

The angles N-S-N, 113.4° , are small in comparison with the angles N-P-N (120°) in $(\text{NPCl}_2)_3$. This will be due, as in $(\text{NSF})_4$, to the relatively great p character of the sulphur hybrids used for the σ bonds and to the strong repulsion of the exocyclic lone pair electrons on the sulphur atoms.

The lone pair electrons are in equatorial positions. It is noteworthy that in all cyclic N-S compounds investigated so far, $(\text{NSF})_4$, $\alpha(\text{NSOCl})_3$ and $(\text{NSCl})_3$, strongly repelling groups [the lone pair electrons in the S(IV) compounds or the double bonds to the oxygen atoms in $\alpha(\text{NSOCl})_3$] are pointing away from the mean plane of the ring.

All calculations were carried out on the digital computer ZEBRA, with programs devised by Dr D. W. Smits.

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References

- ALTONA, C. (1964). *Acta Cryst.* **17**, 1282.
 COCHRAN, W. (1951). *Acta Cryst.* **4**, 408.
 CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
 FREEMAN, A. J. (1959). *Acta Cryst.* **12**, 261.
 GOEHRING, M. (1957). *Ergebnisse und Probleme der Chemie der Schwefelstickstoffverbindungen*. Berlin: Akademie Verlag.
 HASSEL, O. & RÖMMING, C. (1962). *Quart. Rev. Chem. Soc. Lond.* **16**, 1.
 HAZELL, A. C., WIEGERS, G. A. & VOS, A. (1966). *Acta Cryst.* **20**, 186.
 SCHRÖDER, H. & GLEMSER, O. (1959). *Z. anorg. Chem.* **298**, 78.
 SMITS, D. W. & WIEBENGA, E. H. (1953). *J. Sci. Instrum.* **30**, 280.
 TOMIIE, Y. & STAM, C. H. (1958). *Acta Cryst.* **11**, 126.
 TRUTER, M. R. (1962). *J. Chem. Soc.* p. 3400.
 WIEBENGA, E. H. & SMITS, D. W. (1950). *Acta Cryst.* **3**, 265.
 WIEGERS, G. A. & VOS, A. (1963a). *Acta Cryst.* **16**, 152.
 WIEGERS, G. A. & VOS, A. (1963b). *Acta Cryst.* **16**, A40.

Acta Cryst. (1966). **20**, 197

The Crystal and Molecular Structure of Acetyl-bromoacetyldihydroenmein

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The crystal structure of acetyl-bromoacetyldihydroenmein, $\text{C}_{24}\text{H}_{31}\text{O}_8\text{Br}$, has been determined in order to elucidate the molecular structure and absolute configuration of enmein, $\text{C}_{20}\text{H}_{26}\text{O}_6$, a principal bitter constituent of *Isodon trichocarpus* Kudo. The derivative was prepared through a series of reactions and it crystallized in a structure with the space group $P2_12_12_1$ and the unit-cell dimensions,

$$a = 9.78, b = 15.25, c = 16.13 \text{ \AA.}$$

The crystal structure was solved by the heavy atom method and refined by the method of least squares. The final reliability index for 2237 observed reflexions was 0.10.

The present analysis, which established the structure of enmein including its absolute configuration, furnishes useful information for chemical investigations which have been carried out in parallel with the X-ray study.

Introduction

Enmein, $\text{C}_{20}\text{H}_{26}\text{O}_6$, is a diterpene bitter principle isolated from *Isodon trichocarpus* Kudo (Ikeda & Kanatomo, 1958; Takahashi, Fujita & Koyama, 1958; Naya, 1958) and its structural study by chemical methods has been carried out by several research groups (Ikeda & Kanatomo, 1958; Takahashi, Fujita & Koyama, 1958; Naya, 1958; Kanatomo, 1958; Takahashi, Fujita & Koyama, 1960; Kanatomo, 1961; Kubota, Matsuura, Tsutsui & Naya, 1961). In 1961, Kubota and his collaborators proposed the structure (I) (Fig. 1) for enmein (Kubota, Matsuura, Tsutsui & Naya, 1961), but later, they suggested that the planar structure (II) is also a

probable one (Kubota, Matsuura, Tsutsui & Naya, 1963).

In order to give a crucial proof for the chemical structure and to establish the stereochemistry of enmein, the present authors have performed the X-ray study of acetyl-bromoacetyldihydroenmein (III) and determined the molecular structure of enmein including its absolute configuration as (IV), in conformity with the result of recent chemical investigations (Kubota, Matsuura, Tsutsui, Uyeo, Takahashi, Irie, Numata, Fujita, Okamoto, Natsume, Kawazoe, Shudo, Ikeda, Tomoeda, Kanatomo, Kosuge & Adachi, 1964). A preliminary short note on the present work has already appeared elsewhere (Iitaka & Natsume, 1964).

Experimental

Crystals of acetyl-bromoacetyldihydroenmein, which were grown from benzene-chloroform solutions, were colourless prisms elongated along the *c* axis. The density was measured by flotation in a mixture of benzene and carbon tetrachloride. The cell dimensions and space group were determined from rotation and Weissenberg photographs taken with Cu $K\alpha$ radiation.

Crystal data

Acetyl-bromoacetyldihydroenmein, $C_{24}H_{31}O_8Br$

Mol.wt. 527.4, m.p. 233~235°C.

Orthorhombic,

$a=9.78 \pm 0.02$, $b=15.25 \pm 0.02$, $c=16.13 \pm 0.02$ Å.

$U=2406$ Å³.

$D_m=1.464$ g.cm⁻³, $D_x=1.456$ g.cm⁻³, $Z=4$.

Linear absorption coefficient for Cu $K\alpha$ radiation, $\mu=21.4$ cm⁻¹.

$F(000)=1096$.

Absent spectra: $h00$ when h is odd, $0k0$ when k is odd, $00l$ when l is odd.

Space group: $P2_12_12_1$.

The three-dimensional intensity data of $0kl \sim 7kl$, $h0l \sim h1l$ and $hk0 \sim hk10$ were collected from equi-inclination Weissenberg photographs taken about the *a*, *b* and *c* axes using the multiple-film technique with Cu $K\alpha$ radiation. The intensities of several thousands of reflexions were estimated by visual comparison with a standard scale. The X-ray specimens used for the measurements had dimensions of the order of 0.15 mm × 0.25 mm in cross section. Since the μR value was about 0.5, no absorption correction was applied. All the intensities were corrected for Lorentz and polarization factors and they were put on a single scale. A total of 2958 independent structure factors were finally evaluated. A Wilson plot was then used to estimate an approximate scale factor and an overall temperature

factor. The value $B=5.5$ Å² was obtained. The following atomic scattering factors were used for the present structure determination: for bromine, those of Thomas & Umeda (1957); for oxygen and carbon, those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955).

