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The Crystal Structure of 2-Cyano-5-bromobenz[f][1,3]oxazepine

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The crystal structure of 2-cyano-5-bromobenz[f][1,3]oxazepine has been investigated by three-dimensional single crystal X-ray diffraction methods. The crystals are orthorhombic, space group $P2_12_12_1$, with unit cell dimensions $a = 10.563 \pm 0.002$ Å, $b = 21.865 \pm 0.005$ Å, $c = 3.978 \pm 0.001$ Å. There are four molecules in the unit cell.

Atomic structural parameters has been derived, by Patterson, heavy atom and least squares refinement methods, from 577 independent reflections whose intensities had been visually estimated from the photographs taken of three equi-inclination Weissenberg layers. The final R-value is 0.115.

The interatomic distances in the oxazepine ring indicate delocalization of the π-electrons within that system. The bond angle at the carbon atom in the cyanide group is 167° (4°), and the values obtained for the C≡N and the C–CN distances 1.08 (0.05) and 1.52 (0.05) Å, respectively, differ somewhat from accepted values.

This work is related to an investigation dealing with the formation and structure of the seven-membered rings which are obtained in the photolysis of quinoline N-oxides [1] and isoquinoline N-oxides.[2]

Preliminary crystal data and a c-axis projection of the crystal structure of 2-cyano-5-bromobenz[f][1,3]oxazepine (I) (Fig. 1) have previously been described in this periodical,[3] and an X-ray crystal structure analysis of a related compound (2-phenyl-7-bromobenz[d][1,3]oxazepine (II) has recently been completed.[4]

The present three-dimensional analysis of I was performed to obtain more conclusive information about the geometry of the oxazepine ring and also to compare the structure of I with that of II.

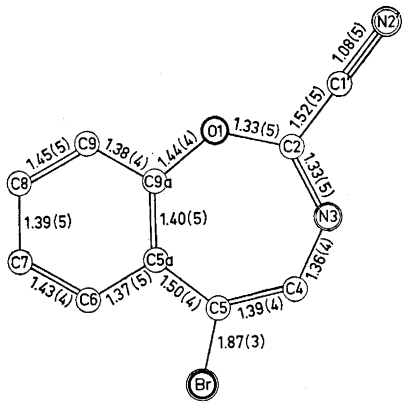

Fig. 1. Schematic drawing of 2-cyano-5-bromobenz[f][1,3]oxazepine. Distances in in Å.

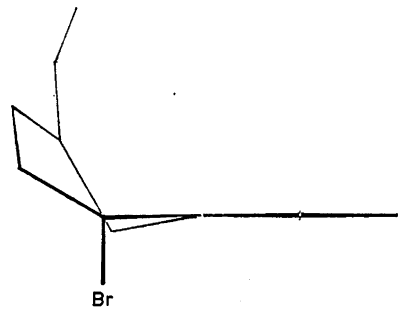

Fig. 2. A drawing of the molecule with the plane of the benzene ring perpendicular to the plane of the paper.

EXPERIMENTAL

The compound (I) was prepared by C. Lohse, as previously described.[3]

Accurate unit cell dimensions were determined by a least squares refinement [5] of measurements, taken from Guinier powder diagrams made with Cu$K\alpha$ radiation and with quartz as an internal standard.

From a needle-shaped crystal, a piece of dimensions $0.15 \times 0.15 \times 0.40$ mm^3 was cut. This crystal piece was oscillated around the needle axis, and equi-inclination Weissenberg photographs of the $hk0$, $hk1$, and $hk2$ reflections were taken, using Cu$K\alpha$ radiation by the multiple-film technique. The intensities of the diffracted spectra were estimated visually by comparison with a photographic scale.[6]

The usual Lorentz and polarization corrections were applied,[7] but no absorption corrections were made. 577 independent reflections out of 910 possible were recorded with non-zero amplitudes. These reflections were brought on to a common scale, to form a single data set by comparing their amplitudes with those measured from an $0kl$ precession photograph, taken with the same crystal.

The following reflections were systematically absent: $h00$ when h is odd, $0k0$ when k is odd, and $00l$ absent when l is odd, so the space group was assumed to be $P2_12_12_1$, even though the last extinction condition was based on very few reflections and hence was doubtful. However, the three-dimensional arrangement of bromine atoms deduced from the Patterson projections $\varrho(u, v)$ and $\varrho(v, w)$ lent further support to the assumption made, and this was subsequently confirmed by the successful structure analysis in this space group.

The density of the crystals was determined by flotation in an aqueous solution of CsCl (1.82 g/cm^3). With four molecules in the unit cell the calculated density is 1.77 g/cm^3.

STRUCTURE DETERMINATION

The first calculation of a three-dimensional electron density map used 217 selected coefficients, for which phase angles were derived from the bromine atomic coordinates (0.250, 0.418, 0.250), obtained from the $\varrho(u, \varrho)$ and $\varrho(v, w)$ Patterson projections. The bromine atoms (in semi-special positions) do not

contribute to reflections with $h+k=2n+1$, so these were omitted from the synthesis. The R-value for the reflections was = 22.7 % $[R=\sum(|F_o|-|F_c|)/\sum|F_o|]$.

