Crystal and Molecular Structure of 1-(4-Bromophenyl)azetidin-2-one

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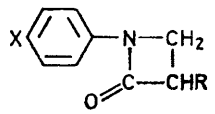
Crystals of the title compound are monoclinic with a = 10·175, b = 7·403, c = 11·804 Å, β = 99·8° space group $P2_1/a$, with Z = 4. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares technique to R 0·058 from diffractometer data consisting of 1814 reflections. Both the β-lactam and the phenyl rings are essentially planar, the torsion angle about the bond joining the two rings being 5·5°.

EVER since the identification of the four-membered β-lactam rings in the molecules of the antibiotics penicillin [1] and cephalosporin C2 [2] by X-ray diffraction techniques, the properties of compounds containing such rings have been of considerable interest. The four-membered ring has the same chemical constitution as a *cis*-peptide linkage, and the synthesis of β-lactams from α- and β-amino-acids has been reported.[3,4] We report here an X-ray study of the structure of 1-(4-bromophenyl)-azetidin-2-one (I). The only other accurate X-ray study



(I) X = Br, R = H
(II) X = Cl, R = Pr^i

of a β-lactam derivative concerns the structure of 1-(*p*-chlorophenyl)-3-isopropylazetidin-2-one (II).[5]

EXPERIMENTAL

A fine needle-shaped crystal of (I) was used for the determination of crystal parameters on a goniostat.

Crystal Data.—C_9H_8NOBr, M = 225·9. Monoclinic, a = 10·175(2), b = 7·403(2), c = 11·804(3) Å, β = 99·8°, U = 876 Å^3, D_m = 1·72, Z = 4, D_c = 1·71. Space group $P2_1/a$. Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 63·3 cm^{-1}.

Intensity data were collected by the stationary-crystal–stationary-counter method using balanced nickel–cobalt filter pairs. First, the data set was measured manually on a General Electric XRD 3 diffractometer. A second set of data was collected on a General Electric XRD 490 automatic diffractometer from a larger crystal. The two sets of data were scaled and averaged to yield 1814 unique reflection amplitudes within the copper sphere. Of these, 1627 (*ca.* 89%) were considered observed and used in structure determination, after placing the data on an absolute scale by Wilson's method.

Structure Determination and Refinement.—The bromine positions were easily derived from a three-dimensional sharpened Patterson map. The molecule was unambiguously located in the bromine-phased electron-density map. The molecule was planar with its plane almost parallel to the *ac* plane. After a few cycles of isotropic least-squares refinement of the atomic parameters, an electron-density difference map was calculated which revealed all the hydrogen atom positions. The structure was further refined with the non-hydrogen atoms ascribed anisotropic thermal parameters; unit weights were assigned in the initial stages and $1/\sigma$ type weighting in the final cycles (where σ represents the standard deviation in $|F_o|$ based mainly on counting statistics). The final R was 0·058, the parameter shifts at this stage being $<0{\cdot}1\ \sigma$. Final positional and thermal parameters are listed in Tables 1 and 2.† The molecule as seen

TABLE 1

Fractional co-ordinates and the estimated standard deviations

	x	y	z
Br	0·1348(1)	0·1180(1)	0·1137(1)
O	0·7760(3)	0·1140(4)	0·5020(3)
N(1)	0·7264(3)	0·1204(3)	0·3011(2)
C(1)	0·8385(3)	0·1189(4)	0·2389(3)
C(2)	0·9318(3)	0·1168(4)	0·3560(4)
C(3)	0·8046(3)	0·1163(3)	0·4070(3)
C(4)	0·5892(3)	0·1238(3)	0·2600(3)
C(5)	0·5440(3)	0·1427(3)	0·1427(3)
C(6)	0·4106(3)	0·1418(4)	0·1008(3)
C(7)	0·3215(3)	0·1236(3)	0·1746(3)
C(8)	0·3627(3)	0·1068(4)	0·2914(3)
C(9)	0·4975(3)	0·1078(3)	0·3337(3)
H(1)	0·838(75)	0·019(61)	0·191(67)
H(2)	0·838(69)	0·226(56)	0·189(63)
H(3)	0·980(34)	0·016(28)	0·368(31)
H(4)	0·981(45)	0·223(37)	0·373(41)
H(5)	0·608(51)	0·152(42)	0·089(47)
H(6)	0·366(62)	0·171(50)	0·017(56)
H(7)	0·297(69)	0·083(56)	0·334(62)
H(8)	0·525(61)	0·076(49)	0·418(55)