Determination of the structure

The positions of the bromine atoms were at first determined by the two-dimensional Patterson and sharpened Patterson syntheses projected along the *a*, *b* and *c*

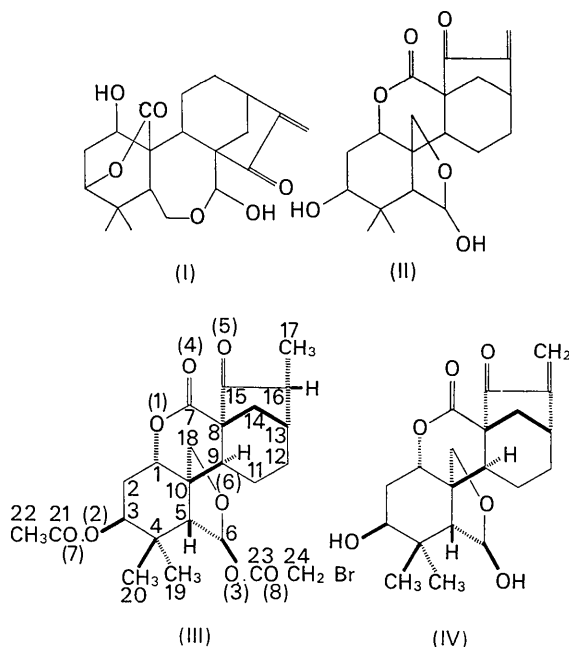


Fig. 1. (I), (II) Proposed structures for enmein. (III) Acetyl-bromoacetyldihydroenmein. (IV) Established structure of enmein, in absolute configuration.

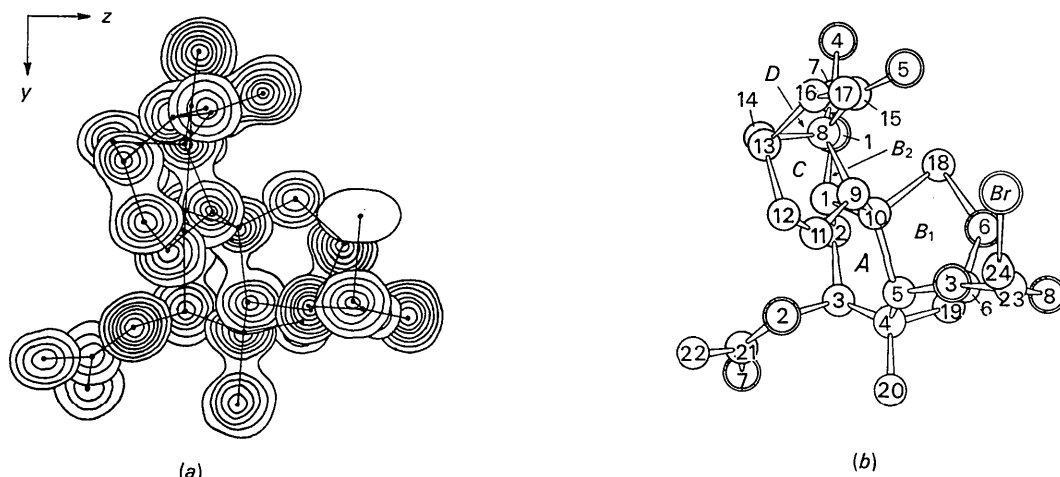


Fig. 2. (a) Composite electron-density contour sections parallel to (100). Contours are drawn at 2, 3, 4, ... e.Å⁻³; those for the bromine atom are not drawn. (b) Atomic configuration of the acetyl-bromoacetyldihydroenmein molecule illustrating the contour map of (a). The figure shows the absolute configuration. Single circles indicate carbon and double circles indicate oxygen atoms.

axes. The electron-density projections obtained showed too severe overlapping to derive information on the arrangement of light atoms. Further study was, therefore, carried out by the three-dimensional analysis.

The coordinates of the bromine atoms obtained from the two-dimensional analysis were refined using the sections of the three-dimensional sharpened Patterson functions at $u=\frac{1}{2}$, $v=\frac{1}{2}$ and $w=\frac{1}{2}$. The first three-dimensional Fourier synthesis utilizing the phase angles given by the contributions of bromine atoms revealed well defined peaks of twelve light atoms [C(6), C(8), C(9), C(10), C(12), C(15), C(18), O(3), O(4), O(5), O(6) and O(8)]. These were included in the next structure factor calculation assuming all were carbon atoms. In this way, eight more atoms [C(1), C(4), C(5), C(11), C(16), C(17), O(1) and O(2)] were found in the second Fourier map. The third set of similar calculation revealed a further six atoms [C(2), C(7), C(14), C(19), C(20) and C(23)]. A subsequent difference Fourier calculation based on the structure factors including the contributions of the above twenty-seven atoms, with which $R=0.42$, showed up the last six atoms [C(3), C(13), C(21), C(22), C(24) and O(7)]. On the basis of peak height considerations, it was possible to distinguish all oxygen atoms from carbon, except the O(7) atom in the acetate group. O(7) was tentatively identified because of its short interatomic distance to C(21). In the course of least-squares refinement, however, fairly large changes in the bond lengths C(21)–O(7) and C(21)–C(22) took place, so that the above assignment had to be changed as described later. A final Fourier synthesis was then computed. The superimposed contour sections illustrating the three-dimensional electron-density distribution drawn parallel to the a axis are shown in Fig. 2. For correction of a pronounced effect due to the anisotropic thermal vibration of the bromine atom in the c direction, two bromine atoms of $\frac{1}{2}$ weight were placed along the c axis. The R value at this stage was 0.20.

