

Crystallographic Studies of High-Density Organic Compounds: 3,5-Diamino-2,4,6-trinitrobenzamide

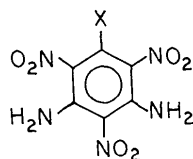
BY HERMAN L. AMMON AND SOVAN K. BHATTACHARJEE

Department of Chemistry, University of Maryland, College Park, Maryland 20742, USA

(Received 5 November 1981; accepted 23 February 1982)

Abstract. $C_7H_6N_6O_7$, $M_r = 286.2$, monoclinic, $P2_1/n$, $a = 16.557(1)$, $b = 10.2453(4)$, $c = 5.9400(1)$ Å, $\beta = 91.840(6)^\circ$, $D_c = 1.89$ Mg m $^{-3}$ for $Z = 4$; Cu $K\alpha$ ($\lambda = 1.5418$ Å) diffractometer data; 1645 unique intensities; 1536 intensities 3σ above background; $R = 0.036$. The benzene ring appears to be slightly folded and there are substantial deviations of the substituents from the plane of the ring. The amide group is twisted 70° out-of-plane and the nitro-group torsion angles are 4, 17 and 35° . There are strong N–H...O intramolecular and weaker intermolecular contacts in the crystal structure. Packing-coefficient calculations suggest that the high crystal density is due to an efficient intermolecular packing arrangement which reduces empty space.

Introduction. The densities of organic crystals containing only elements from the first and second rows of the periodic table (H to F) are usually in the 1.1–1.3 Mg m $^{-3}$ range. A dramatic increase in density often accompanies nitro-group substitution, with many poly-nitro organics having values as high as 1.8–2.0 Mg m $^{-3}$. We are investigating the crystal structures of a number of high-density nitro organics in an attempt to understand what molecular and crystal properties are responsible for exceptional densities. The subject of this report, 3,5-diamino-2,4,6-trinitrobenzamide (I), is the third compound in our series of diaminotrinitroaromatics, the other compounds being the phenol (II) (Bhattacharjee & Ammon, 1981) and the fluoro analog (III) (Ammon, Bhattacharjee & Holden, 1982).



- (I) X = C(=O)NH₂,
(II) X = OH
(III) X = F

The compound was obtained from Dr M. Chaykovsky, Naval Surface Weapons Center, Silver

Spring, Maryland. It was recrystallized from nitromethane as transparent yellow-orange parallelepipeds. 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-monochromated Cu radiation. A $0.33 \times 0.17 \times 0.12$ mm crystal was mounted along the body-diagonal of the crystal (a) 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 12 reflections manually centered at $\pm 2\theta$ (average $|2\theta_o - 2\theta_c| = 0.002^\circ$).

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 $1.6^\circ + 0.29^\circ \tan \theta$. Four standards were measured every 100 reflections to monitor intensity fluctuations. 1897 reflections were measured to a 2θ maximum of 127° giving 1645 unique reflections after averaging. 1536 were 3σ above background. The structure was solved with the XRAY system's (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) direct-methods subprogram PHASE. An E map calculated with 226 phases revealed the positions of the 20 C, N and O atoms. H atoms were located from a difference map. The structure was refined by the method of full-matrix least squares with anisotropic temperature factors for the C, N and O atoms and isotropic terms for H. The quantity minimized was $\sum w(F_o - F_c)^2$, where $w = [1/\sigma(F)]^2$. Reflections for which $I_c < 3\sigma(I)$ were not included in the refinement. Scattering factors for C, N and O were calculated from the analytical expressions of Cromer & Mann (1968); the H terms were interpolated from the tabulated values of Stewart, Davidson & Simpson (1965). A correction for secondary extinction was applied during the latter stages of 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 are 0.036 and 0.038 respectively. Atomic coordinates and

Table 1. Fractional coordinates and isotropic temperature factors (\AA^2)

An asterisk denotes U_{eq} , the equivalent value of the anisotropic temperature coefficients, calculated from the expression $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$. The U_{ij} values have been deposited.