TABLE 2

Thermal parameters of atoms

(*a*) Anisotropic * (× 10^4)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	82	357	147	−23	13	29
O(1)	131	500	68	76	31	−21
N(1)	73	290	65	5	37	4
C(1)	72	405	79	3	37	11
C(2)	92	299	94	7	−1	1
C(3)	102	294	70	10	24	−4
C(4)	84	221	73	−1	45	−8
C(5)	95	036	66	−4	52	14
C(6)	95	361	66	−4	53	14
C(7)	75	220	100	−14	25	2
C(8)	87	330	92	20	72	41
C(9)	103	315	69	19	63	25

(*b*) Isotropic (× 10^3)

	U_{iso}		U_{iso}
H(1)	87	H(5)	56
H(2)	79	H(6)	71
H(3)	28	H(7)	79
H(4)	46	H(8)	71

* T = exp $-2\pi^2$ ($U_{11}h^2a^{*2}$ + $U_{22}k^2b^{*2}$ + $U_{33}l^2c^{*2}$ + $2U_{12}hka^*b^*$ + $2U_{13}hla^*c^*$ + $2U_{23}klb^*c^*$).

† Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20822 (8 pp.). For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

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[5] R. Parthasarathy, *Acta Cryst.*, 1970, *B*, **26**, 1283.

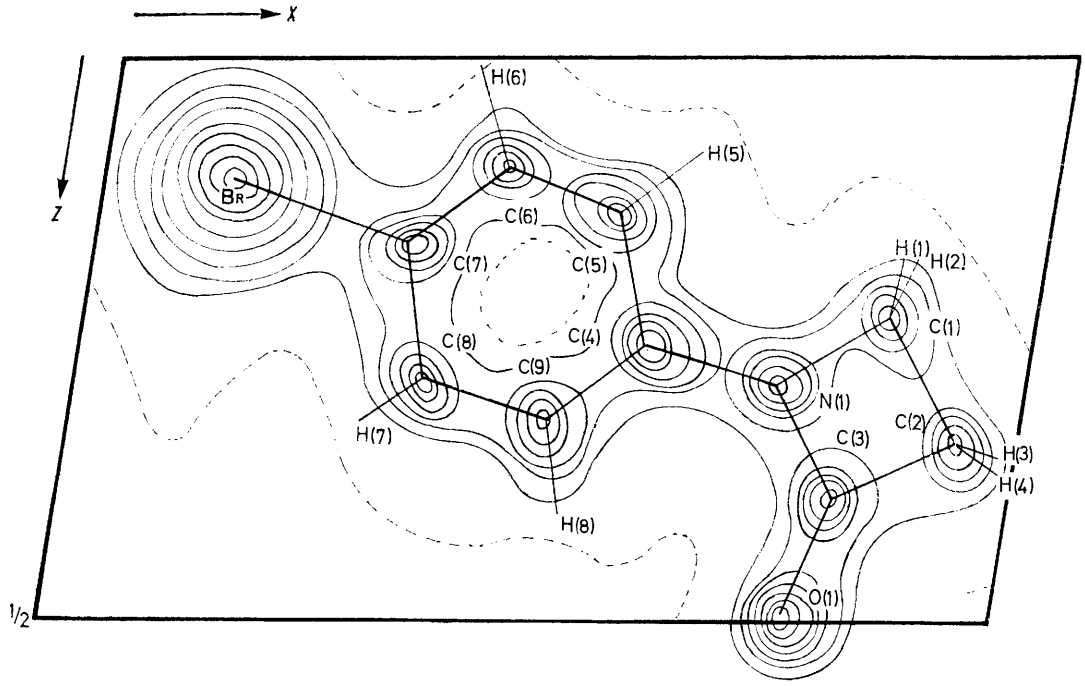

FIGURE 1 Electron-density section at $y = 0{\cdot}13$ showing the atomic positions. Contours are at equal but arbitrary intervals except around bromine

in the section at $y = 0{\cdot}13$ of the final three-dimensional electron-density map is shown in Figure 1. Bond distances and angles are given in Table 3. For comparison, the corresponding values observed in the structure of (II) are given in parentheses. Bond distances and angles involving non-hydrogen atoms are considered accurate to 0·007 Å and 0·3° respectively.

