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A Single-Crystal Neutron Diffraction Refinement of Benzamide at 15 and 123 K

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Abstract

C_7H_7NO, $P2_1/c$ with $Z = 4$, cell dimensions at 15K [123K] are $a = 5{\cdot}529(1)$ [$5{\cdot}549(1)$], $b = 5{\cdot}033(1)$ [$5{\cdot}033(1)$], $c = 21{\cdot}343(3)$ [$21{\cdot}548(4)$] Å, $\beta = 88{\cdot}73(1)$ [$89{\cdot}22(1)$]°, $V = 593{\cdot}77(1)$ [$601{\cdot}74(1)$] Å^3, $D_m = 1{\cdot}358$ [$1{\cdot}337$] g cm^{-3}. 2364 [2377] symmetry-independent reflections were measured at the Brookhaven High Flux Reactor [λ = 1·0411(1) Å]. Structure refinement gave values of $R(F^2) = 0{\cdot}044$ [0·063]. A rigid-body thermal motion analysis was applied. The internal modes for the C—H and N—H bonds were calculated. The benzene ring has a small B_5^2 distortion, with benzene C—C bond lengths, corrected for thermal motion, ranging from 1·392(1) to 1·401(1) Å. The internal ring angles are 119·7(1) to 120·1(1)°. The amide bond lengths are C—C 1·498(1), C=O 1·246(1) and C—N 1·341(1) Å. Benzene C—H bond lengths range from 1·084(2) to 1·089(2) Å and N—H bond lengths are 1·013(2) and 1·022(2) Å. The plane of the amide group makes an angle of 25·2(1)° with the mean plane of the benzene ring.

Introduction

The crystal structure of benzamide was determined by single-crystal X-ray analysis at room temperature by Blake & Small (1972). We report a neutron diffraction refinement at 15 and 123K to provide more precise molecular dimensions and for later use in a charge-density analysis based on X-ray data at those temperatures.

Experimental

Crystals of benzamide (Sigma Chemical Co.) were grown from benzene solution by slow evaporation. A crystal with dimensions 3·1 × 1·0 × 1·4 mm was selected for diffraction measurements. The data were collected at the Brookhaven High Flux Beam Reactor on the H6M four-circle diffractometer using a monochromated neutron beam obtained by reflection from Be(002) planes and calibrated against a reference KBr crystal (a_0 = 6·6000 Å at 295K). The temperature of the sample crystal was held within 0·5° of 15 and 123K inside a closed-cycle helium refrigerator.‡ Measurements were made first at 15 K and then at 123K. The lattice parameters, given in Table 1, were determined by least-squares fits to $\sin^2\theta$ vaues for 30 reflections with $52 < 2\theta < 57°$.

Table 1. *Crystal data for benzamide*

$C_6H_5CONH_2$; space group $P2_1/c$; $Z = 4$, molecular symmetry 1.

	Neutron data (λ = 1·0411 Å) (this work)		X-ray data (λ = 1·5418 Å) (Blake & Small, 1972)
	15K	123K	295K
a (Å)	5·529 (1)	5·549 (1)	5·607 (2)
b (Å)	5·033 (1)	5·033 (1)	5·046 (2)
c (Å)	21·343 (3)	21·548 (4)	22·053 (8)
β (°)	88·73 (1)	89·22 (1)	89·34
V (Å^3)	593·77 (1)	601·74 (1)	623·90
D_x (g cm^{-3})	1·355	1·337	1·288
μ_n (cm^{-1})	1·857		

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Table 2. *Atomic coordinates* ($\times 10^5$) *and anisotropic thermal parameters* ($\text{Å}^2 \times 10^4$) *for benzamide at* 15 K (*first line*) *and* 123 K (*second line*)