From the map, 7 atomic positions were determined, and these were used in a second cycle of structure factor calculation ($R=19.8$ %) and Fourier synthesis (217 reflections used again). From this distribution, all the 14 atomic positions of the structure were obtained.

The postulated structure was refined in two parts. In the first, calculations were performed on a GIER computer, using the step method of Bhuiya and Stanley.[8] All 577 observed reflections were included, the x-, y-, and B-values for all atoms were those from the two-dimensional analysis,[3] and only the z-coordinates were refined ($\Delta z=0.02$). After two cycles, R changed from 30.91 % to 16.34 %.

The method of least squares was used in the second part of the refinement, which was performed on an IBM 7094 computer. The function minimized was $\sum w_i(F_o-F_c)^2$ with weights w of unity given to all reflections i. Layer line scale factors, atomic positional coordinates and individual isotropic temperature factors were refined. No further changes in the parameters were indicated after 5 cycles of full matrix refinement, when the final R was 11.50 %.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Within the experimental limits the molecule of 2-cyano-5-bromobenz[f][1,3] oxazepine consists of a normal benzene ring fused to a non-planar 2,5-substituted seven-membered oxazepine ring. All the atoms of the molecule lie in one or both of two planes (D and B) (Fig. 1). The benzene ring, O(1) and C(5) are in plane D, while, to a rough approximation, atoms O(1), C(2), C(1'), N(2'), N(3), C(4), C(5), and Br lie in plane B. These two planes intersect in a line through O(1) – C(5), and are at an angle of about 45° to each other (Figs. 1 – 3). The distances from the atoms in the oxazepine ring to a least squares plane,[9] calculated through the atoms in the benzene ring, are given in Table 1.

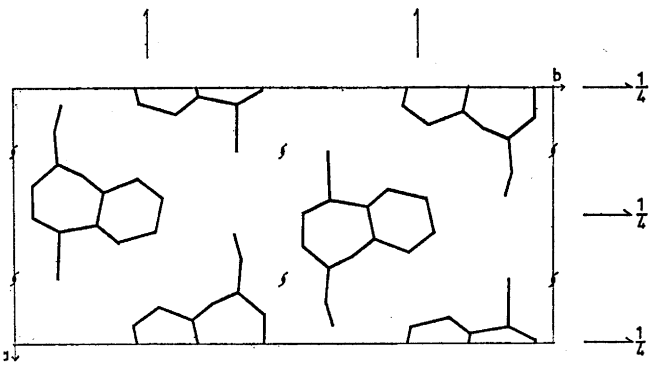

Fig. 3. Packing view of the crystal structure (c-axis projection).

Table 1. Distances (in Å) from the plane D of the benzene ring to the atoms in the compound I. The six benzene ring atoms C(5a) to C(9a) were used, to define the least-squares plane (D).

C5a	−0.03	O1	−0.18
C6	0.03	C2	0.86
C7	−0.02	C1′	1.73
C8	0.01	N2′	2.31
C9	−0.01	N3	1.21
C9a	0.02	C4	0.52
		C5	−0.04
		Br	−0.78

The equation of the least squares plane (D), in the unit cell co-ordinate system, is $4.3442\,x + 4.4036\,y - 3.5373\,z = 0.40687$.

Table 2. Calculated interatomic distances (in Å) within the molecule. Estimated standard deviations in brackets.

N2′−C1′	1.08	(0.05)	C5a−C9a	1.40	(0.05)
C1′−C2	1.52	(0.05)	C5a−C6	1.37	(0.05)
C2−N3	1.33	(0.05)	C6−C7	1.43	(0.04)
N3−C4	1.36	(0.04)	C7−C8	1.40	(0.05)
C4−C5	1.39	(0.04)	C8−C9	1.45	(0.05)
C5−Br	1.88	(0.03)	C9−C9a	1.38	(0.04)
C5−C5a	1.51	(0.04)	C9a−O1	1.44	(0.04)
			O1−C2	1.33	(0.05)

From a comparison of the molecular interatomic distances (Table 2) obtained in this analysis and the "typical distances" listed in the *International Tables for X-Ray Crystallography* [10] it can be seen that the intramolecular bonds, C(9a)−O(1) and C(5)−C(5a), appear to be single bonds, while O(1)−C(2), C(2)−N(3), N(3)−C(4), and C(4)−C(5) are best characterized as partial double bonds, indicating some delocalization of π-electrons over the system O(1)−C(2)−N(3)−C(4)−C(5). This differs from the related compound II,[4] in which there is evidence for localized double bonds in the ring (Table 5).

The distances and the angles associated with the cyano group deviate from the usual values.

		Found	Normal [10]
Angle	C(2)−C(1′)−N(2′)	167° (4°)	180°
Distance	C(2)−C(1′)	1.52 Å (0.05)	1.44 Å (0.01)
	C(1′)−N(2′)	1.08 Å (0.05)	1.158 Å (0.002)

X−C≡N angles deviating significantly from 180° have been observed before, an outstanding example being in $P(CN)_3$ [11] (172° ± 3). Further examples are in tetraphenylarsonium-3-fluoro-1,1,4,5,5-pentacyano-2-azapentadienide [12] and in 1,2,3-tricyanocyclopropane.[13]

It is difficult to estimate the influence of a structure on C−C≡N angle, and in the present work, no clear reason for the non linearity can be given.