TABLE 3

Bond distances (Å) and angles (deg) in (I), with corresponding values for (II) in parentheses

(*a*) Distances

N(1)–C(1)	1·459(1·481)	C(1)–H(1)	0·93
N(1)–C(3)	1·363(1·367)	C(1)–H(2)	0·98
N(1)–C(4)	1·399(1·409)	C(2)–H(3)	0·89
C(1)–C(2)	1·539(1·575)	C(2)–H(4)	0·94
C(2)–C(3)	1·518(1·518)	C(5)–H(5)	0·98
C(3)–O(1)	1·207(1·210)	C(6)–H(6)	1·04
C(4)–C(5)	1·390	C(8)–H(7)	0·92
C(5)–C(6)	1·363		
C(6)–C(7)	1·368	C(1) · · · C(3)	2·073(2·100)
C(7)–C(8)	1·376		
C(8)–C(9)	1·378	N(1) · · · C(2)	2·081(2·094)
C(9)–C(4)	1·385		
C(7)–Br	1·914		

(*b*) Bond angles (deg.)

C(1)–N(1)–C(3)	94·5(95·0)	C(2)–C(1)–H(1)	106
C(1)–N(1)–C(4)	130·2(131·8)	C(2)–C(1)–H(2)	119
C(3)–N(1)–C(4)	135·3(132·6)	N(1)–C(1)–H(1)	112
N(1)–C(1)–C(2)	87·9(86·5)	N(1)–C(1)–H(2)	113
C(1)–C(2)–C(3)	85·4(85·5)	H(1)–C(1)–H(2)	106
C(2)–C(3)–N(1)	92·0(93·0)	C(1)–C(2)–H(3)	113
C(2)–C(3)–O(1)	136·5(136·1)	C(1)–C(2)–H(4)	114
N(1)–C(3)–O(1)	131·1(130·9)	C(3)–C(2)–H(3)	115
C(5)–C(4)–N(1)	119·2	C(3)–C(2)–H(4)	112
C(5)–C(4)–C(9)	119·4	H(3)–C(2)–H(4)	114
N(1)–C(4)–C(9)	121·3	C(4)–C(5)–H(5)	120
C(4)–C(5)–C(6)	120·5	C(6)–C(5)–H(5)	120
C(5)–C(6)–C(7)	119·8	C(5)–C(6)–H(6)	126
C(6)–C(7)–C(8)	121·7	C(7)–C(6)–H(6)	114
C(7)–C(8)–C(9)	118·5	C(7)–C(8)–H(7)	116
C(8)–C(9)–C(4)	120·5	C(9)–C(8)–H(7)	125
Br–C(7)–C(6)	119·1	C(8)–C(9)–H(8)	117
Br–C(7)–C(8)	119·2	C(4)–C(9)–H(8)	122

DISCUSSION

Description of the Structure.—The β-lactam system and the bonds around the nitrogen atom are planar. It is seen that in (I) the contacts N(1) · · · C(2) and C(1) · · · C(3) are shorter, while the C(1)–C(2) bond assumes a value closer to normal carbon–carbon single-bond distances in comparison with the corresponding values in (II). One could consider the β-lactam ring as being derived in principle from a *cis*-peptide by the linkage of α-carbons of adjacent units. In fact, bond distances in the β-lactam unit in (I) and (II) agree remarkably well with the dimensions for the average *cis*-peptide unit in the structures of *cyclo*-Pro-Pro-Pro and *cyclo*-Pro-Pro-Hyp, which consist only of *cis*-peptides.[6] This correspondence is graphically brought out in Figure 2. The results of the least-squares planes and torsion angle calculations are given in Tables 4 and 5. It is seen that the lactam and