Standard deviations given in parentheses refer to the least significant digit. The temperature expression is given by $T = \exp(-2\pi^2\Sigma_i^3\Sigma_j^3h_ih_ja_i^*a_j^*U_{ij})$. Isotropic extinction factor g = 0·206 (9) × 10⁴ rad⁻¹ for 15 K data, 0·220 (11) × 10⁴ rad⁻¹ for 123 K data.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N	22364 (9)	23934 (10)	2772 (2)	85 (2)	50 (2)	80 (2)	−3 (2)	−28 (2)	9 (2)
	22277 (12)	23983 (13)	2795 (3)	219 (3)	124 (2)	204 (2)	−7 (2)	−66 (2)	9 (2)
O	19525 (14)	−19610 (14)	5351 (4)	78 (3)	42 (3)	93 (2)	−12 (2)	−34 (2)	1 (2)
	19589 (21)	−19510 (20)	5334 (5)	237 (5)	103 (4)	261 (5)	−15 (4)	−107 (4)	−11 (3)
C1	47559 (11)	6609 (13)	10983 (3)	55 (2)	43 (2)	54 (2)	−5 (2)	−14 (2)	3 (2)
	47492 (15)	6764 (17)	10953 (4)	150 (4)	115 (3)	167 (2)	−6 (3)	−28 (3)	−13 (3)
C2	64802 (11)	26920 (13)	10515 (3)	66 (2)	58 (2)	67 (2)	−18 (2)	−16 (2)	11 (2)
	64748 (17)	26935 (19)	10486 (4)	194 (4)	175 (4)	195 (5)	−53 (3)	−29 (3)	2 (3)
C3	82538 (11)	29300 (13)	15027 (3)	60 (2)	66 (2)	80 (2)	−18 (2)	−15 (2)	3 (2)
	82423 (17)	29445 (20)	14980 (5)	176 (4)	209 (4)	234 (5)	53 (3)	−37 (3)	−29 (3)
C4	82915 (12)	11604 (13)	20061 (3)	65 (2)	73 (3)	70 (2)	−7 (2)	−22 (2)	2 (2)
	82792 (17)	11971 (21)	19992 (5)	170 (4)	223 (4)	243 (5)	−5 (3)	−69 (3)	−33 (3)
C5	65490 (12)	−8397 (13)	20597 (3)	74 (2)	64 (2)	71 (2)	10 (2)	−21 (2)	16 (2)
	65380 (18)	−7923 (20)	20525 (4)	209 (4)	200 (4)	227 (5)	−4 (3)	−85 (4)	25 (3)
C6	47998 (12)	−11044 (12)	16046 (3)	67 (2)	47 (2)	70 (2)	−11 (2)	−22 (2)	12 (2)
	47921 (17)	−10644 (18)	16000 (4)	183 (4)	145 (4)	208 (5)	−19 (3)	−61 (3)	27 (3)
C7	28666 (11)	2697 (12)	6144 (3)	58 (2)	34 (2)	57 (2)	−2 (2)	−13 (2)	0 (2)
	28637 (16)	2791 (16)	6140 (4)	169 (4)	106 (3)	167 (5)	−2 (3)	−39 (3)	−9 (3)
H2	64797 (31)	40619 (35)	6580 (8)	266 (7)	213 (7)	191 (7)	−68 (6)	−52 (5)	100 (5)
	64685 (46)	40519 (53)	6556 (11)	466 (13)	398 (12)	344 (9)	170 (10)	−68 (9)	144 (9)
H3	96052 (29)	45037 (34)	14579 (8)	207 (7)	204 (7)	264 (7)	−109 (6)	−46 (5)	21 (6)
	95821 (44)	45049 (54)	14538 (12)	377 (12)	422 (13)	494 (14)	−212 (10)	−72 (10)	10 (11)
H4	96720 (30)	13445 (38)	23605 (8)	214 (7)	270 (8)	198 (7)	−55 (6)	−106 (5)	23 (6)
	96479 (43)	13881 (57)	23501 (12)	352 (11)	490 (14)	423 (12)	−72 (10)	−207 (10)	2 (10)
H5	65401 (31)	−21902 (36)	24557 (8)	257 (7)	218 (7)	195 (7)	−38 (6)	−63 (5)	98 (5)
	65328 (48)	−21417 (55)	24475 (12)	479 (13)	425 (13)	416 (12)	−68 (11)	−179 (10)	173 (10)
H6	34517 (29)	−26746 (34)	16351 (8)	210 (7)	183 (6)	251 (7)	−92 (6)	−47 (5)	54 (5)
	34514 (43)	−26302 (48)	16299 (12)	389 (11)	302 (10)	457 (12)	−151 (9)	−142 (9)	115 (9)
H7	8507 (29)	21824 (33)	−309 (7)	212 (6)	187 (6)	208 (7)	−6 (5)	−104 (5)	15 (5)
	8546 (39)	21870 (43)	−281 (10)	355 (10)	268 (9)	337 (9)	7 (8)	−161 (8)	12 (8)
H8	26663 (31)	42643 (31)	4172 (80	261 (7)	110 (6)	242 (7)	−24 (5)	−66 (5)	−8 (5)
	26573 (41)	42622 (40)	4160 (10)	376 (11)	194 (8)	380 (9)	−37 (8)	−98 (8)	2 (8)