Refinement of the structure

Further refinement of the structure was performed on an IBM 7090 computer with a modified version of the full-matrix least-squares refinement program, ORFLS (Busing, Martin & Levy, 1962). With the original ORFLS program executed on the 32K machine, the maximum number of atoms was restricted to 20 and the maximum number of parameters which can be refined was 100. The present structure, however, contains 33 atoms in an asymmetric unit (excluding hydrogen atoms) with 298 parameters to be refined, including individual anisotropic temperature factors. The program was therefore modified so as to be able to deal with the maximum number of atoms 50 and to vary blocks of parameters successively during each cycle of refinement. The whole parameters were divided into three blocks, each consisting of 100 parameters; one scale factor and 11 atoms with anisotropic tem-

perature factors. These groups of parameters were selected by parameter selection cards read at the beginning of each inner loop. One complete cycle of refinement was performed by calculating such three inner loops. The computing process of the first inner loop was as follows: select the parameters of the bromine, the 8 oxygen atoms, the 2 carbon atoms [C(1) and C(2)] and an overall scale factor; obtain derivatives for the 100 parameters; solve the normal equations and adjust the parameters. The refinement then proceeded to the second inner loop, by taking the next 100 parameter [C(3)~C(13)], and so on.

Because of the limited capacity of the core memories, the number of observations which could be stored was restricted to 2100. The experimentally unobserved reflexions and some of the observed reflexions were therefore not included in the refinement. The hydrogen atoms were also excluded from the calculation. The weighting system chosen was such that the weight of each observation is unity. X-ray dispersion correction for bromine atom was not applied.

In the first cycle, calculated as a program test using 1160 reflexions, R dropped from 0.189 to 0.126. After two more complete cycles of refinement with 2085 reflexions, successive changes in the parameters became less than the estimated standard deviations, and R thereby dropped to 0.096. Comparison with the initial values showed that many parameters had changed by amounts larger than five times their final estimated standard deviations. Thus, some of the bond lengths and angles had changed by amounts 0.15 Å and 7°, respectively. The final fractional atomic coordinates and temperature factors are given in Tables 1 and 2, and their standard deviations estimated from the last least-squares inverse matrix are also given in these tables. The standard deviations differ slightly according to the atoms: *e.g.* for carbon atoms, $\sigma(x/a)$ are in the range 0.0010 to 0.0017, $\sigma(y/b)$ are 0.0007~0.0010, $\sigma(z/c)$ are 0.0007~0.0012; for oxygen atoms, $\sigma(x/a)$ are in the range 0.0008~0.0011, $\sigma(y/b)$ are 0.0005~0.0008, $\sigma(z/c)$ are 0.0005~0.0007. The averages of the standard deviations of the positional parameters in Å units may then be estimated as follows. For bromine atom $\sigma(r)=0.002$ Å, for carbon atoms $\sigma(r)=0.013$ Å and for oxygen atoms $\sigma(r)=0.009$ Å.

The final R index calculated for all 2237 observed reflexions was 0.099 and that calculated for all 2958 reflexions including non-observed reflexions was 0.164. The set of structure factors calculated with the final parameters listed in Tables 1 and 2 is given in Table 3 together with the observed structure factors.

Absolute configuration

The absolute configuration of the molecule has already been proposed on the basis of optical rotatory dispersion data and conformational analysis (Kubota, Matsuura, Tsutsui, Uyeo, Takahashi, Irie, Numata, Fujita, Okamoto, Natsume, Kawazoe, Shudo, Ikeda,

Tomoeda, Kanatomo, Kosuge & Adachi, 1964). In this connection an X-ray study of the absolute configuration was performed by the anomalous dispersion method (Bijvoet, Peerdeman & van Bommel, 1951). The dispersion correction of the bromine scattering factor for Cu K radiation was given by Dauben & Templeton (1955) as $\Delta f' = -0.9$ and $\Delta f'' = 1.5$. The structure factors were calculated assuming that the atomic parameters of Tables 1 and 2 are referred to a right-handed set of axes. The equivalent positions of the atoms were located corresponding to space group $P2_12_12_1$, No. 19 in *International Tables for X-ray Crystallography* (1952).

Of the 50 pairs of reflexions for which the intensity differences between $I(hkl)$ and $I(h\bar{k}l)$ were expected to

be discernible, 30 pairs showed significant differences in the l th layer Weissenberg photographs. Some of the results are shown in Table 4. The comparison between observed and calculated intensities indicated that the assumed configuration was actually correct. The absolute configuration of the molecule is then established as Fig. 1 (III), which coincides with the configuration which has been proposed by chemical methods. In this paper, all figures are drawn in such a way that they represent the correct configuration.

Discussion of the structure

The bond distances and angles in the molecule, calculated from the coordinates of Table 1, are shown in

Table 1. *The final fractional atomic coordinates and their standard deviations*

Atom	x/a	$\sigma(x/a)$	y/b	$\sigma(y/b)$	z/c	$\sigma(z/c)$
Br	0.82796	± 0.00020	0.52129	± 0.00011	0.32739	± 0.00017
C(1)	0.1081	± 0.0010	0.4882	± 0.0007	0.5850	± 0.0007
C(2)	0.9682	0.0012	0.5303	0.0008	0.5905	0.0008
C(3)	0.9870	0.0012	0.6298	0.0009	0.5959	0.0010
C(4)	0.0643	0.0012	0.6593	0.0008	0.6740	0.0009
C(5)	0.2075	0.0011	0.6122	0.0007	0.6777	0.0008
C(6)	0.2378	0.0012	0.3926	0.0009	0.2683	0.0008
C(7)	0.2014	0.0013	0.3422	0.0008	0.5938	0.0007
C(8)	0.1632	0.0012	0.6136	0.0007	0.0820	0.0008
C(9)	0.1491	0.0010	0.5181	0.0007	0.1255	0.0007
C(10)	0.2097	0.0011	0.5121	0.0007	0.6549	0.0007
C(11)	0.0758	0.0012	0.4564	0.0007	0.0635	0.0008
C(12)	0.9431	0.0012	0.4964	0.0007	0.0259	0.0009
C(13)	0.9644	0.0014	0.5942	0.0008	-0.0025	0.0009
C(14)	0.1229	0.0013	0.6115	0.0008	0.9884	0.0007
C(15)	0.0447	0.0015	0.6650	0.0007	0.1218	0.0008
C(16)	0.9211	0.0012	0.6624	0.0008	0.0635	0.0008
C(17)	0.7874	0.0017	0.6563	0.0010	0.1071	0.0011
C(18)	0.1699	0.0013	0.4682	0.0008	0.7368	0.0007
C(19)	0.9717	0.0013	0.6446	0.0010	0.7493	0.0009
C(20)	0.9058	0.0014	0.2608	0.0008	0.8292	0.0011
C(21)	0.0131	0.0015	0.6991	0.0008	0.4589	0.0010
C(22)	0.1156	0.0012	0.7173	0.0009	0.3874	0.0007
C(23)	0.0262	0.0013	0.3882	0.0007	0.3360	0.0009
C(24)	0.8736	0.0012	0.3971	0.0008	0.3215	0.0012
O(1)	0.0860	0.0008	0.3942	0.0005	0.5932	0.0005
O(2)	0.0701	0.0009	0.6551	0.0006	0.5240	0.0005
O(3)	0.0903	0.0008	0.3926	0.0005	0.2618	0.0005
O(4)	0.1865	0.0009	0.2640	0.0005	0.5972	0.0006
O(5)	0.0504	0.0010	0.7015	0.0005	0.1890	0.0005
O(6)	0.2155	0.0009	0.5291	0.0005	0.8017	0.0005
O(7)	0.8929	0.0011	0.7231	0.0008	0.4653	0.0007
O(8)	0.0788	0.0010	0.3811	0.0006	0.4030	0.0005