The e.s.d. of the last significant digit is given in parentheses.

	x	y	z	U
C(1)	0.3895 (1)	0.2354 (2)	0.6149 (3)	0.023 (3)*
C(2)	0.3083 (1)	0.2381 (2)	0.6721 (3)	0.023 (1)*
C(3)	0.2461 (1)	0.1833 (2)	0.5274 (3)	0.027 (2)*
C(4)	0.2721 (1)	0.1070 (2)	0.3418 (3)	0.020 (2)*
C(5)	0.3561 (1)	0.0819 (2)	0.3058 (3)	0.026 (2)*
C(6)	0.4119 (1)	0.1602 (2)	0.4351 (3)	0.026 (4)*
C(7)	0.4539 (1)	0.3126 (2)	0.7492 (3)	0.024 (4)*
N(7)	0.4497 (1)	0.4419 (2)	0.7201 (3)	0.026 (4)*
N(8)	0.2887 (1)	0.3006 (2)	0.8798 (3)	0.030 (4)*
N(9)	0.1685 (1)	0.2040 (2)	0.5677 (4)	0.031 (3)*
N(10)	0.2137 (1)	0.0547 (2)	0.1862 (3)	0.023 (3)*
N(11)	0.3817 (1)	-0.0042 (2)	0.1586 (4)	0.029 (5)*
N(12)	0.4952 (1)	0.1679 (2)	0.3649 (3)	0.032 (4)*
O(7)	0.50410 (8)	0.2550 (2)	0.8667 (2)	0.032 (3)*
O(8A)	0.3426 (1)	0.3177 (2)	1.0235 (2)	0.033 (4)*
O(8B)	0.2187 (1)	0.3341 (2)	0.9155 (3)	0.044 (3)*
O(10A)	0.2356 (1)	-0.0024 (2)	0.0142 (3)	0.026 (5)*
O(10B)	0.14065 (9)	0.0688 (2)	0.2136 (3)	0.029 (2)*
O(12A)	0.53030 (9)	0.2723 (2)	0.3859 (3)	0.035 (5)*
O(12B)	0.52776 (9)	0.0702 (2)	0.2853 (3)	0.051 (4)*
H(7A)	0.414 (2)	0.474 (3)	0.608 (5)	0.060 (9)
H(7B)	0.490 (2)	0.488 (3)	0.790 (5)	0.063 (9)
H(9A)	0.158 (2)	0.250 (3)	0.699 (5)	0.053 (8)
H(9B)	0.133 (2)	0.169 (3)	0.470 (5)	0.054 (8)
H(11A)	0.439 (2)	-0.017 (3)	0.153 (5)	0.08 (1)
H(11B)	0.346 (2)	-0.038 (3)	0.056 (5)	0.08 (1)

thermal parameters are listed in Table 1.* All calculations were done on Univac 1108 and 1100/40 computers at the University of Maryland's Computer Science Center with the XRAY system (Stewart *et al.*, 1976) of crystallographic programs.

Discussion. An *ORTEP* drawing (Johnson, 1971) of the molecule is shown in Fig. 1. The maximum and average deviations of the six ring atoms from their least-squares plane at 0.090 and 0.057 \AA are larger than observed in the phenol (II) and fluoro (III) derivatives (Table 2). The out-of-plane distances show that the benzene ring is folded along a line from C(2) to C(5). Additionally, the ring substituents deviate substantially from the plane, and the pattern of deviations is one which clearly allows these groups a little more 'room' in the intramolecular environment. While the phenol shows a similar pattern, the fluoro derivative is more or less flat.

Bond lengths and angles are listed in Table 3. As in (II) and (III) the molecule exhibits the characteristics of

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36753 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

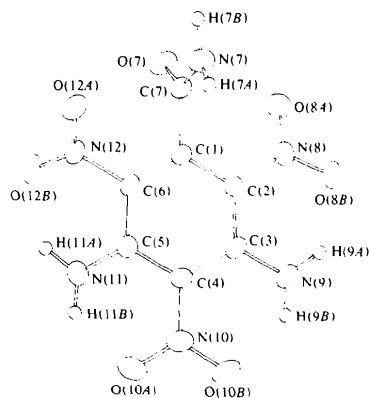


Fig. 1. An *ORTEP* drawing of (I) with the C, N and O atoms depicted as 50% probability boundary ellipsoids. H atoms are shown as 0.1 \AA radius circles.

Table 2. Out-of-plane distances (\AA) of (I), (II), and (III) from the least-squares plane of the six ring atoms

	(I)*	(II)	(III)
C(1)	0.039	0.009	0.015
C(2)	-0.081	-0.059	-0.010
C(3)	0.033	0.042	-0.006
C(4)	0.051	0.020	0.017
C(5)	-0.090	-0.069	-0.012
C(6)	0.048	0.056	-0.004
X†	0.143	-0.039	0.117
N(8)	-0.294	-0.182	-0.030
N(9)	0.117	0.118	-0.039
N(10)	0.221	0.027	0.104
N(11)	-0.289	-0.228	-0.059
N(12)	0.297	0.220	0.003
O(7)	-0.783	-	-
N(7)	1.308	-	-

* E.s.d.'s are approximately 0.008 \AA .