Intensity data for reflections ($+h$, $+k$, $\pm l$; $h \leq 8$, $k \leq 7$, $|l| \leq 30$) were measured by the $\omega/2\theta$ step-scan method. Scan widths were fixed at $\Delta 2\theta = 3{\cdot}2°$ for $\sin\theta/\lambda < 0{\cdot}406$ Å⁻¹, and were varied as $\Delta 2\theta = (2{\cdot}639 + 2{\cdot}195\tan\theta)°$ at higher angles up to $(\sin\theta/\lambda)_{\max}$ of 0·787 Å⁻¹. Counts were accumulated at each step for a preset number of counts of the direct beam requiring ~1·5 s. Between 65 and 90 steps (N) were taken per scan with at least 10% of N at each end being for background counts. The intensities of two test reflections, monitored after every 50 scans, were constant within 3%. Integrated intensities, I, were obtained by subtracting from the cumulative scan counts the background counts estimated from the first and last 10% of the scans. The variances $\sigma^2(I)$ were estimated from counting statistics. Absorption corrections (de Meulenaer & Tompa, 1965; Templeton & Templeton, 1973) were applied using the μ/ρ value of 2475 m² kg⁻¹ for bound hydrogen at λ = 1·0411 Å (McMullan & Koetzle, 1979). Transmission factors ranged from 0·752 to 0·845. The F_o^2 ($= I.\sin 2\theta$) values of equivalent $0kl$ reflections were averaged [R_{int} = 0·011 (15K) and 0·013 (123K) for 198 pairs], to give 2364 (15K) and 2377 (123K) reflections for the structure refinements.

Initial atomic parameters for the 15K model were the coordinates of Blake & Small (1972) and assumed isotropic U values (0·01 Å² for C, N, O, and 0·02 Å² for H). The refined 15K parameters were taken as starting values for refinement against the 123K data. The residuals $\Sigma w|F_o^2 - F_c^2|^2$ were minimized by full-matrix least-squares methods with weights $w = [\sigma^2(F_o^2) + (0{\cdot}02F_o^2)^2]^{-1}$. Coherent neutron-scattering lengths were taken from Koester (1977). The variable parameters were: positional and anisotropic thermal parameters of the 16 non-equivalent atoms, one scale factor and the isotropic secondary-extinction parameter for a type I crystal with Lorentzian distribution in mosaic spread (Becker & Coppens, 1974). Use of anisotropic extinction parameters resulted in no significant improvement in agreements. The indices of fit at convergence ($P_i/\sigma_i < 0{\cdot}01$) were $R(F^2)$ = 0·044, 0·063, $wR(F^2)$ = 0·057, 0·068, S = 1·11, 1·05 for the 15 and 123K data respectively. In final $\Delta\rho$ maps, the largest residuals $|\rho|$ were 1·3% (15K), 1·6% (123K) of $\rho_{\max}$ at the N atom and were within the estimated noise levels of both maps. Extinction corrections ($\times F_o{}^2$) > 1·05 were applied to 127 (15K) and 69 (123K) observations, the largest being 1·51 for reflection $10\bar{4}$ in both data sets. The final nuclear positional and thermal parameters are in Table 2.* The structure determinations were carried out with the least-squares program

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* Lists of observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54030 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Rigid-body thermal motion analysis of benzamide*

Origin at center of mass, l_1 parallel to C2—C3; l_2 is 8° from C2···C6, l_3 is $l_1 \times l_2$. R.m.s. ($U_{ij\,\mathrm{obs}} - U_{ij\,\mathrm{calc}}$) = 0·0004(4) Å^2 at 15 K, 0·0008(9) Å^2 at 123 K.

	l_1		l_2		l_3	
	15 K	123 K	15 K	123 K	15 K	123 K
T (translational) (Å^2 × 10^4)	47 (1)	132 (3)				
	3 (1)	18 (2)	41 (1)	139 (3)		
	1 (1)	−4 (2)	9 (1)	−32 (3)	63 (2)	160 (4)
ω (vibrational) (rad^2 × 10^5)	164 (11)	545 (2)				
	−3 (3)	6 (8)	36 (4)	103 (9)		
	2 (4)	4 (10)	4 (3)	19 (6)	33 (3)	101 (7)
S (cross-tensor) (rad Å × 10^6)	−5 (6)	57 (14)	−29 (9)	169 (19)	5 (6)	78 (14)
	3 (5)	32 (12)	−12 (5)	4 (10)	−1 (3)	−25 (8)
	7 (4)	39 (8)	13 (3)	90 (6)	7 (3)	61 (8)

of Lundgren (1982) and other programs in use at Brookhaven National Laboratory. The atomic notation and thermal ellipsoids at 15 and 123 K are shown in Fig. 1.