Mean standard deviations

Br	0.00020 (0.0020 Å)	0.00011 (0.0017 Å)	0.00017 (0.0027 Å)
C	0.00126 (0.0123 Å)	0.00079 (0.0120 Å)	0.00085 (0.0137 Å)
O	0.00093 (0.0091 Å)	0.00056 (0.0086 Å)	0.00054 (0.0087 Å)

Br, $\sigma(r) = 0.0021$ Å; C, $\sigma(r) = 0.013$ Å; O, $\sigma(r) = 0.009$ Å

Mean estimated standard deviations in bond lengths

$\sigma(\text{Br}-\text{C}) = 0.013$ Å; $\sigma(\text{C}-\text{C}) = 0.018$ Å; $\sigma(\text{C}-\text{O}) = 0.015$ Å

Mean estimated standard deviations in tetrahedral bond angles

$\sigma(\text{C}-\text{C}-\text{C}) = 1.2^\circ$

Table 2. *The final anisotropic temperature factors and their standard deviations*The thermal parameters are of the form $T = \exp \{ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \}$.

Br	β_{11} 0.0180 (± 0.0002)	β_{22} 0.0058 (± 0.0001)	β_{33} 0.0133 (± 0.0002)	β_{12} 0.0019 (± 0.0001)	β_{13} 0.0005 (± 0.0002)	β_{23} 0.0002 (± 0.0001)
C(1)	71 (11)	39 (5)	38 (5)	-11 (7)	-10 (7)	-6 (5)
C(2)	75 (13)	50 (6)	58 (7)	-14 (8)	4 (8)	-3 (6)
C(3)	79 (13)	49 (7)	58 (8)	24 (8)	9 (9)	10 (6)
C(4)	83 (13)	44 (5)	47 (6)	18 (7)	3 (9)	2 (6)
C(5)	84 (12)	30 (4)	43 (6)	-1 (6)	15 (8)	-2 (5)
C(6)	74 (13)	48 (6)	43 (7)	-2 (8)	-9 (8)	-3 (6)
C(7)	118 (16)	38 (5)	27 (6)	-12 (8)	-6 (8)	-1 (5)
C(8)	81 (12)	34 (5)	30 (6)	-7 (7)	5 (8)	1 (5)
C(9)	64 (11)	31 (4)	30 (5)	6 (7)	-4 (6)	-2 (4)
C(10)	82 (12)	29 (4)	29 (6)	-8 (7)	10 (7)	-5 (4)
C(11)	84 (13)	31 (5)	53 (7)	-1 (7)	-23 (8)	-2 (5)
C(12)	83 (13)	37 (5)	53 (7)	1 (7)	-22 (9)	2 (5)
C(13)	111 (16)	41 (6)	39 (7)	0 (8)	-9 (9)	3 (5)
C(14)	114 (15)	42 (5)	32 (6)	-3 (8)	0 (8)	8 (5)
C(15)	139 (18)	30 (5)	34 (6)	6 (8)	3 (9)	5 (5)
C(16)	79 (13)	44 (6)	40 (6)	8 (7)	4 (8)	-1 (5)
C(17)	156 (22)	64 (8)	78 (9)	6 (12)	-1 (13)	-5 (8)
C(18)	114 (14)	52 (6)	20 (5)	-16 (9)	5 (8)	-4 (5)
C(19)	117 (15)	72 (9)	35 (6)	4 (10)	30 (9)	1 (6)
C(20)	145 (18)	42 (5)	70 (9)	-29 (9)	15 (12)	-1 (7)
C(21)	157 (18)	41 (6)	83 (9)	20 (9)	-38 (11)	-11 (6)
C(22)	141 (13)	82 (7)	38 (5)	-9 (8)	2 (7)	11 (5)
C(23)	115 (15)	31 (5)	59 (7)	-6 (7)	6 (10)	-3 (6)
C(24)	87 (13)	45 (6)	94 (11)	12 (7)	31 (11)	9 (8)
O(1)	87 (9)	41 (4)	41 (4)	-23 (5)	-5 (5)	3 (3)
O(2)	96 (10)	61 (5)	45 (5)	17 (6)	-4 (6)	12 (4)
O(3)	84 (9)	44 (4)	33 (4)	-5 (5)	2 (5)	4 (3)
O(4)	127 (11)	38 (4)	57 (5)	-15 (6)	6 (7)	-3 (4)
O(5)	157 (12)	44 (4)	36 (4)	8 (6)	0 (7)	-3 (4)
O(6)	134 (11)	46 (4)	33 (4)	-10 (6)	9 (6)	5 (3)
O(7)	146 (13)	95 (8)	81 (7)	41 (9)	-23 (8)	28 (6)
O(8)	138 (12)	67 (5)	35 (4)	-16 (7)	7 (6)	6 (4)