† X = C(7) in (I), O in (II) and F in (III).

both nitro- and amino-group substitutions (Holden & Dickinson, 1977). The average of the four benzene-ring bond lengths at the amino-group substitutions is 1.434 (3) \AA , while in (II) and (III) the values are 1.434 (9) and 1.433 (7) \AA , respectively. The averages of the internal C—C angles at the benzene-ring atoms bearing the amino and nitro substituents are [116.2 (2), 122.2 (2)°], [116.5 (6), 121.4 (6)°] and [116.4 (4), 122.1 (4)°] in (I), (II) and (III), respectively.

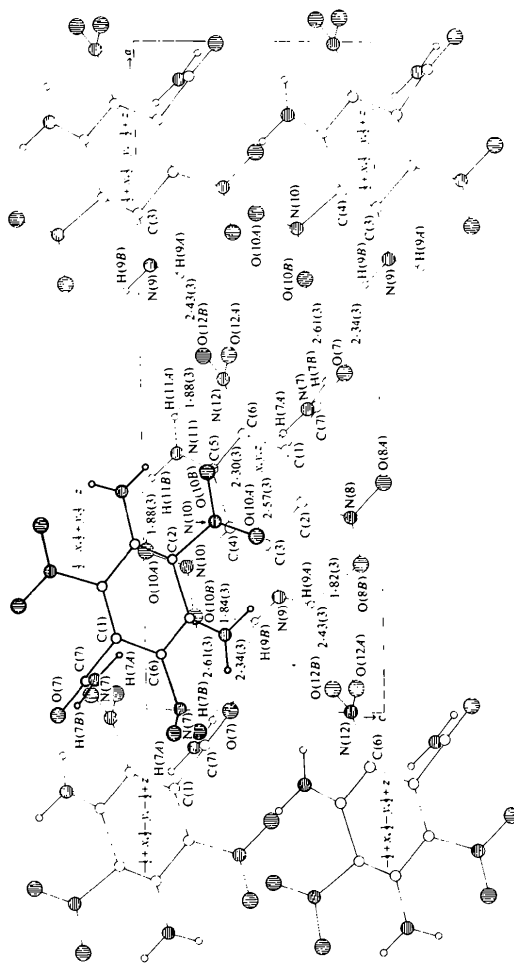
The N(10), N(8) and N(12) nitro groups are twisted by angles of 4.5 (3), 17.5 (3) and 34.8 (2)°, respectively, out of the benzene-ring plane. As we noted in the phenol structure (II), changes in the nitro-group torsion angles, C—N distances and O—N—O angles can be readily rationalized in terms of varying amounts of negative-charge delocalization to the three substituents. For example, a small torsion angle goes hand-in-hand with a short C—N distance, indicating enhanced C—N π -bond character and therefore increased negative charge on the NO₂ O atoms.