Table 3. Calculated interatomic angles within the molecule (°). Estimated standard deviations in brackets. Order of atoms: end, apex, end.

N2′ – C1′ – C2	167	(4)	C5 – C5a – C6	120	(3)
C1′ – C2 – N3	115	(4)	C9a – C5a – C6	119	(3)
C1′ – C2 – O1	114	(3)	C5a – C6 – C7	118	(3)
O1 – C2 – N3	130	(4)	C6 – C7 – C8	123	(3)
C2 – N3 – C4	120	(3)	C7 – C8 – C9	117	(3)
N3 – C4 – C5	124	(3)	C8 – C9 – C9a	119	(3)
C4 – C5 – C5a	128	(3)	C9 – C9a – C5a	123	(3)
C4 – C5 – Br	116	(3)	C5a – C9a – O1	119	(3)
Br – C5 – C5a	116	(2)	C9 – C9a – O1	116	(3)
C5 – C5a – C9a	121	(3)	C9a – O1 – C2	109	(3)

Table 4. Atomic co-ordinates and their estimated standard deviations, expressed as fractions of the corresponding unit cell edges, and the atomic isotropic thermal parameters in Å².

	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B	$\sigma(B)$
N2′	0.064	0.087	0.726	0.003	0.001	0.01	3.2	0.6
C1′	0.164	0.079	0.675	0.003	0.002	0.01	2.8	0.8
C2	0.306	0.084	0.607	0.004	0.002	0.01	3.6	0.9
N3	0.375	0.039	0.736	0.002	0.001	0.01	2.3	0.6
C4	0.504	0.040	0.699	0.003	0.001	0.01	2.4	0.7
C5	0.576	0.093	0.697	0.003	0.001	0.01	1.9	0.6
Br	0.7526	0.0821	0.690	0.0004	0.0001	0.001	2.9	0.1
C5a	0.530	0.158	0.724	0.003	0.001	0.01	1.6	0.6
C6	0.603	0.201	0.884	0.003	0.001	0.01	2.0	0.7
C7	0.559	0.262	0.891	0.003	0.001	0.01	2.4	0.7
C8	0.439	0.280	0.776	0.003	0.001	0.01	2.7	0.7
C9	0.364	0.233	0.618	0.003	0.001	0.01	2.4	0.7
C9a	0.409	0.174	0.609	0.003	0.001	0.01	2.0	0.7
O1	0.338	0.1305	0.4120	0.002	0.0008	0.007	1.9	0.4

Table 5. Interatomic distances (in Å) within the seven-membered oxazepine ring in the compound 2-phenyl-7-bromobenz[d][1,3]oxazepine (II). Estimated standard deviations in brackets.

N1 – C2	1.25 (2)
C2 – O3	1.40 (2)
O3 – C4	1.41 (3)
C4 – C5	1.27 (3)
C5 – C5a	1.44 (3)
C5a – C9a	1.45 (3)

Table 6 lists cyano-group distances for this work and that of others. It indicates the connection between C – CN and C≡N distances in any one carbon-bound cyano group (special factors may be of importance when the cyano group is attached to a carbon atom forming a carbon-carbon triple bond). These distances are direct reflections of the relative proportions of the resonance structures (A): $X-C\equiv N \longleftrightarrow \overset{+}{X}=C=\overline{N}$. High infrared C≡N

Table 6. List of observed C≡N/C–N distances. For cyano groups belonging to the same molecule, mean values are sometimes used (■).

	C≡N distance	C–CN distance	Reference number	Compound
1.	1.03	1.60	14	1:2 Copper(II) nitrate-methylcyanide complex
2.	1.04	1.54	14	1:2 Copper(II) nitrate-methylcyanide complex
3.	1.08	1.52	15 this work	2-Cyano-5-bromobenz[f][1,3]oxazepine
4.	1.10	1.48	16	2-Bromo-4′-dimethylamino-α-cyanostilbene
5.	1.113	1.472	17	Complex of pyrene and tetracyanoethylene
6.	1.124	1.464	17	Complex of pyrene and tetracyanoethylene
7.	1.118	1.483	18	Bis-succinodinitrile-copper(I)perchlorate
8.	1.12	1.45	19	9-Dicyanomethylene-2,4,7-trinitro-fluorene
9. ■	1.126	1.445	20	Tetracyanocyclobutane
10.	1.126	1.436	21	Triphenylmethylphosphonium bis(1,2-dicyanoethylene-1,2-dithiolato)niccolate(III)
11.	1.13	1.44	22	Molecular addition compound of methyl-cyanide and boron trifluoride
12. ■	1.131	1.426	23	Tetracyanoethylene-naphthalene complex
13.	1.134	1.436	24	1,4-Bis(dicyanomethylene)cyclohexane
14.	1.135	1.432	21	Triphenylmethylphosphonium bis(1,2-dicyanoethylene-1,2-dithiolato)niccolate(III)
15.	1.134	1.413	25	Potassium *p*-nitrophenyldicyanomethide
16.	1.14	1.43	26	Hydrogencyanide tetramer
17. ■	1.14	1.425	27	Tetraphenylphosphonium bis (tetracyano-quinodimethanide)
18. ■	1.140	1.423	28	2:1 complex of 7,7,8,8-tetracyano-quinodimethane and *N*,*N*,*N*′,*N*′-tetra-methyl-*p*-phenylenediamine
19.	1.140	1.421	29	Oxonium cyanoanilate
20.	1.146	1.423	25	Potassium *p*-nitrophenyldicyanomethide
21.	1.148	1.429	21	Triphenylmethylphosphonium bis(1,2-dicyanoethylene-1,2-dithiolato(niccolate(III)
22.	1.148	1.436	30	2,5-Dimethyl-7,7-dicyanonorcaradiene
23.	1.153	1.436	30	2,5-Dimethyl-7,7-dicyanonorcaradiene
24	1.15	1.43	31	9-Cyanoanthracene
25.	1.152	1.432	24	1,4-Bis(dicyanomethylene)cyclohexane
26.	1.15	1.42	19	9-Dicyanomethylene-2,7-dinitrofluorene
27. ■	1.152	1.419	32	Cesium tetracyanoquinodimethanide
28. ■	1.159	1.396	33	2-Dimethylsulfuranylidenemalononitrile
29. ■	1.17	1.41	34	Tetracyanothiophene
30.	1.21	1.38	35	Rubidium salt of dinitroacetonitrile
31.	1.14	1.38	36	Cyanoacetylene
32.	1.14	1.37	37	Dicyanoacetylene

