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Structural Studies of Benzene Derivatives.
III.* The Crystal and Molecular Structure of *p*-Nitrobenzamide

BY FERNANDA DI RIENZO AND ALDO DOMENICANO

Istituto di Chimica Farmaceutica e Tossicologica, Università di Roma, Città Universitaria, 00185 Roma, Italy and Laboratorio di Strutturistica Chimica del CNR 'Giordano Giacomello', 00016 Monterotondo Stazione, Italy

AND ELISABETTA FORESTI SERANTONI

Istituto di Mineralogia e Petrografia, Università di Bologna, Piazza S. Donato 1, 40127 Bologna, Italy

The structure of *p*-nitrobenzamide has been determined by X-ray diffraction analysis from 1158 independent non-zero reflexions measured on an automated single-crystal diffractometer. Crystals are monoclinic, space group $P2_1/c$, with $a = 7.643$ (1), $b = 6.766$ (1), $c = 13.847$ (2) Å, $\beta = 91.34$ (1)°, $Z = 4$. The structure has been solved by direct methods and refined by full-matrix least squares to a final R of 0.038. The symmetry of the C hexagon is lowered from D_{6h} (6/*mmm*) to C_{2v} (*mm*) as a result of substitution. The internal angles at the *ipso* atoms are $\alpha_{NO_2} = 122.6$ (2)° and $\alpha_{CONH_2} = 119.1$ (2)°. The carboxamido group is almost coplanar with the benzene nucleus, an unusual conformation for a benzamide derivative. The molecules are hydrogen bonded in crystallographically centrosymmetric pairs through their $-CONH_2$ groups; much weaker hydrogen bonds connect the two $-NH_2$ groups of each pair to two $-NO_2$ groups of adjacent pairs.

Introduction

As a part of our research programme of accurate determination of the molecular structures of benzene derivatives (Colapietro, Di Rienzo, Domenicano, Foresti Serantoni & Riva di Sanseverino, 1976; Domenicano, Foresti Serantoni & Riva di Sanseverino, 1977; Colapietro & Domenicano, 1977) we report here the crystal and molecular structure of *p*-nitrobenzamide, as obtained by X-ray diffraction analysis.

* Part II: Colapietro & Domenicano (1977).

Experimental

Commercial *p*-nitrobenzamide (Fluka) was recrystallized from ethanol. Pale-yellow prisms, suitable for X-ray diffraction work, were grown by evaporation of an acetone solution of the purified product. A crystal, *ca* 0.65 × 0.27 × 0.25 mm, was mounted on a Philips PW 1100 automatic single-crystal diffractometer. Accurate values for the cell parameters were derived by a least-squares fit to the measured θ values for 11 reflexions of the $h00$, $0k0$, $00l$, $h0h$, $\bar{h}0h$, hhh and $\bar{h}hh$ rows, in the θ range 19–43°. The reflexions were

Table 1. *Crystal data*

p-Nitrobenzamide, $C_7H_6N_2O_3$, FW 166·14. Monoclinic, space group $P2_1/c$ (systematic absences: 0k0, k = 2n + 1; h0l, l = 2n + 1), Z = 4, m.p. = 199–200°C.

a = 7·643 (1) Å[a]	V = 715·9 (2) Å³
b = 6·766 (1)	D_c = 1·541 g cm⁻³
c = 13·847 (2)	D_m = 1·54 [b]
β = 91·34 (1)°	

(a) Standard deviations are given in parentheses as units in the last digit. The radiation used was Cu $K\alpha$ (λ = 1·5418 Å).
(b) Measured by flotation in a mixture of carbon tetrachloride and n-hexane.

scanned along both the positive and negative sides of the 2θ circle, in order to correct for the zero scale error. Crystal data are given in Table 1.

The intensities were measured in the ω–2θ scan mode, with graphite-monochromatized Cu $K\alpha$ radiation. The scan width was 1·4°, the scan time 28 s; the background was measured for 5 s at each end of the scan. The size of the collimator employed was 0·8 mm. 1544 reflexions in the θ range 3–75° were measured, and 1165 having $I > 5\sigma(I)$ were considered as observed and used in subsequent calculations. Three standard reflexions were monitored every 220 reflexions; their intensities proved to be constant within ±2·1%. The intensities were corrected for Lorentz and polarization effects, but not for extinction or absorption (μ for Cu $K\alpha$ is 10·7 cm⁻¹).