Table 3. Observed and calculated structure factors

H	K	L	[Obs]	[Calc]	Anal	Real	H	K	L	[Obs]	[Calc]	Anal	Real	H	K	L	[Obs]	[Calc]	Anal	Real	H	K	L	[Obs]	[Calc]	Anal	Real
1	0	0	59.14	54.01	56.01	0.00	0	14	0	33.84	35.99	-35.99	0.00	4	8	1	9.26	12.77	1.30	12.71	1	4	2	90.57	89.07	-88.38	-11.07
4	0	0	63.35	53.43	53.43	0.00	1	14	0	16.31	15.62	0.00	15.62	4	8	1	19.29	17.21	-15.11	-8.24	2	4	2	47.39	46.07	-42.77	-23.11
8	0	0	62.35	1.22	1.22	0.00	2	14	0	25.96	5.61	5.61	0.00	10	8	1	6.22	3.88	2.87	1.95	3	4	2	27.25	28.01	-44.59	27.43
12	0	0	4.64	81.40	81.40	0.00	3	14	0	14.38	14.16	-14.16	0.00	11	8	1	13.36	6.42	-6.42	-1.12	4	4	2	76.93	75.98	-16.68	-4.20
16	0	0	8.13	5.46	5.46	0.00	4	14	0	9.11	9.42	9.42	0.00	12	8	1	34.30	30.90	0.00	30.90	5	4	2	28.76	26.66	-28.37	4.08
20	0	0	81.99	74.07	0.00	-74.07	5	14	0	0.00	0.00	0.00	-74.07	1	9	1	56.11	55.27	-26.88	-26.88	7	4	2	24.62	24.16	-27.85	4.11
24	0	0	16.94	24.03	24.03	0.00	7	14	0	6.39	6.28	0.00	-6.28	3	9	1	9.84	10.07	9.84	-2.12	4	4	2	16.44	15.82	-14.64	-5.99
28	0	0	38.65	0.00	0.00	0.00	8	14	0	0.00	2.09	2.09	0.00	4	9	1	27.68	26.68	0.00	0.00	5	4	2	8.73	8.73	-6.21	-6.21
32	0	0	14.62	24.13	24.13	0.00	1	13	0	5.53	6.17	0.00	-6.17	5	9	1	7.83	6.77	-1.31	6.64	10	4	2	0.00	3.02	-0.32	3.01
36	0	0	33.82	32.72	0.00	-32.72	2	15	0	10.25	9.06	-9.06	0.00	6	9	1	1.72	4.65	-4.36	1.62	11	4	2	3.59	5.16	0.91	-5.08
40	0	0	16.41	12.40	12.40	0.00	3	15	0	12.60	9.06	0.00	-9.06	7	10	1	14.53	13.82	-9.55	-9.01	2	5	2	0.00	3.75	-4.65	-1.46
44	0	0	52.07	49.97	0.00	-49.97	4	15	0	21.09	23.08	23.08	0.00	1	9	1	10.83	10.65	0.25	-10.65	10	5	2	1.59	3.49	0.00	3.49
48	0	0	9.72	9.12	9.12	0.00	5	15	0	9.02	8.90	0.00	-8.90	8	10	1	12.74	12.08	8.81	8.26	1	5	2	90.26	89.94	-88.00	-16.49
52	0	0	16.07	16.35	0.00	-16.35	6	15	0	0.00	2.71	2.71	0.00	17	9	1	6.48	3.80	-0.48	-3.77	2	5	2	58.28	53.09	-59.00	-32.32
56	0	0	1.98	2.60	2.60	0.00	7	15	0	0.00	2.17	0.00	-2.17	11	9	1	6.35	7.20	6.66	2.74	3	5	2	50.00	47.70	-38.99	-27.49
60	0	0	1.77	1.77	0.00	-1.77	8	15	0	3.24	3.90	-3.90	0.00	10	10	1	29.96	25.43	-25.43	0.00	4	5	2	43.56	43.27	-41.05	-13.65
64	0	0	2.15	7.03	0.00	-7.03	9	15	0	20.81	21.83	0.00	-21.83	12	10	1	37.70	39.88	-17.15	36.61	5	5	2	17.17	13.64	-11.61	-4.20
68	0	0	143.13	144.68	144.68	0.00	1	16	0	14.48	19.86	0.00	-19.86	2	10	1	21.67	24.37	23.57	6.17	5	5	2	28.26	27.85	-4.23	-27.32
72	0	0	109.33	109.33	0.00	-109.33	2	16	0	0.00	3.14	3.14	0.00	3	10	1	15.83	24.37	-24.32	3.91	7	5	2	11.78	12.11	8.83	-8.83
76	0	0	102.95	106.03	-106.03	0.00	3	16	0	1.27	5.19	0.00	-5.19	4	10	1	47.79	46.78	39.28	-25.59	5	5	2	11.30	11.30	-9.59	-9.59
80	0	0	17.91	14.16	0.00	-14.16	4	16	0	7.86	8.84	0.00	-8.84	5	10	1	15.94	14.53	12.23	7.81	9	5	2	10.32	10.07	9.64	-2.91
84	0	0	24.88	19.09	-19.09	0.00	5	16	0	13.59	9.34	0.00	-9.34	6	10	1	28.00	23.87	-23.31	-5.37	10	5	2	7.87	8.06	-6.25	-5.08
88	0	0	52.11	54.61	0.00	-54.61	6	16	0	0.00	2.39	-2.39	0.00	7	10	1	4.64	6.73	-6.73	0.00	11	5	2	0.00	4.91	-4.39	-2.19
92	0	0	50.70	49.86	49.86	0.00	7	16	0	0.00	0.94	0.00	-0.94	8	10	1	8.73	6.18	6.16	0.50	12	5	2	5.68	5.97	-0.74	-5.93
96	0	0	16.00	11.20	0.00	-11.20	8	16	0	11.44	0.00	0.00	-11.44	9	10	1	12.74	8.18	-8.18	-4.81	13	5	2	14.58	17.17	-17.17	0.00
100	0	0	18.99	16.36	-16.37	0.00	9	16	0	1.62	-1.62	0.00	1.62	10	11	1	4.65	9.07	0.00	9.07	1	6	2	53.98	52.87	-34.79	-39.81
104	0	0	10.33	13.35	0.00	-13.35	10	17	0	0.00	0.36	0.00	-0.36	1	11	1	43.45	41.94	-13.17	-39.82	2	6	2	27.19	31.12	27.29	-14.94
108	0	0	7.99	7.99	0.00	-7.99	11	17	0	11.79	0.00	0.00	-11.79	2	11	1	16.07	15.75	15.75	0.00	3	6	2	10.33	10.33	-8.61	-8.61
112	0	0	3.99	6.51	0.00	-6.51	12	17	0	3.94	6.33	0.00	-6.33	3	11	1	30.33	27.97	-6.32	27.25	4	6	2	30.72	30.72	0.97	10.74
116	0	0	1.54	1.34	1.34	0.00	13	17	0	0.00	3.00	3.00	0.00	4	11	1	15.17	18.30	-7.23	17.03	5	6	2	13.56	14.51	14.13	-3.31
120	0	0	84.36	91.64	0.00	-91.64	14	17	0	11.25	10.55	0.00	-10.55	5	11	1	7.08	7.17	7.17	0.00	6	6	2	10.33	10.33	-8.39	-8.39
124	0	0	76.26	72.18	-72.18	0.00	15	18	0	3.77	3.29	3.29	0.00	6	11	1	18.35	17.37	-0.99	17.34	7	6	2	22.73	19.23	-18.52	-5.16
128	0	0	9.76	82.13	82.13	0.00	16	18	0	0.00	1.25	0.00	-1.25	7	11	1	13.83	12.48	-5.07	-11.60	8	6	2	10.85	11.04	6.03	-9.25
132	0	0	12.43	6.80	0.00	-6.80	17	18	0	2.14	5.96	0.00	-5.96	8	11	1	5.92	8.16	-5.88	5.65	9	6	2	6.42	4.42	1.81	4.03
136	0	0	20.44	20.44	0.00	-20.44	18	18	0	7.16	7.04	0.00	-7.04	9	11	1	11.83	10.80	-10.80	0.00	10	6	2	0.00	0.95	0.95	0.00
140	0	0	46.98	45.97	0.00	-45.97	19	19	0	74.15	0.00	0.00	-74.15	10	11	1	21.47	20.48	-15.81	-15.81	11	6	2	8.01	8.01	-7.19	-7.19
144	0	0	0.00	4.66	-4.66	0.00	20	19	0	0.00	1.18	1.18	0.00	11	12	1	21.05	22.66	0.79	-22.65	12	7	2	36.87	29.78	0.00	-29.78
148	0	0	0.00	8.44	-8.44	0.00	21	19	0	61.46	0.00	0.00	-61.46	12	12	1	16.09	16.09	-16.09	0.00	13	7	2	26.65	31.98	-23.25	-21.96
152	0	0	8.29	5.93	5.93	0.00	22	20	0	77.32	83.20	0.00	-83.20	13	12	1	12.95	11.39	-16.75	-0.05	14	7	2	51.10	46.91	46.87	-13.94
156	0	0	0.00	4.20	-4.20	0.00	23	20	0	61.46	0.00	0.00	-61.46	14	12	1	24.23	24.09	-24.09	-0.14	15	7	2	19.59	20.04	-19.27	8.82
160	0	0	15.77	15.79	0.00	-15.79	24	20	0	68.27	67.47	0.00	-67.47	15	12	1	2.72	3.52	-3.12	1.62	16	7	2	21.97	14.87	-0.45	-14.86
164	0	0	115.11	104.36	-104.36	0.00	25	21	0	21.25	18.61	0.00	-18.61	16	12	1	7.59	7.47	-7.21	1.93	17	7	2	15.88	17.17	-17.17	0.00
168	0	0	86.80	84.67	0.00	-84.67	26	21	0	35.75	35.75	0.00	-35.75	17	13	1	2.02	2.02	-2.02	-2.02	18	7	2	3.38	3.38	-3.38	-3.38
172	0	0	86.80	84.67	0.00	-84.67	27	21	0	21.37	21.01	0.00	-21.01	18	13	1	10.36	11.06	0.00	-11.06	4	7	2	16.54	18.76	13.34	-13.19
176	0	0	84.67	84.67	0.00	-84.67	28	21	0	36.40	35.77	0.00	-35.77	19	13	1	24.41	24.99	-5.59	-26.40	5	7	2	0.00	0.21	-0.09	-0.19
180	0	0	65.84	63.16	0.00	-63.16	29	21	0	22.00	22.18	0.00	-22.18	20	13	1	11.86	11.86	0.00	0.00	6	7	2	7.27	6.88	-6.88	-6.88
184	0	0	54.03	54.92	54.92	0.00	30	21	0	3.65	5.00	0.00	-5.00	21	13	1	14.87	15.88	-14.49	6.49	7	7	2	0.00	2.99	-2.58	-1.51
188	0	0	20.15	15.44	0.00	-15.44	31	21	0	0.00	0.77	0.00	-0.77	22	13	1	9.90	11.73	-11.73	-0.24	8	7	2	14.86	18.00	-18.00	0.00
192	0	0	0.00	1.30	-1.30	0.00	32	21	0	97.63	43.14	0.00	-43.14	23	13	1	17.86	17.86	-17.86	-0.24	9	7	2	6.82	6.82	-6.82	-6.82
196	0	0	2.71	1.60	-1.60	0.00	33	21	0	102.81	109.44	0.00	-109.44	24	13	1	9.18	9.00	-3.06	-8.46	10	7	2	17.20	35.45	-19.03	-29.70
200	0	0	75.00	73.00	0.00	-73.00	34	21	0	30.17	31.74	-31.74	5.60	25	13	1	10.32	12.21	-11.12	5.02	11	7	2	0.00	5.35	0.71	-4.21
204	0	0	61.75	56.11	56.11	0.00	35	21	0	102.40	124.74	0.00	-124.74	26	13	1	27.13	28									