intensity is obtained when the right resonance form is dominant,[38,39] so that a very low infrared frequency might be expected from 2-cyano-5-bromobenz[f][1,3]oxazepine. Indeed, no IR-band has been observed at the frequency expected for this band.

All intermolecular distances are equal to or greater than the sum of the corresponding van der Waals radii.

Table 7. Observed and calculated structure factors.

h	k	l	F_o	F_c
0	2	0	34.91	49.77
0	4	0	60.00	72.72
0	6	0	140.59	177.33
0	8	0	76.43	72.68
0	10	0	28.25	31.05
0	12	0	83.57	88.98
0	14	0	35.87	39.25
0	16	0	39.46	47.65
0	18	0	48.74	65.31
0	20	0	26.64	34.92
0	22	0	27.40	28.50
0	24	0	32.85	44.79
0	26	0	16.77	21.61
1	25	0	10.54	18.30
1	23	0	8.71	13.57
1	21	0	7.63	7.81
1	19	0	17.09	20.44
1	18	0	15.00	13.96
1	17	0	38.54	48.11
1	16	0	9.92	10.19
1	15	0	11.63	12.63
1	14	0	18.08	12.65
1	13	0	52.49	55.38
1	12	0	9.92	12.96
1	11	0	79.56	79.82
1	8	0	65.15	59.86
1	7	0	85.06	88.10
1	6	0	13.08	11.13
1	5	0	53.64	65.63
1	4	0	11.46	14.12
1	3	0	7.12	7.39
1	2	0	61.28	65.00
1	1	0	42.30	46.53
2	0	0	52.39	55.96
2	1	0	19.76	18.12
2	2	0	74.33	87.30
2	3	0	11.59	10.99
2	4	0	79.28	78.65
2	5	0	13.25	5.01
2	6	0	111.29	111.94
2	7	0	20.28	19.41
2	8	0	45.23	43.52
2	9	0	55.05	48.57
2	10	0	51.09	45.25
2	12	0	67.94	69.27
2	13	0	13.91	14.90
2	14	0	47.38	50.81
2	15	0	17.45	14.65
2	17	0	7.37	5.49
2	18	0	49.28	54.79
2	19	0	13.29	14.39
2	20	0	28.23	33.23
2	21	0	15.16	18.89
2	22	0	7.35	10.56
2	24	0	19.56	25.13
2	26	0	7.32	12.28
3	26	0	16.35	2.32
3	23	0	17.97	25.08
3	20	0	7.64	10.13
3	19	0	40.33	54.78
3	18	0	17.07	13.22
3	17	0	21.20	21.81
3	15	0	8.63	8.38
3	14	0	8.29	8.16
3	13	0	56.08	61.73
3	12	0	12.36	7.12
3	11	0	54.06	54.19
3	10	0	36.44	34.73
3	9	0	22.52	20.20
3	8	0	21.37	20.86
3	7	0	75.06	76.63
3	6	0	7.87	1.17
3	5	0	89.71	87.60
3	4	0	17.01	17.56
3	3	0	18.37	18.73
3	2	0	20.12	20.52
3	1	0	102.11	107.45
4	0	0	54.08	51.89
4	1	0	45.96	43.14
4	2	0	70.69	64.73
4	3	0	46.89	40.88
4	4	0	55.33	46.58
4	5	0	10.92	5.00
4	6	0	88.97	78.16
4	7	0	43.19	35.58
4	8	0	50.53	44.88
4	10	0	24.74	24.04
4	12	0	75.90	73.14
4	13	0	8.33	9.16
4	14	0	39.90	36.02
4	15	0	12.62	10.19
4	16	0	25.91	25.82
4	17	0	7.62	8.96
4	18	0	33.07	35.64
4	19	0	19.54	18.41
4	20	0	16.85	16.26
4	24	0	15.00	21.61
5	23	0	19.43	26.25
5	19	0	27.70	35.06
5	17	0	36.47	39.27
5	13	0	58.53	54.61
5	12	0	17.67	11.99
5	11	0	31.07	30.41
5	10	0	6.47	12.08
5	8	0	17.06	8.87
5	7	0	67.66	65.26
5	6	0	12.64	16.25
5	5	0	76.85	72.31
5	4	0	11.99	9.80
5	3	0	13.40	13.52
5	1	0	120.69	110.54
6	0	0	91.20	76.64
6	1	0	16.47	14.44
6	2	0	17.59	18.14
6	4	0	22.12	23.24
6	5	0	6.14	3.75
6	6	0	82.74	73.97
6	7	0	7.87	5.03
6	8	0	47.79	48.45
6	9	0	28.34	28.68
6	10	0	46.43	46.45
6	11	0	8.75	8.93
6	12	0	67.47	66.17
6	14	0	24.61	21.30
6	15	0	12.13	9.16
6	16	0	21.75	22.38
6	18	0	29.48	30.11
6	20	0	15.48	13.42
7	20	0	10.95	10.31
7	19	0	32.76	37.50
7	17	0	30.38	32.32
7	16	0	11.93	6.19
7	15	0	19.51	22.25
7	13	0	43.73	40.99
7	12	0	13.18	16.40
7	11	0	53.12	47.04
7	10	0	27.17	24.76
7	9	0	8.90	12.65
7	7	0	72.44	63.97
7	6	0	10.88	13.64