Structure determination and refinement

The structure was solved by the iterative application of Σ_2 relations (Karle & Karle, 1966), with 189 reflexions with $|E| \geq 1·50$. An E map clearly showed all the non-H atoms of the molecule. A structure factor calculation based on the atomic positions from this map and with $\bar{B}$ = 2·96 Å² from a Wilson plot gave an R of 0·247. This was reduced to 0·137 by block-diagonal isotropic least-squares refinement, and then to 0·086 by anisotropic refinement (unit weights). At this stage a difference synthesis computed from terms with sin $\theta/\lambda \leq 0·40$ showed all the H atoms as well-defined peaks. Their introduction in a structure factor calculation lowered R to 0·068.

The final refinement of all the atomic parameters, including the positional and isotropic thermal parameters of the H atoms, was carried out by full-matrix least squares. The function minimized was $\Sigma w(|F_o| - K|F_c|)^2$, with $w = \sin \theta/\lambda$; seven strong, low-θ reflexions, which appeared to be severely affected by extinction, were excluded from the refinement. The final R and R_w for the 1158 reflexions used in the refinement were 0·038 and 0·040, respectively (refinement

1). In the last cycle all the shifts were less than 0·02σ. The number of observations per refined parameter was 1158/133 = 8·7.

An alternative refinement was carried out with the weighting function $w = 1/\sigma^2(F_o)$, with the experimental $\sigma(F_o)$ derived from the counting statistics (refinement 2). It converged to higher values for both R and R_w (0·040 and 0·067, respectively), and also gave a somewhat larger dispersion for the mean values of the minimized function over ranges of either F_o or sin θ/λ. A similar result has been obtained in the refinement of the crystal structure of p-phenylenediamine dihydrochloride (Domenicano, Foresti Serantoni & Riva di Sanseverino, 1977). The standard deviations on the atomic parameters obtained from refinements 1 and 2 are quite similar. Comparison of the two molecular geometries shows that all the differences between corresponding bond distances and angles are lower (and generally much so) than 3·5σ.* Although the individual differences are far from significant, the geometry of the C hexagon from refinement 1 is closer to perfect C_{2v} (mm) symmetry than that from refinement 2. We point

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* The differences in the values of the internal angles at the *ipso* atoms, α_{NO_2} and α_{CONH_2}, are about 1σ.

Table 2. *Final coordinates* ($\times 10^5$) *for non-hydrogen atoms*

Estimated standard deviations from the final full-matrix least-squares cycle are given in parentheses as units in the last digit.

	x	y	z
O(1)	53912 (19)	85251 (20)	40033 (9)
O(2)	81978 (22)	−3132 (23)	22075 (10)
O(3)	96208 (21)	−9484 (23)	35302 (10)
N(1)	65646 (24)	79577 (27)	54761 (11)
N(2)	86777 (21)	1172 (24)	30300 (10)
C(1)	69451 (21)	55171 (26)	41955 (11)
C(2)	66239 (25)	50644 (29)	32253 (12)
C(3)	71793 (24)	33027 (29)	28372 (12)
C(4)	80832 (22)	20013 (26)	34338 (11)
C(5)	84381 (25)	23976 (28)	43978 (12)
C(6)	78586 (24)	41671 (28)	47754 (12)
C(7)	62434 (22)	74461 (26)	45570 (12)

Table 3. *Final coordinates* ($\times 10^4$) *and isotropic thermal parameters for hydrogen atoms*

Estimated standard deviations from the final full-matrix least-squares cycle are given in parentheses as units in the last digit.

	x	y	z	B (Å²)
H(2)	6029 (31)	6034 (38)	2843 (17)	2·0 (5)
H(3)	6901 (30)	2956 (35)	2157 (17)	1·9 (4)
H(5)	9060 (31)	1507 (38)	4791 (17)	2·1 (5)
H(6)	8102 (29)	4405 (35)	5453 (17)	1·8 (4)
H(1N)	6051 (33)	9058 (43)	5665 (18)	2·3 (5)
H(2N)	7168 (33)	7181 (39)	5891 (18)	2·2 (5)

out here that the weighting scheme $w = \sin \theta/\lambda$ should, in principle, yield more accurate positional parameters for the non-H atoms.

