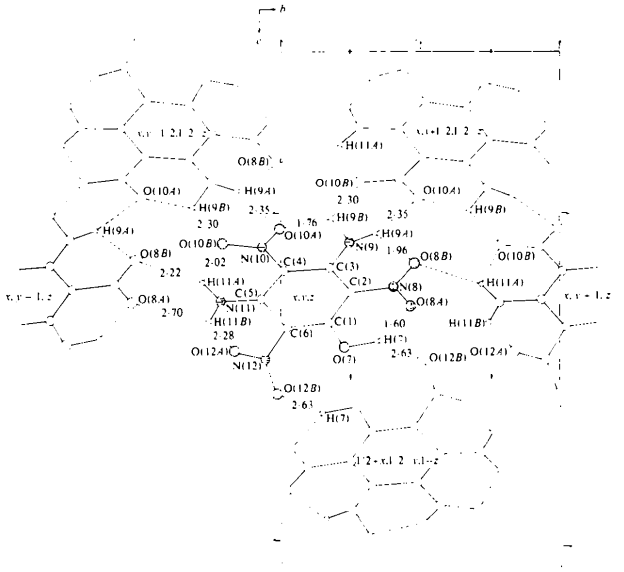


Fig. 2. Intermolecular packing viewed down **a**. All non-bonded distances less than 2·70 Å have been indicated by broken lines (e.s.d.'s are 0·06–0·07 Å). The intermolecular distances of 2·70 [H(11*B*)···O(8*A*)] and 2·63 Å [H(7)···O(12*B*)] are not hydrogen-bonded contacts. A number of the angles (°) associated with the intra- and intermolecular hydrogen contacts are: O(7)–H(7)···O(8*A*) = 143 (5), O(7)–H(7)···O(12*B*) = 110 (5), O(8*A*)···H(7)···O(12*B*) = 90 (3), N(9)–H(9*A*)···O(8*B*) = 128 (5), N(9)–H(9*A*)···O(10*A*)^{i} = 126 (6), O(10*A*)···H(9*A*)···O(8*B*) = 100 (2), N(9)–H(9*B*)···O(10*B*)^{i} = 120 (5), N(9)–H(9*B*)···O(10*A*) = 120 (5), O(10*B*)···H(9*B*)···O(10*A*) = 105 (3), N(11)–H(11*A*)···O(10*B*) = 117 (6), N(11)–H(11*A*)···O(8*B*)^{ii} = 148 (7), O(8*B*)···H(11*A*)···O(10*B*) = 96 (3), N(11)–H(11*B*)···O(12*A*) = 120 (6). Superscripts i and ii refer to molecules at $x, y + \frac{1}{2}, -z + \frac{1}{2}$ and $-x, y - \frac{1}{2}, -z + \frac{1}{2}$ respectively.

H(7) (–OH group) appear not to be associated with intermolecular hydrogen bonds, with O···H distances of 2·63 Å [to O(12*B*)] and 2·70 Å [to O(8*A*)] respectively.

Along **a**, molecules which are separated by the cell repeat have no C···C contacts less than 3·6 Å and there are no hydrogen bonds. The molecules are thus stacked in layers in which the normal to the benzene ring is inclined by 44° from **a**. The predicted length of the *a* axis of 4·73 Å, based on a 3·4 Å thick benzene ring angled at 44°, is close to the observed value of 4·97 Å.

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(*p*-Methylphenoxy)acetic Acid

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Abstract. $C_9H_{10}O_3$, monoclinic, $P2_1/c$, $Z = 4$, $a = 13{\cdot}890\,(16)$, $b = 5{\cdot}248\,(2)$, $c = 12{\cdot}072\,(2)$ Å, $\beta = 103{\cdot}00\,(13)°$, $D_o = 1{\cdot}326$, $D_c = 1{\cdot}316$ Mg m^{-3}. The structure was solved by direct methods using Sayre's equation and refined to $R = 0{\cdot}0865$ for 511 reflections by full-matrix least squares with anisotropic temperature factors. The molecules form dimers across centres of symmetry with O–H···O bonds of

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