7	5	0	75.71	70.79
7	4	0	10.56	6.16
7	2	0	16.69	15.63
7	1	0	72.83	63.15
8	2	0	39.26	35.87
8	3	0	11.40	10.18
8	4	0	12.58	10.32
8	6	0	40.52	31.86
8	8	0	33.75	31.02
8	9	0	12.04	9.59
8	10	0	7.66	5.12
8	11	0	17.19	20.56
8	12	0	19.58	20.74
8	13	0	19.46	14.46
8	14	0	9.22	10.62
8	15	0	9.02	7.12
8	16	0	8.74	9.95
8	18	0	20.94	23.56
8	20	0	6.70	9.65
9	19	0	17.09	16.86
9	17	0	20.34	18.73
9	13	0	34.38	35.42
9	11	0	42.93	38.99
9	9	0	19.55	16.92
9	7	0	33.07	29.69
9	6	0	24.88	26.30
9	5	0	41.95	38.74
10	6	0	53.42	46.09
10	7	0	12.98	10.89
10	8	0	7.41	4.42
10	9	0	8.94	11.08
10	10	0	7.15	8.18
10	12	0	33.03	31.25
10	13	0	10.23	9.40
10	14	0	21.29	22.20
10	16	0	9.20	8.16
0	2	1	148.29	182.60
0	3	1	97.14	99.34
0	4	1	136.85	148.54
0	5	1	9.55	8.50
0	6	1	41.51	37.53
0	7	1	30.53	23.80
0	8	1	79.58	67.47
0	9	1	29.38	28.86
0	10	1	116.69	107.90
0	11	1	31.51	26.22
0	12	1	7.67	10.37
0	13	1	17.21	15.04
0	14	1	71.21	71.24
0	15	1	26.09	25.24
0	16	1	43.21	46.91
0	17	1	9.63	13.79
0	18	1	17.08	15.12
0	20	1	34.54	42.66
0	21	1	25.00	29.92
0	22	1	25.95	34.82
0	26	1	18.97	24.69
1	23	1	10.94	16.15
1	21	1	16.94	22.86
1	19	1	14.13	17.75
1	18	1	12.10	10.49
1	17	1	31.32	35.93
1	16	1	19.86	21.91
1	15	1	19.10	49.70
1	14	1	24.34	25.81
1	12	1	10.96	11.19
1	11	1	33.91	34.35
1	13	1	17.36	18.27
1	10	1	40.10	35.55
1	9	1	78.37	70.22
1	8	1	22.48	20.61
1	7	1	57.00	46.80
1	6	1	16.66	15.24
1	5	1	13.29	14.57
1	4	1	62.73	55.00
1	3	1	88.40	87.85
1	2	1	33.64	30.71
1	1	1	39.55	45.80
1	0	1	95.44	84.92
2	0	1	63.46	56.42
2	1	1	47.16	41.55
2	2	1	65.94	63.03
2	3	1	48.43	45.87
2	4	1	71.74	76.13
2	5	1	43.41	40.09
2	6	1	15.76	14.66
2	7	1	42.91	35.76
2	8	1	109.09	94.14
2	9	1	32.68	33.47
2	10	1	63.34	58.03
2	11	1	24.51	23.12
2	12	1	16.93	17.27
2	13	1	13.27	9.53
2	14	1	45.67	44.89
2	15	1	28.91	28.73
2	16	1	44.01	47.69
2	17	1	23.90	25.27
2	18	1	17.20	19.05
2	20	1	22.18	26.00
2	21	1	9.69	15.07
2	22	1	19.74	26.53
3	23	1	8.46	16.51
3	22	1	11.10	13.71
3	21	1	30.84	42.29
3	17	1	18.48	20.74
3	16	1	13.68	17.10
3	15	1	38.17	49.08
3	14	1	11.11	13.34
3	13	1	23.05	21.82
3	11	1	37.29	36.61
3	10	1	27.82	28.21
3	9	1	76.52	70.05
3	8	1	25.13	20.82
3	7	1	30.12	28.48
3	6	1	13.10	13.58
3	5	1	71.51	63.32
3	4	1	25.11	21.03
3	3	1	94.10	94.24
3	2	1	48.71	40.64
3	1	1	54.36	51.05
3	0	1	28.49	26.73
4	0	1	9.51	10.35
4	1	1	28.02	24.43
4	2	1	24.87	68.42
4	3	1	31.87	31.22
4	4	1	78.16	71.74
4	5	1	24.39	22.93
4	6	1	22.30	19.51
4	7	1	27.26	26.45
4	8	1	49.18	43.24
4	9	1	36.46	36.79
4	10	1	63.30	55.73
4	11	1	16.89	16.34
4	12	1	10.75	11.04
4	13	1	14.40	14.37
4	14	1	37.04	37.92
4	15	1	20.51	21.94
4	16	1	38.20	42.24
4	17	1	17.28	19.90
4	19	1	12.09	13.66
4	20	1	16.65	18.90
4	22	1	18.40	25.13
4	23	1	7.99	10.22
5	23	1	12.67	16.97
5	21	1	16.34	23.32
5	20	1	14.61	17.67
5	19	1	16.66	18.14
5	17	1	18.67	18.87
5	16	1	12.23	14.31
5	15	1	40.21	43.12
5	14	1	16.86	16.82
5	13	1	27.75	31.69
5	12	1	11.35	12.50
5	11	1	42.16	43.86
5	10	1	17.41	11.72
5	9	1	54.90	52.73
5	8	1	29.94	27.09
5	7	1	25.57	23.40
5	6	1	10.83	8.08
5	5	1	58.17	52.13
5	4	1	28.16	25.60
5	3	1	86.72	76.83