Discussion

Thermal motion analysis and corrections

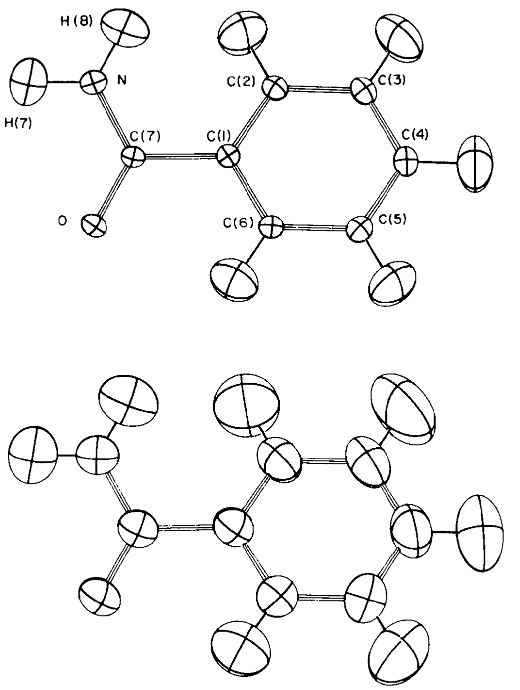

Fig. 1. Atomic notation and thermal ellipsoids for benzamide. Upper figure, 15 K; lower figure, 123 K.

Table 4. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°) *for benzamide*

Bond lengths

	From neutron data (this work)			From X-ray data (Blake & Small, 1972)
	15 K	123 K	Corrected for thermal motion*	Corrected for thermal motion at 295 K
C1—C2	1·400 (1)	1·398 (1)	1·401	1·392 (4)
C1—C6	1·400 (1)	1·397 (1)	1·401	1·389 (4)
C1—C7	1·498 (1)	1·497 (1)	1·498	1·501 (4)
C2—C3	1·395 (1)	1·393 (1)	1·395	1·398 (5)
C3—C4	1·396 (1)	1·393 (1)	1·397	1·378 (5)
C4—C5	1·396 (1)	1·395 (1)	1·398	1·390 (5)
C5—C6	1·392 (1)	1·391 (1)	1·392	1·400 (5)
C7—O	1·244 (1)	1·243 (1)	1·245	1·249 (3)
C7—N	1·339 (1)	1·337 (1)	1·340	1·342 (3)
C2—H2	1·087 (2)	1·088 (3)	1·094†	
C3—H3	1·092 (2)	1·085 (3)	1·091	
C4—H4	1·090 (2)	1·083 (3)	1·091	
C5—H5	1·085 (2)	1·089 (3)	1·087	
C6—H6	1·087 (2)	1·085 (3)	1·089	
N—H7	1·026 (2)	1·022 (3)	1·023	
N—H8	1·018 (2)	1·013 (3)	1·011	

Bond angles (e.s.d.'s 0·1°)

	15 K	123 K
Benzene ring		
C2—C1—C6	119·7	119·5
C1—C2—C3	120·1	120·2
C2—C3—C4	120·0	120·0
C3—C4—C5	120·1	120·0
C4—C5—C6	120·0	120·1
C1—C6—C5	120·1	120·2
Amide group		
C2—C1—C7	122·1	122·1
C6—C1—C7	118·2	118·4
C1—C7—N	117·3	117·3
C1—C7—O	120·3	120·3
O—C7—N	122·3	122·3
H2—C2—C1 (e.s.d.'s 0·2°)	120·4	120·2
H2—C2—C3	119·4	119·6
H3—C3—C2	119·5	119·5
H3—C3—C4	120·6	120·5
H4—C4—C3	120·2	120·2
H4—C4—C5	119·8	119·8
H5—C5—C4	120·5	120·4
H5—C5—C6	119·5	119·5
H6—C6—C5	120·9	120·9
H6—C6—C1	119·0	118·9
H7—N—C7	118·0	118·1
H8—N—C7	121·0	121·2
H7—N—H8	117·8	117·7

Selected torsion angles (e.s.d.'s 0·1°)

	15 K	123 K
C2—C1—C7—O	154·3	153·6
C2—C1—C7—N	−25·4	−26·0
C6—C1—C7—O	−24·6	−25·3
C6—C1—C7—N	155·8	155·1
O—C7—N—H7	5·0	4·9
O—C7—N—H8	164·4	164·8

* Mean of corrected values from 15 and 123 K data.

† The libration-motion corrections ⟨+0·020 Å⟩ and anharmonic corrections ⟨−0·020 Å⟩ cancel.