Table 3 (cont.)

Table with multiple columns of numerical data, organized in a grid-like structure with rows and columns of numbers.

Table 3 (cont.)

5	16	5	8-87	4-95	8-24	0-10	5	11	6	5-17	7-39	-7-10	-2-04	10	7	7	3-60	6-13	5-31	3-08	5	4	8	11-36	9-65	8-40	-8-475	
0	17	5	4-51	3-62	0-00	3-62	7	11	6	2-97	3-18	-0-95	3-03	11	7	7	0-00	6-28	4-98	6-00	4	8	6	6-69	6-27	-5-81	-2-36	
0	17	5	9-09	11-68	0-00	0-00	7	11	6	12-37	11-66	-11-45	0-04	11	7	7	0-00	4-98	4-98	4-98	3	4	8	8-05	9-26	9-26	-0-72	
2	17	5	3-87	4-72	-3-64	-3-64	0	11	6	3-26	4-69	2-95	0-00	0	8	7	0-00	7-05	7-05	7-05	3	4	8	0-00	2-74	-1-30	-2-41	
3	17	5	5-66	6-69	5-03	4-80	0	12	6	4-06	9-67	9-67	0-00	2	8	7	18-02	17-27	9-01	14-73	3	4	8	10-00	3-36	-3-16	-1-13	
4	17	5	6-78	4-46	6-78	0-00	0	12	6	20-41	22-00	7-33	20-74	3	8	7	17-56	19-48	-19-16	-3-41	3	4	8	5-26	4-46	-3-16	-1-13	
5	17	5	2-50	5-43	4-67	2-74	0	12	6	9-93	10-30	10-02	-2-21	4	8	7	10-65	8-75	8-12	3-24	3	4	8	14-36	10-36	0-00	17-92	
0	18	5	0-00	1-44	1-44	0-00	0	12	6	22-24	22-90	12-12	-18-96	5	8	7	9-71	10-04	-2-49	9-72	1	5	5	11-95	15-34	-5-14	-14-45	
1	18	5	3-26	0-21	-0-21	-0-21	0	12	6	0-00	0-00	0-00	0-00	6	8	7	21-36	24-89	-7-71	-7-71	2	5	5	15-45	11-71	-2-74	-0-71	
2	18	5	0-00	2-31	-0-07	-2-09	0	12	6	0-00	7-77	4-72	0-80	7	8	7	4-66	4-58	-1-22	4-42	3	5	5	12-77	11-54	-5-01	-10-39	
3	18	5	8-95	8-13	-0-44	-8-12	0	12	6	0-00	3-72	-3-37	-1-58	8	8	7	8-29	8-01	-3-60	-7-15	4	5	5	10-29	9-05	-6-89	-5-56	
4	18	5	3-59	3-59	0-00	0-00	0	12	6	0-00	4-69	4-69	0-00	9	8	7	4-09	4-09	0-00	-0-00	5	5	5	18-76	16-62	-4-74	-20-24	
0	19	5	1-91	10-71	0-00	10-71	0	12	6	1-71	3-68	3-75	-3-08	10	8	7	3-24	1-19	-1-19	-0-83	6	5	5	6-05	6-02	-6-84	5-96	
1	19	5	2-80	4-53	1-70	4-19	0	13	6	2-56	4-30	-0-54	-0-29	11	9	7	21-21	23-77	0-00	20-77	7	5	5	21-55	17-73	1-04	-17-70	
0	20	5	0-00	0-00	0-00	0-00	0	13	6	0-00	0-00	0-00	0-00	12	9	7	32-33	32-36	-21-37	-14-73	8	5	5	5-05	5-96	5-05	0-15	
1	20	5	5-99	3-45	3-45	0-00	0	13	6	5-87	3-98	-2-59	-3-02	2	9	7	21-05	23-21	-18-36	-14-17	9	5	5	4-63	5-73	5-55	0-00	
2	20	5	2-32	27-48	-27-48	0-00	0	13	6	2-25	3-56	0-14	-3-58	3	9	7	7-75	8-76	-2-81	-2-81	10	5	5	21-28	18-91	-18-91	0-00	
3	20	5	35-78	33-95	-33-95	0-00	0	13	6	4-27	10-02	6-47	-7-47	4	9	7	24-48	24-32	24-24	-14-97	10	5	5	38-92	37-60	6-54	-37-03	
4	20	5	0-95	1-42	-1-42	0-00	0	13	6	7-54	8-77	8-66	1-34	5	9	7	20-44	21-14	20-29	3-40	0	6	5	21-28	18-91	-18-91	0-00	
5	20	5	5-62	6-36	6-36	0-00	0	13	6	6-85	6-26	-5-90	8-07	6	9	7	0-00	2-91	0-95	2-75	1	6	5	26-94	18-93	-18-93	-18-45	
6	20	5	0-00	29-15	28-61	28-61	0-00	0	13	6	0-00	4-73	-3-71	2-94	7	9	7	14-44	18-93	5-76	-18-03	2	6	5	38-92	37-60	6-54	-37-03
7	20	5	1-46	0-32	0-32	0-00	0	13	6	4-81	5-15	-2-60	4-45	8	9	7	8-57	6-38	5-59	-3-07	3	6	5	12-17	9-69	9-65	0-00	
8	20	5	6-66	6-94	-6-94	0-00	0	13	6	13-04	12-04	-11-84	-0-20	9	9	7	6-18	2-76	2-57	-0-39	4	6	5	20-76	16-36	3-29	0-00	
9	20	5	0-00	1-24	1-24	0-00	0	14	6	0-00	1-74	1-74	0-00	10	9	7	2-75	4-91	-3-28	3-65	5	6	5	18-27	15-24	3-71	-18-86	
10	20	5	3-02	7-69	-7-69	0-00	0	14	6	8-97	9-69	-3-84	8-90	11	10	7	21-50	20-49	-20-49	0-00	6	6	5	8-13	8-97	6-69	3-97	
11	20	5	0-00	1-95	1-95	0-00	0	14	6	15-20	1-20	1-20	0-00	12	10	7	15-85	18-45	5-33	15-92	7	6	5	14-42	14-99	-13-98	-5-41	