Table 7. Continued.

h	k	l	F_o	F_c
5	2	1	50.65	45.60
5	1	1	54.36	43.62
5	0	1	22.48	22.70
6	0	1	7.86	5.55
6	1	1	16.71	12.32
6	2	1	72.01	65.53
6	3	1	25.35	22.52
6	4	1	61.14	51.42
6	5	1	14.34	12.90
6	6	1	16.91	16.33
6	8	1	61.37	51.56
6	9	1	31.45	30.21
6	10	1	49.64	53.22
6	11	1	20.18	19.05
6	12	1	11.83	11.54
6	13	1	19.71	18.69
6	14	1	28.17	28.04
6	15	1	14.14	20.07
6	16	1	34.45	38.25
6	20	1	18.35	21.84
6	22	1	15.43	19.32
7	21	1	18.60	20.35
7	20	1	9.53	9.73
7	19	1	8.41	11.00
7	17	1	22.85	24.89
7	16	1	16.69	18.64
7	15	1	38.11	41.54
7	14	1	12.19	11.36
7	13	1	15.80	14.25
7	11	1	23.20	21.38
7	10	1	16.94	16.68
7	9	1	78.07	69.06
7	8	1	20.15	19.39
7	7	1	37.98	33.90
7	6	1	13.02	12.01
7	5	1	42.08	37.70
7	4	1	32.92	32.75
7	3	1	63.95	56.24
7	2	1	32.33	28.98
7	1	1	28.38	23.70
8	1	1	20.18	18.15
8	2	1	41.58	39.31
8	3	1	13.55	9.88
8	4	1	36.07	32.65
8	5	1	22.77	19.25
8	6	1	22.94	21.79
8	7	1	12.07	9.81
8	8	1	28.07	28.29
8	9	1	7.05	12.36
8	10	1	15.80	13.85
8	11	1	12.22	10.81
8	12	1	14.02	14.07
8	13	1	9.79	10.71
8	14	1	17.96	18.53
8	16	1	12.68	14.24
8	17	1	6.03	2.67
8	20	1	13.89	17.17
9	17	1	14.63	12.35
9	16	1	11.17	10.35
9	15	1	29.07	28.37
9	14	1	8.80	9.46
9	13	1	12.93	12.37
9	12	1	9.41	9.93
9	11	1	27.20	25.51
9	10	1	20.72	20.20
9	9	1	36.28	35.23
9	8	1	9.94	9.88
9	7	1	15.78	11.67
9	5	1	9.99	8.79
9	4	1	9.99	11.66
9	3	1	46.25	42.94
9	2	1	19.93	19.66
9	1	1	28.16	23.22
10	2	1	29.56	23.83
10	3	1	15.54	14.40
10	4	1	36.61	33.63
10	5	1	13.76	12.78
10	7	1	16.52	16.71
10	8	1	26.57	26.03
10	9	1	15.96	12.98
10	10	1	33.03	31.01
10	14	1	23.80	22.60
10	15	1	11.03	9.42
10	16	1	20.96	20.40
11	13	1	10.82	9.03
11	11	1	12.56	10.76
11	10	1	13.22	12.78
11	9	1	22.51	18.30
11	8	1	13.02	14.64
11	7	1	13.38	14.96
11	5	1	15.24	16.55
0	5	2	47.05	48.49
0	6	2	67.70	70.48
0	7	2	73.79	75.48
0	8	2	51.07	46.08
0	9	2	11.80	9.11
0	10	2	18.50	17.87
0	11	2	46.75	43.89
0	12	2	52.13	46.55
0	13	2	60.50	59.83
0	14	2	20.66	13.83
0	15	2	27.27	28.18
0	16	2	32.88	38.31
0	17	2	17.61	18.02
0	18	2	25.77	28.93
0	19	2	27.85	30.20
0	20	2	6.38	10.77
0	22	2	12.75	11.11
0	23	2	13.80	16.27
1	23	2	10.33	13.83
1	20	2	6.35	12.57
1	19	2	19.64	23.21
1	18	2	19.95	26.29
1	17	2	22.09	23.95
1	16	2	9.32	12.87
1	14	2	22.58	22.45
1	13	2	43.07	42.16
1	12	2	22.35	23.21
1	11	2	32.02	34.53
1	10	2	15.59	14.13
1	9	2	6.92	5.17
1	8	2	31.08	30.46
1	7	2	44.93	42.95
1	6	2	33.91	36.69
1	5	2	45.24	48.32
1	4	2	39.80	42.72
1	3	2	20.70	17.43
1	2	2	31.53	37.02
1	1	2	38.45	48.12
2	0	2	22.13	24.90
2	1	2	33.47	39.39
2	2	2	30.14	27.38
2	3	2	22.69	22.38
2	4	2	27.70	27.17
2	5	2	51.42	50.78
2	6	2	60.72	57.43