Table 3. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

C(1)–C(2)	1.398 (3)	C(7)–O(7)	1.220 (2)
C(1)–C(6)	1.378 (3)	N(8)–O(8A)	1.227 (2)
C(1)–C(7)	1.530 (3)	N(8)–O(8B)	1.235 (2)
C(2)–C(3)	1.435 (3)	N(10)–O(10A)	1.241 (3)
C(3)–C(4)	1.429 (3)	N(10)–O(10B)	1.234 (2)
C(4)–C(5)	1.437 (3)	N(12)–O(12A)	1.223 (2)
C(5)–C(6)	1.429 (3)	N(12)–O(12B)	1.238 (2)
C(2)–N(8)	1.436 (3)	N(7)–H(7A)	0.93 (3)
C(3)–N(9)	1.332 (3)	N(7)–H(7B)	0.91 (3)
C(4)–N(10)	1.420 (3)	N(9)–H(9A)	0.93 (3)
C(5)–N(11)	1.322 (3)	N(9)–H(9B)	0.88 (4)
C(6)–N(12)	1.456 (2)	N(11)–H(11A)	0.95 (3)
C(7)–N(7)	1.338 (3)	N(11)–H(11B)	0.90 (3)
C(1)–C(2)–C(3)	121.6 (2)	C(1)–C(7)–O(7)	119.9 (2)
C(2)–C(3)–C(4)	116.7 (2)	C(1)–C(7)–N(7)	114.3 (2)
C(3)–C(4)–C(5)	121.9 (2)	C(2)–N(8)–O(8A)	118.8 (2)
C(4)–C(5)–C(6)	115.6 (2)	C(2)–N(8)–O(8B)	120.7 (2)
C(5)–C(6)–C(1)	123.1 (2)	C(4)–N(10)–O(10A)	120.2 (2)
C(6)–C(1)–C(2)	118.9 (2)	C(4)–N(10)–O(10B)	121.3 (2)
C(6)–C(1)–C(7)	119.6 (2)	C(6)–N(12)–O(12A)	118.0 (2)
C(2)–C(1)–C(7)	121.5 (2)	C(6)–N(12)–O(12B)	119.6 (2)
C(1)–C(2)–N(8)	117.6 (2)	O(7)–C(7)–N(7)	125.7 (2)
C(3)–C(2)–N(8)	120.8 (2)	C(7)–N(7)–H(7A)	118 (2)
C(2)–C(3)–N(9)	120.5 (2)	C(7)–N(7)–H(7B)	115 (2)
C(4)–C(3)–N(9)	122.8 (2)	C(3)–N(9)–H(9A)	116 (2)
C(3)–C(4)–N(10)	119.6 (2)	C(3)–N(9)–H(9B)	116 (2)
C(5)–C(4)–N(10)	118.5 (2)	C(5)–N(11)–H(11A)	117 (2)
C(4)–C(5)–N(11)	123.4 (2)	C(5)–N(11)–H(11B)	119 (2)
C(6)–C(5)–N(11)	120.9 (2)	H(7A)–N(7)–H(7B)	126 (3)
C(5)–C(6)–N(12)	118.6 (2)	H(9A)–N(9)–H(9B)	128 (2)
C(1)–C(6)–N(12)	118.2 (2)	H(11A)–N(11)–H(11B)	123 (3)

Bond lengths and angles in the amide portion of the molecule have typical values for this functional group. The group is essentially isolated from any π -electron interactions with the benzene ring by virtue of the 70° torsion about C(1)–C(7). The C(1)–C(7) distance of 1.530 (3) Å is long for a C(sp^2)–C(sp^2) single bond, providing further evidence for the absence of p -orbital effects. For comparison, the C(2)–C(3) distance in (planar), 1,3-butadiene is 1.463 Å (Kuchitsu, Fukuyama & Morino, 1968), while in benzanilide [Ph–C(=O)–NH–Ph] the aromatic C–C(carbonyl) bond is 1.484 (8) Å with a 31° twist (Kashino, Ito & Haisa, 1979).

A packing diagram is shown in Fig. 2. The pattern of strong intramolecular N–H...O interactions between adjacent NH₂ and NO₂ groups is repeated here. Because of the out-of-plane amide group, the packing scheme is quite different from those observed in the phenol (II) and fluoro (III) derivatives, in which the molecules pack in sheets with essentially no sheet-to-sheet interactions. There are sheets of molecules in (I), essentially normal to the b axis, but the amide groups provide the necessary link for hydrogen bonding between sheets. This link occurs between molecules related by the twofold screw operation: from the molecule at x, y, z to the one at $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$, the N–H(7A)...O(10A) and N–H(7A)...O(10B) distances are 2.57 (3) and 2.30 (3) Å, respectively. Within the sheets, there are close contacts involving the

Fig. 2. Packing view down b ; some contact distances (Å) and e.s.d.'s (in parentheses) are given.

N(9) amino group: (x, y, z) H(9B)...O(7) $(-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z) = 2.34 (3) \text{ \AA}$, (x, y, z) H(9A)...O(12A) $(-\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z) = 2.43 (3) \text{ \AA}$. There are no double hydrogen-bonded contacts between NH₂ and NO₂ groups similar to those observed in (II) and (III).

Dr J. Holden of the Naval Surface Weapons Center has performed a series of packing calculations, based on the atomic radii of Kitaigorodsky (1973), for over 40 polynitro-organic compounds. The packing coefficients ($PC = \text{total molecular volume/unit-cell volume}$) range from 0.70 in [FC(NO₂)₂CH₂-OC(=NH)]₂ to 0.81 in 1,3,5-triamino-2,4,6-trinitrobenzene. This parameter should be sensitive to the extent of close intermolecular contacts, and may be expected to reflect more subtle factors, such as molecular 'shape', which could lead to efficient arrangements of molecular packing. The PC 's calculated for (I)–(III), 0.79, 0.79 and 0.80, respectively, are near the top of the range of these values. It appears unlikely that there are any significant shape factors to be taken into account in these aromatic compounds, and we con-

clude that close contacts are responsible for reducing the amount of free space in the unit cells and, thus, for the high crystal densities.