12	20	5	7-54	10-43	-10-43	0-00	0	14	6	15-61	1-57	0-68	-15-25	13	10	7	9-10	11-14	-9-48	5-88	8	6	5	0-00	4-10	4-19	-0-99	
0	21	6	55-79	51-14	0-00	51-14	0	14	6	2-21	1-36	1-23	-0-57	14	10	7	13-31	13-34	-1-31	13-57	9	6	5	0-00	4-28	2-63	3-29	
1	21	6	75-88	72-07	83-52	0-00	0	14	6	18-62	13-90	-1-18	13-45	15	10	7	9-54	5-02	1-63	8-07	10	6	5	3-62	3-05	-2-96	1-38	
2	21	6	90-62	88-63	77-80	-82-68	0	14	6	8-65	7-70	-7-62	-1-11	16	10	7	7-44	9-79	7-19	-6-65	11	6	5	5-32	6-93	0-00	-6-34	
3	21	6	34-49	35-44	-12-75	-33-06	0	14	6	3-54	3-63	5-50	0-97	17	10	7	8-99	9-57	-0-53	-2-52	12	7	5	12-31	10-91	-4-88	-10-36	
4	21	6	1-14	31-44	-4-61	-1-14	0	14	6	5-60	7-35	-6-40	-3-04	18	10	7	3-61	6-00	-3-61	-6-00	13	7	5	34-78	35-96	33-74	-7-50	
5	21	6	41-57	42-83	-11-40	-11-23	0	15	6	10-16	10-80	0-00	-10-80	19	10	7	8-01	8-30	-4-5	-7-25	14	7	5	10-44	4-89	-1-22	-8-41	
6	21	6	26-65	26-65	0-00	0-00	0	15	6	11-72	12-61	-0-00	-11-72	20	10	7	6-54	6-11	-3-40	-5-08	15	7	5	10-44	4-89	-1-22	-8-41	
7	21	6	18-53	14-06	-13-23	-4-77	0	15	6	5-54	8-17	-8-02	1-55	21	10	7	1-81	1-79	-4-86	-1-73	16	7	5	9-84	6-72	-8-63	1-27	
8	21	6	22-94	23-01	-20-53	-10-38	0	15	6	8-21	8-12	7-65	-2-71	22	10	7	4-21	11-13	0-00	-11-13	17	7	5	10-83	13-69	-0-36	13-69	
9	21	6	11-17	11-17	-0-29	-10-26	0	15	6	3-75	3-75	0-00	0-00	23	10	7	20-61	20-61	-12-62	-12-62	18	7	5	0-00	11-40	-11-40	0-00	
10	21	6	4-12	5-08	-4-24	-4-24	0	15	6	8-23	7-22	-5-68	-4-18	24	11	7	12-81	14-18	-6-05	-12-62	19	7	5	0-00	5-94	0-70	5-30	
11	21	6	9-91	10-79	-0-34	-10-79	0	15	6	1-70	1-96	1-11	1-61	25	11	7	17-99	17-56	-3-62	-17-14	20	7	5	0-00	3-58	3-15	1-70	
12	21	6	43-16	46-80	-46-80	0-00	0	15	6	18-83	21-52	-2-52	-18-83	26	11	7	21-52	21-52	0-00	-21-52	21	7	5	0-00	12-17	9-69	9-65	
13	21	6	59-05	58-81	-27-62	-51-92	0	15	6	0-00	0-98	-0-98	0-00	27	11	7	25-34	25-71	7-94	24-18	22	7	5	0-00	10-00	8-08	0-00	
14	21	6	77-55	75-38	-74-80	-12-13	0	15	6	1-56	1-98	-0-46	-1-92	28	11	7	2-13	2-05	-1-99	0-49	23	7	5	2-63	7-96	-7-92	-0-87	
15	21	6	4-14	4-14	0-00	0-00	0	15	6	18-63	17-78	-1-85	-17-78	29	11	7	4-66	3-84	1-27	-3-62	24	7	5	0-00	4-10	4-19	-0-99	
16	21	6	5-25	7-65	7-65	0-37	0	15	6	5-48	5-69	1-73	-5-63	30	11	7	7-15	5-48	2-95	-1-83	25	7	5	2-63	7-96	-7-92	-0-87	
17	21	6	24-22	24-25	9-50	-22-31	0	15	6	8-05	7-84	4-67	-6-23	31	11	7	4-66	3-84	1-27	-3-62	26	7	5	11-79	10-98	-0-77	10-95	
18	21	6	34-29	34-29	-0-44	-0-44	0	15	6	3-89	3-11	-3-04	-0-63	32	11	7	12-58	12-97	5-75	-11-62	27	7	5	0-00	9-04	-5-28	-2-96	
19	21	6	36-14	35-53	-14-09	-32-61	0	15	6	0-00	2-36	0-00	-2-36	33	11	7	10-70	9-33	6-11	-11-62	28	7	5	2-60	4-79	-0-52	-4-76	
20	21	6	12-11	13-48	-11-23	-7-85	0	15	6	3-43	-3-43	0-00	0-00	34	11	7	11-36	10-27	-1-10	-1-10	29	7	5	0-00	0-00	0-00	0-00	
21	21	6	4-39	0-82	0-73	-0-38	0	15	6	9-40	5-34	-8-49	0-91	35	11	7	0-00	0-00	4-83	-3-25	3-57	30	7	5	0-00	1-92	1-96	1-12
22	21	6	2-98	0-82	0-73	-0-38	0	15	6	6-09	6-09	4-43	0-76	36	11	7	7-54	7-84	7-81	0-76	31	7	5	0-00	2-91	-2-98	-0-56	
23	21	6	16-37	20-13	0-00	20-13	0	15	6	5-59	4-68	-1-74	-2-02	37	11	7	5-12	6-19	-4-82	-4-82	32	7	5	9-94	12-49	0-00	12-49	
24	21	6	46-77	44-05	-12-90	-42-12	0	15	6	7-61	3-95	-1-49	-3-66	38	11	7	6-92	6-90	-4-27	-4-89	33	7	5	9-84	11-87	-1-71	-11-75	
25	21	6	33-68	33-68	0-00	0-00	0	15	6	6-09	6-09	4																