2	7	2	55.22	53.90
2	8	2	30.11	25.92
2	9	2	13.50	13.29
2	10	2	28.48	22.72
2	11	2	44.87	44.18
2	12	2	41.80	40.24
2	13	2	34.23	34.93
2	14	2	19.06	20.25
2	15	2	15.97	14.00
2	17	2	24.03	26.90
2	18	2	25.65	26.88
2	19	2	17.18	20.52
2	20	2	15.35	16.66
3	20	2	6.11	14.27
3	19	2	22.10	26.43
3	18	2	19.67	23.10
3	17	2	25.76	25.81
3	15	2	6.60	7.16
3	14	2	11.23	12.85
3	13	2	26.04	27.09
3	12	2	35.14	37.10
3	11	2	34.87	35.85
3	10	2	13.86	14.84
3	9	2	13.26	9.97
3	8	2	32.29	28.38
3	7	2	49.32	45.82
3	6	2	42.84	43.20
3	5	2	52.90	53.43
3	4	2	4.29	8.58
3	3	2	32.78	28.18
3	2	2	25.63	18.12
3	1	2	51.13	53.50
3	0	2	69.00	70.38
4	0	2	62.39	53.93
4	1	2	48.54	45.51
4	2	2	22.85	16.26
4	3	2	25.17	18.14
4	4	2	39.95	33.21
4	5	2	43.27	37.51
4	6	2	41.23	36.70
4	7	2	34.91	30.69
4	8	2	27.36	24.11
4	9	2	15.31	10.43
4	10	2	14.66	13.20
4	11	2	23.92	24.11
4	12	2	35.36	36.01
4	13	2	25.16	23.07
4	14	2	28.02	27.85
4	15	2	14.89	15.40
4	17	2	25.47	27.02
4	18	2	21.29	20.78
4	19	2	16.34	17.23
4	20	2	14.33	13.92
5	20	2	10.93	10.66
5	19	2	15.49	15.28
5	18	2	18.50	18.39
5	17	2	21.22	21.83
5	16	2	19.67	19.70
5	15	2	6.64	6.38
5	14	2	22.11	18.57
5	13	2	38.10	32.53
5	12	2	39.88	36.60
5	11	2	28.83	24.46
5	10	2	20.94	19.40
5	9	2	6.16	7.24
5	8	2	37.54	31.59
5	7	2	46.50	42.41
5	6	2	50.77	46.78
5	5	2	34.84	27.56
5	4	2	22.52	17.29
5	2	2	31.34	25.52
5	1	2	50.39	47.80
5	0	2	46.56	44.00
6	0	2	47.07	46.33
6	1	2	39.67	35.34
6	2	2	22.78	18.69
6	3	2	15.70	15.86
6	4	2	33.42	28.79
6	5	2	41.29	35.42
6	6	2	57.67	48.16
6	7	2	22.66	20.95
6	8	2	15.65	13.38
6	9	2	6.48	5.08
6	10	2	27.87	24.76
6	11	2	28.13	22.39
6	12	2	32.64	29.92
6	13	2	24.00	24.21
6	14	2	21.89	19.96
6	16	2	12.63	13.55
6	18	2	23.75	21.49
6	19	2	22.80	21.10
7	13	2	23.07	19.16
7	17	2	16.65	13.99
7	16	2	11.75	10.36
7	14	2	15.53	14.20
7	13	2	25.13	23.68
7	12	2	37.85	34.25
7	11	2	38.17	32.62
7	10	2	13.33	12.52
7	9	2	6.66	6.05
7	8	2	17.54	16.05
7	7	2	43.13	34.37
7	6	2	49.34	47.67
7	5	2	42.51	38.70
7	4	2	17.02	14.10
7	3	2	16.91	13.91
7	2	2	33.65	27.62
7	1	2	31.06	25.12
7	0	2	26.87	23.53
8	0	2	39.22	29.98
8	1	2	21.99	22.93
8	2	2	28.16	29.41
8	3	2	9.40	8.09
8	4	2	9.41	9.27
8	5	2	18.85	19.61
8	6	2	22.11	19.78
8	7	2	17.61	14.52
8	8	2	17.54	15.29
8	11	2	6.40	10.16
8	12	2	15.33	13.33
8	13	2	14.87	12.57
8	15	2	5.55	4.87
8	16	2	5.20	7.58
9	14	2	13.35	9.63
9	13	2	22.76	20.58
9	12	2	23.22	19.33
9	11	2	17.57	15.63
9	10	2	14.79	11.60
9	9	2	8.75	12.31
9	8	2	16.69	17.46
9	7	2	16.93	15.57
9	6	2	17.11	16.08
9	5	2	17.25	19.93
9	4	2	17.35	17.45
10	6	2	32.79	22.08
10	7	2	24.47	25.40
10	8	2	18.63	16.52
10	9	2	12.16	8.73
10	10	2	12.79	11.57