This work was supported by the Naval Sea Systems Command, under task 61153N SR024-03 and, in part, through the facilities of the Computer Science Center of the University of Maryland. Our thanks to Dr J. Holden for the packing calculations and for many fruitful discussions.

References

- AMMON, H. L., BHATTACHARJEE, S. K. & HOLDEN, J. R. (1982). *Acta Cryst.* **B38**, 1851–1854.
 BHATTACHARJEE, S. K. & AMMON, H. L. (1981). *Acta Cryst.* **B37**, 2082–2085.

- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 HOLDEN, J. R. & DICKINSON, C. (1977). *J. Phys. Chem.* **81**, 1505–1514.
 JOHNSON, C. K. (1971). *ORTEP II*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 KASHINO, S., ITO, K. & HAISA, M. (1979). *Bull. Chem. Soc. Jpn.* **52**(2), 365–369.
 KITAIGORODSKY, A. I. (1973). In *Molecular Crystals and Molecules*. New York: Academic Press.
 KUCHITSU, K., FUKUYAMA, T. & MORINO, Y. (1968). *J. Mol. Struct.* **1**, 463–479.
 STEWART, J. M., MACHIN, P. A., DICKINSON, C., AMMON, H. L., HECK, H. S. & FLACK, H. (1976). The XRAY system – version of 1976. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1982). **B38**, 2086–2089

N-(*p*-Aminobenzoyl)-L-glutamic Acid Hydrochloride

BY CHANDANA CHATTERJEE, J. K. DATTA GUPTA AND N. N. SAHA

Crystallography and Molecular Biology Division, Saha Institute of Nuclear Physics, Calcutta-700 009, India

(Received 10 September 1981; accepted 25 February 1982)

Abstract. $C_{12}H_{15}N_2O_5^+ \cdot Cl^-$, $M_r = 302.70$, monoclinic, $P2_1$, $a = 11.819$ (3), $b = 4.924$ (1), $c = 12.085$ (1) Å, $\beta = 102.4$ (1)°, $V = 686.82$ Å³, $Z = 2$, $D_x = 1.46$, D_m (floatation in benzene/bromoform) = 1.47 Mg m⁻³, μ (Cu $K\alpha$) = 2.704 mm⁻¹. The structure was solved by direct methods and refined to a final R value of 0.065 for 1022 reflections. The *p*-aminobenzoic acid part of the molecule is linked to the glutamic acid through a peptide-like linkage with an amide C–N distance of 1.340 (9) Å. C ^{δ} in the glutamic acid side chain is *gauche* to C ^{α} ($\chi^2 = 74^\circ$), and the α -carboxyl C atom is *trans* to C ^{γ} , the torsion angle C–C ^{α} –C ^{β} –C ^{γ} being -177° . The α -N deviates from the plane of the α -carboxyl group, and ψ^1 has a value of 22.5°.

Introduction. *p*-Aminobenzoyl-L-glutamic acid (PABG) is a sulfanilamide antagonist and is a major portion of folic acid. It is well known that the antibacterial action of sulfonamide is related to its ability to block bacterial synthesis of folic acid. The presence of *p*-aminobenzoic acid (PABA) and glutamic acid moieties in the folic acid molecule is a feature of special biological interest (Herbert, 1966). These are linked through a peptide-like linkage to form PABG.

The present study was undertaken to provide structural data to help interpret the biological function of the molecule.

Thin, spear-shaped crystals were obtained by the slow cooling of a solution of a stoichiometric amount of PABG in 0.1 *M* hydrochloric acid. Preliminary oscillation and Weissenberg photographs using Cu $K\alpha$ radiation showed the crystals to be monoclinic, space group $P2_1$. Refined cell parameters and their standard deviations were derived from a least-squares fit to the setting angles of 25 reflections centered on an Enraf–Nonius CAD-4 diffractometer.

A crystal of dimensions 0.28 × 0.13 × 0.03 mm was used for collecting intensity data on the diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. All reflections in the range $2 < \theta < 60^\circ$ were measured with an $\omega/2\theta$ scan, a variable scan speed and a scan range of $(0.7 + 0.14 \tan \theta)^\circ$. Three standard reflections were monitored after each group of 50 measurements; they did not show any noticeable change in intensity. Of the 1169 reflections measured, 1023 were considered observed with $F_o > 2\sigma(F)$, where $\sigma(F)$ is the e.s.d. based on counting statistics, and these were corrected for Lorentz and polarization effects, but no correction was made for absorption.