The scattering factors of Cromer & Mann (1968) were used for O, N, and C. For H the values used were those of Hanson, Herman, Lea & Skillman (1964).

All calculations were carried out on the Univac 1110 computer of the Università di Roma with local crystallographic programs (Domenicano, 1968; Carruthers & Spagna, 1975).

Results and discussion

Tables 2 and 3 give the final atomic parameters from refinement 1.* Bond lengths and angles calculated from these parameters are given in Fig. 1; no corrections have been applied for thermal-motion effects. The equation of the least-squares plane through the six C atoms of the ring and the displacements of all the atoms from this plane are given in Table 4. Torsion angles are reported in Table 5.

The six-membered C ring

The symmetry of the C ring is C_{2v} (mm) within experimental error. The deviations from D_{6h} ($6/mmm$)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as a Supplementary Publication No. SUP 32839 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
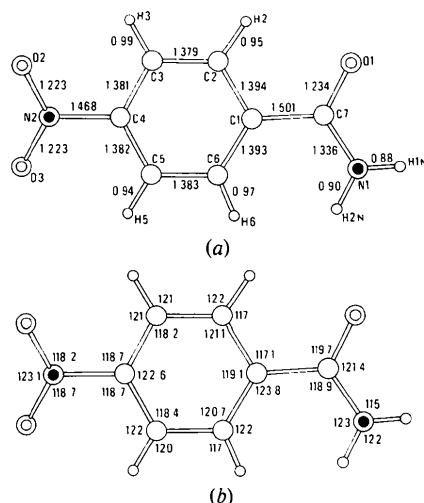
symmetry are highly significant (up to 16σ), and involve all the ring. Two out of the six C–C bonds, C(1)–C(2) and C(1)–C(6), are somewhat longer than the other four [$1\cdot393$–$1\cdot394$ vs $1\cdot379$–$1\cdot383$ Å; σ(C–C) = $0\cdot002$–$0\cdot003$ Å]. All the internal angles deviate significantly from the ideal value of $120°$ (Fig. 1b); the pronounced alternation of larger and smaller values should be noted.

Of particular interest are the C–C–C angles at the *ipso* atoms, α, since they are known to be sensitive to the electronic properties of the substituents (Domenicano, Vaciago & Coulson, 1975a,b; Domenicano, Mazzeo & Vaciago, 1976). The value of α_{NO_2}, $122\cdot6$ (2)°, is just marginally greater than the mean value, $122\cdot1$ (1)°, calculated from a number of reliable data on *para*-substituted nitrobenzenes (Domenicano, Vaciago & Coulson, 1975a).

The value of α_{CONH_2} is $119\cdot1$ (2)°. Only a few derivatives of benzene having the –CONH$_2$ functional group have been studied with reasonable accuracy by X-ray crystallography. The best structural results are

Table 4. Deviations from planarity

Equation of the least-squares plane through the six C atoms of the ring (referred to the crystallographic axes)

$$6\cdot6379x + 2\cdot9290y - 3\cdot6239z = 4\cdot7076$$

Displacements (Å) of atoms from the plane (the standard deviations in the atomic positions are $0\cdot0014$–$0\cdot0018$ Å for the non-H atoms, $0\cdot023$–$0\cdot026$ Å for the H atoms)

C(1)*	−0·002	C(7)	−0·034	H(2)	0·03
C(2)*	0·004	N(1)	−0·004	H(3)	−0·04
C(3)*	−0·003	N(2)	−0·011	H(5)	0·01
C(4)*	0·000	O(1)	−0·083	H(6)	−0·02
C(5)*	0·002	O(2)	−0·158	H(1N)	−0·09
C(6)*	−0·001	O(3)	0·122	H(2N)	0·02

* Atoms defining the least-squares plane.

Fig. 1. Molecular geometry of p-nitrobenzamide: (a) bond lengths (Å), (b) bond angles (°). Estimated standard deviations are $0\cdot002$ Å for C–N, C–O and N–O bonds, $0\cdot002$–$0\cdot003$ Å for C–C bonds, $0\cdot02$–$0\cdot03$ Å for C–H and N–H bonds, $0\cdot14$–$0\cdot17°$ for angles not involving H atoms, $1\cdot4$–$1\cdot7°$ for angles involving H atoms.