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REFERENCES

1. Buchardt, O., Jensen B. and Kjøller Larsen, I. *Acta Chem. Scand.* **21** (1967) 1841.
2. Buchardt, O., Lohse, C., Duffield, A. M. and Djerassi, C. *Tetrahedron Letters* **29** (1967) 2741.
3. Simonsen, O., Lohse, C. and Buchardt, O. *Acta Chem. Scand.* **24** (1970) 268.
4. Jensen, B. *Private communication.*
5. An Algol program (S 1) by V. Schousboe-Jensen, Bygning 207, Danmarks tekniske højskole, DK – 2800 Lyngby 1969.
6. *International Tables of X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III, p. 141.
7. An Algol program (D 17) by J. Danielsen and S. E. Rasmussen, Kemisk Institut, Aarhus universitet, DK – 8000 Aarhus 19XX.
8. Bhuiya, A. K. and Stanley, E. *Acta Cryst.* **16** (1963) 981.
9. Schomaker, V. *et al. Acta Cryst.* **12** (1959) 600.
10. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III, p. 276.
11. Emerson, K. and Britton, D. *Acta Cryst.* **17** (1964) 1134.
12. Palenik, J. G. *Acta Cryst.* **20** (1966) 471.
13. Hartman, A. and Hirshfeld, F. L. *Acta Cryst.* **20** (1966) 80.
14. Duffin, B. *Acta Cryst.* **B 24** (1968) 396.
15. This work, p. 2669.
16. van Meersche, M. and Leroy, G. *Bull. Soc. Chim. Belges* **69** (1960) 204.
17. Ikemoto, I. and Kuroda, H. *Acta Cryst.* **B 24** (1968) 383.
18. Blount, J. F. and Freeman, H. F. *Acta Cryst.* **B 25** (1969) 1518.
19. Silverman, J., Krukonis, A. P. and Yannoni, N. F. *Acta Cryst.* **B 24** (1968) 1481.
20. Greenberg, B. and Post, B. *Acta Cryst.* **B 24** (1968) 918.
21. Fritchie, C. J., Jr. *Acta Cryst.* **20** (1966) 107.
22. Hoard, J. L., Owen, T. B., Buzzel, A. and Salmon, O. N. *Acta Cryst.* **3** (1950) 130.
23. Williams, R. M. and Wallwork, S. C. *Acta Cryst.* **22** (1967) 899.
24. Iwasaki, F. and Aihara, A. *Acta Cryst.* **B 26** (1970) 91.
25. Sass, R. L. and Bugg, C. *Acta Cryst.* **23** (1967) 282.
26. Penford, B. R. and Lipscomb, W. N. *Tetrahedron Letters* **6** (1960) 17.
27. Goldstein, P., Seff, K. and Trueblood, K. N. *Acta Cryst.* **B 24** (1968) 778.
28. Hanson, A. W. *Acta Cryst.* **B 24** (1968) 768.
29. Andersen, E. K. *Private communication.*
30. Fritchie, C. J., Jr. *Acta Cryst.* **20** (1966) 27.
31. Rabaud, H. and Clastre, J. *Acta Cryst.* **12** (1959) 911.
32. Fritchie, C. J., Jr. and Arthur, P., Jr. *Acta Cryst.* **21** (1966) 139.
33. Christensen, A. T. and Witmore, W. G. *Acta Cryst.* **B 25** (1969) 73.
34. Rychnovsky, V. and Britton, D. *Acta Cryst.* **B 24** (1968) 725.
35. Grigor'eva, N. V., Margolis, N. V., Shokhor, I. N., Tselinskii, I. V. and Mel'nikov, V. V. *Zh. Strukt. Khim.* **9** (1968) 550.
36. Shallcross, F. V. *Diss. Abstr.* **19** (1959) 2244.
37. Hannan, R. B. and Collin, R. L. *Acta Cryst.* **6** (1953) 350.
38. Skinner, M. W. and Thompson, H. W. *J. Chem. Soc.* **1955** 487.
39. Bellamy, L. J. *Advances in Infrared Group Frequencies*, Methuen, New York 1968, p. 73.

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