A rigid-body thermal motion analysis was calculated using *ORSBA* (Johnson, 1970). The internal motion of the C—H and N—H bonds at 15 K was calculated using the program *FLAP* (Craven & He, 1982). The mean-square amplitudes for the stretching, in-plane half-scissors and wagging motions were 0·0052, 0·0204, 0·0140 Å^2 for the C—H bonds and 0·0050, 0·0171, 0·0134 Å^2 for the N—H bonds. The overall least-squares fit was good with r.m.s. ($U_{ij\,\mathrm{obs}} - U_{ij\,\mathrm{calc}}$) = 0·0004 (4) Å^2 at 15 K and 0·0008 (9) Å^2 at 123 K. The rigid-body parameters are given in Table 3.

The C—C, C—N and C=O bond lengths corrected for librational motion are given in Table 4. The C—H and N—H bond lengths are corrected for riding motion and anharmonic stretching using Δ =

$-3k\Delta U/2$, where ΔU is the difference in thermal motion of the two atoms along the bond and $k = 2{\cdot}0\ \text{Å}^{-1}$ for C—H $2{\cdot}2\ \text{Å}^{-1}$ for N—H.

The molecular structure

The bond lengths, valence angles and selected torsion angles are given in Table 4. The benzene ring bond lengths and angles have *m* symmetry normal to the plane of the benzene ring along the diagonal C1—C4. Both the 15 and 123K and the thermally corrected bond lengths show that C1—C2 = C1—C6 > C3—C4 = C4—C5 > C2—C3 ≃ C5—C6, with small, possibly significant, differences of 0·004 Å $(\sim 4\sigma)$. This is consistent with the trend reported by Domenicano, Vaciago & Coulson (1975) from the crystal structures of monosubstituted benzene derivatives. The bond-length differences are in the same directions and of the same order of magnitude as reported by Domenicano & Vaciago (1979) for some aniline and azobenzene derivatives.

The benzene valence angles are 120·0° within 3σ. There is no significant angle closure as observed in tetraphenylmethane (Robbins, Jeffrey, Chesick, Donohue, Cotton, Frenz & Murillo, 1975) and other compounds containing C_6H_5—CC_3 groups (Domenicano & Vaciago, 1979). The closure of the C2—C1—C6 angle of 119·7(1)° is significant at the 3σ level. The ring has a small boat distortion to B_5^2, with C2 and C5 0·009(1) and 0·013(1) Å respectively above a plane through C1, C3, C4 and C6, within which the displacements are ±0·0006(9) Å. The benzene C—H bond lengths are 1·086 Å within 1σ. H2, H3 and H4 are in the mean plane of the benzene ring within 0·009(2) Å, but H5 and H6 are significantly displaced by +0·031(2) and −0·013(2) Å respectively. H5 is 0·044(3) Å from the mean plane of H2, H3, H4 and H6.

The amide C7 atom is −0·038(1) Å out of the mean benzene ring plane. The amide group is twisted so that the O—C7—C1—C2 torsion angle is 154·3 (1)°. The angle between the amide plane and the mean benzene ring plane is 25·2(3)° at 15K, 25·8 (4)° at 123K. The amide group is non-planar, with H7 and H8 0·076(2) and 0·236(2) Å out of the C1, C7, O, N plane. The twist of the amide group out of the benzene plane and the further displacement of H8 from the amide plane are clearly consequences of the H8···H2 intramolecular interaction. The H8···H2 distance of 2·480(2) Å would be reduced to 1·77 Å for a fully planar molecule.

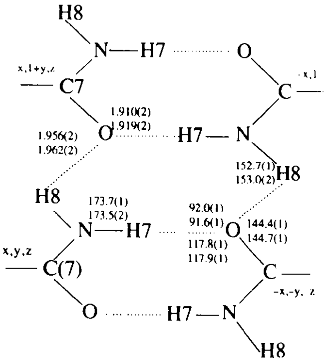

Fig. 2. Hydrogen bonding in the crystal structure of benzamide. Distances are given in Å, angles in °.

The hydrogen bonding

The hydrogen bonding shown in Fig. 2 consists of cyclic dimers linked laterally to form ribbons which extend throughout the crystal in the direction of the *b* axis. This is the axis which shows least contraction on cooling. The two N—H···O=C hydrogen bonds are shorter and longer respectively than the mean value of 1·934 Å for amides reported by Taylor, Kennard & Versichel (1984). As commonly observed, the smaller N—H···O angle is associated with the longer bond. The coordination about the carbonyl O atom is close to being planar with the sum of angles equal to 354°.

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