Table 5. Torsion angles (°)

Signs have been given according to the convention of Klyne & Prelog (1960). Estimated standard deviations are ca $0\cdot2°$.

(a) –NO$_2$ substituent

O(2)–N(2)–C(4)–C(3)	−7·2
O(2)–N(2)–C(4)–C(5)	172·3
O(3)–N(2)–C(4)–C(5)	−7·5
O(3)–N(2)–C(4)–C(3)	173·0

(b) –CONH$_2$ substituent

O(1)–C(7)–C(1)–C(2)	1·6
O(1)–C(7)–C(1)–C(6)	−177·3
N(1)–C(7)–C(1)–C(6)	2·9
N(1)–C(7)–C(1)–C(2)	178·2

Table 6. *Exocyclic* C—C *bond lengths* (Å) *and* α *angles* (°) *in benzamide derivatives*

Estimated standard deviations, σ, are given in parentheses as units in the last digit. The table includes data on benzamide itself and on its *para*-substituted and *N*-monosubstituted derivatives. The condition for inclusion was σ(α) ≤ 0·4°.

No.	Compound	Reference	C—C	α(CONH₂)
1	Benzamide	a	1·496 (3)	119·8 (2)
2	Benzamide (2:1 molecular complex with succinic acid)	b, c	1·495 (4)	119·1 (3)
3	Terephthalamide	d, c	1·489 (5)	119·5 (3)
4	p-Nitrobenzamide	e	1·501 (2)	119·1 (2)
5	Hippuric acid	f	1·496 (6)	120·1 (4)
6	Hippuric acid	g	1·495 (4)	119·5 (3)
7	Benzoyl-DL-leucylglycine ethyl ester	h, c	1·487 (4) 1·484 (4)	119·4 (3) 118·4 (3)
	Weighted mean values	i	1·495 (2) [1]	119·4 (2) [1]

References: (a) Blake & Small (1972). The values given here have been calculated from the atomic coordinates not corrected for libration given in the original paper. (b) Huang, Leiserowitz & Schmidt (1973). (c) The standard deviations have been calculated from the standard deviations of the atomic parameters quoted in the paper. (d) Cobbledick & Small (1972). (e) This work. (f) Ringertz (1971). (g) Harrison, Rettig & Trotter (1972). (h) Timmins (1975). The asymmetric unit contains two crystallographically independent molecules. (i) Mean values and their 'external' () and 'internal' [] standard errors have been calculated as in part I of this series (Domenicano, Foresti Serantoni & Riva di Sanseverino, 1977).

compared in Table 6, which also includes data on compounds where one of the two amidic protons is replaced by an aliphatic C. (The effect of this replacement on the α angle is expected to be undetectably small.) The values of α given in Table 6 fall in a rather narrow range, 118·4–120·1°. The weighted mean value, 119·4 (2)°, may be considered as a 'standard' value for α(CONH₂).

The —NO₂ *substituent*

The geometry of the nitro group is normal. The group is practically coplanar with the C atom of the ring to which it is bonded, C(4), but its plane makes an angle of 7·5° with the least-squares plane of the ring, due to a twist about the exocyclic C(4)—N(2) bond (Table 5).

The —CONH₂ *substituent*

Bond distances and angles in the carboxamido group are consistent with those observed in other aromatic amides. The dihedral angle between the plane through C(7), O(1) and N(1) and the least-squares plane through the C ring is, however, unusually low (2·3°). Crystal structure analyses of several aromatic amides have shown that a marked twist of the carboxamido