TABLE 4

Deviation (Å) of atoms from least-squares planes

Plane (1): C(4)—(9), N(1)

C(4) — 0·007, C(5) 0·005, C(6), 0·001, C(7) — 0·003, C(8) 0·001, C(9) 0·005, H(5) — 0·02, H(6) 0·13, H(7) — 0·09, H(8) — 0·13, Br — 0·04, N(1) — 0·04

Plane (2): C(1)—(4), N(1)

N(1) 0·004, C(1) — 0·004, C(2) 0·004, C(3) — 0·004, O(1) — 0·008, C(4) — 0·015

[6] G. Kartha, G. Ambady, and P. V. Shankar, unpublished data.

the phenyl rings are nearly coplanar, thus confirming results of earlier n.m.r. and u.v. studies.[7]

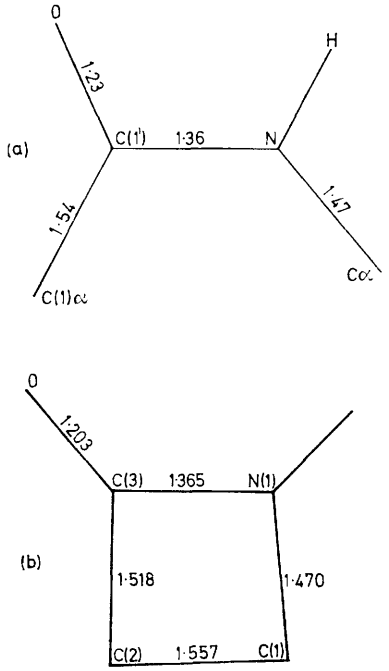

FIGURE 2 Mean bond distances in the *cis*-peptide in the structures of (a) cyclo-Pro-Pro-Pro and *cyclo*-Pro-Pro-Hyp (ref. 6) compared with (b) the mean dimensions of the β-lactam moiety in (I) and (II)

TABLE 5

Torsion angles (deg.) in (I), with the corresponding angles in (II) in parentheses

C(3)–N(1)–C(4)–C(5)	174·8(172·0)
C(1)–N(1)–C(4)–C(5)	−5·5(7·8)
N(1)–C(1)–C(2)–C(3)	0·6(0·6)
C(1)–C(2)–C(3)–N(1)	−0·7(−0·7)
C(2)–C(3)–N(1)–C(1)	0·6(0·7)
C(3)–N(1)–C(1)–C(2)	−0·7(−0·7)

These values relate to one molecule, but, as the structure is centrosymmetric, enantiomeric molecules also occur.

Molecular Packing.—The crystal structure viewed down the *b* axis is shown in Figure 3. The molecules lie in sheets parallel to the *ac* plane, the stacking distance being 3·7 Å. All intermolecular contacts are >3·4 Å.

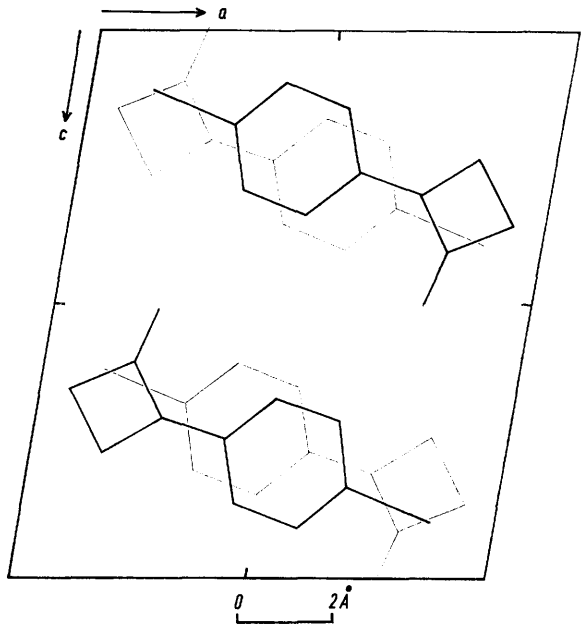

FIGURE 3 Packing of (I) in the unit cell. Molecules are stacked head-to-tail, stacking distance 3·7 Å

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