group is normal with these molecules, even if *ortho* substituents are not present. Twist angles in the range 23–33° have in fact been reported for benzamide (Penfold & White, 1959; Blake & Small, 1972), the 2:1 molecular complex of benzamide with succinic acid (Huang, Leiserowitz & Schmidt, 1973), terephthalamide (Cobbledick & Small, 1972), *p*-fluorobenzamide (Takaki, Taniguchi & Sakurai, 1965), *m*-methylbenzamide (Orii, Nakamura, Takaki, Sasada & Kakudo, 1963), *m*-fluorobenzamide (Taniguchi, Kato, Takaki & Sakata, 1965), *m*-hydroxybenzamide (Katsube, Sasada & Kakudo, 1966). The twist has been attributed to repulsion between an amidic H and an *ortho* H (Penfold
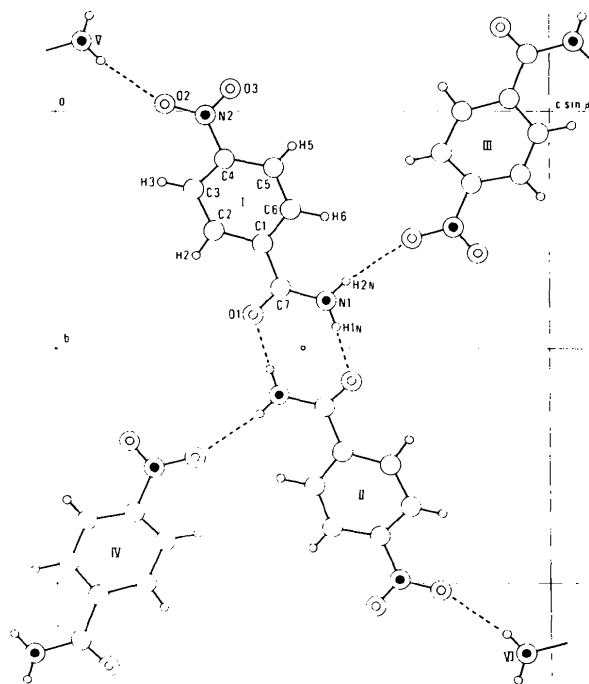

Fig. 2. Projection of the crystal structure down **a**. The broken lines represent intermolecular hydrogen bonds. The symmetry operations relating the different molecules to molecule i (which is at *x*,*y*,*z*) are: (ii) 1 − *x*, 2 − *y*, 1 − *z*; (iii) *x*, ½ − *y*, ½ + *z*; (iv) 1 − *x*, ½ + *y*, ½ − *z*; (v) *x*, ½ − *y*, −½ + *z*; (vi) 1 − *x*, ½ + *y*, ½ − *z*.

Table 7. *Geometry of the hydrogen bonds*

Estimated standard deviations are given in parentheses as units in the last digit. The superscripts ii and iii refer to the symmetry operations given in the caption of Fig. 2.

(a) Distances (Å)

O(1ⁱⁱ)···N(1)	2·910 (2)	O(1ⁱⁱ)···H(1N)	2·03 (3)
O(2ⁱⁱⁱ)···N(1)	3·220 (2)	O(2ⁱⁱⁱ)···H(2N)	2·34 (3)

(b) Angles (°)

O(1ⁱⁱ)···H(1N)—N(1) 173 (2)	O(2ⁱⁱⁱ)···H(2N)—N(1) 167 (2)

& White, 1959). It is more likely, however, that it is due to intermolecular effects resulting from the packing of the molecules (Leiserowitz & Schmidt, 1969); and indeed the crystal packing of p-nitrobenzamide is markedly different from that of the other amides quoted above.

The lack of axial symmetry in the carboxamido group and its being almost coplanar with the benzene ring gives rise to a severe 'in-plane' bending of the C(1)–C(7) bond. The difference between the C(6)–C(1)–C(7) and C(2)–C(1)–C(7) bond angles is 6·7°, to be compared with 3·4° in benzamide (Blake & Small, 1972), 5·2° in the 2:1 molecular complex of benzamide with succinic acid (Huang, Leiserowitz & Schmidt, 1973), 1·9° in terephthalamide (Cobbledick & Small, 1972).

The crystal structure

As generally found with primary amides (Leiserowitz & Schmidt, 1969) the molecules of p-nitrobenzamide are hydrogen bonded in crystallographically centrosymmetric pairs through their –$CONH_2$ groups. The packing of the pairs is novel, however. Whilst in the great majority of cases the centrosymmetric amide pair is found to be connected to adjacent pairs through N–H$\cdots$O=C hydrogen bonds, here the two –NH_2 groups of a pair link two –NO_2 groups from adjacent pairs (Fig. 2). This gives rise to an undulated layer of molecules extending along bc. The translational repeat unit of the layer is $3b$, $1c$; it contains the four molecules shown in Fig. 2. Adjacent layers are held together by van der Waals forces; three layers are comprised in the a thickness of the unit cell.

Geometrical details of the two N–H$\cdots$O hydrogen bonds are given in Table 7. The much greater length of the interpair bond should be noted.

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