Table 3 (cont.)

Table with multiple columns of numerical data, organized in a grid-like structure. The data appears to be a continuation of a list or table from a previous page, containing various numerical values and possibly identifiers.

Table 3 (cont.)

1	4	13	6.31	8.39	-1.43	8.23	2	7	14	0.00	4.40	-4.58	-0.43	3	11	15	0.00	3.04	-2.54	1.66	3	5	17	4.73	3.79	3.76	0.86		
1	4	13	7.36	10.21	-1.33	-7.23	3	7	14	0.00	2.33	1.93	-1.28	4	11	15	0.00	2.01	0.08	-3.81	3	5	17	0.00	0.16	-0.13	-0.29		
1	4	13	7.24	7.80	-7.57	1.86	4	7	14	15.92	13.60	-12.87	-0.07	5	12	15	0.00	2.11	2.11	0.00	4	5	17	3.86	4.61	1.91	-1.19		
1	4	13	16.09	15.61	-3.21	15.37	6	7	14	0.00	3.77	2.13	3.11	7	12	15	3.23	2.08	-0.26	-2.06	5	6	17	0.00	0.94	-0.34	0.06		
1	4	13	7.31	7.01	-0.18	7.01	6	7	14	0.00	4.17	-2.43	-3.59	8	12	15	3.16	2.08	-0.26	-2.06	6	6	17	0.00	6.4	-1.74	-0.82		
1	4	13	7.13	3.09	3.04	0.71	7	7	14	0.00	5.25	4.17	-2.43	9	12	15	3.16	2.08	-0.26	-2.06	7	6	17	0.00	6.63	-1.74	0.41		
1	4	13	0.00	4.40	-4.40	0.00	8	7	14	0.00	8.90	-2.93	-8.19	10	13	15	0.00	2.24	0.00	-2.24	8	6	17	0.00	2.19	2.11	0.42		
1	4	13	8.18	7.70	-0.40	8.18	9	7	14	0.00	6.05	-4.82	-1.88	11	13	15	0.00	2.01	0.00	-2.01	9	6	17	0.00	1.66	-0.21	1.15		
1	4	13	6.36	6.47	7.61	3.72	10	7	14	0.00	3.06	-1.87	-1.37	12	13	15	0.00	2.45	3.50	-3.49	10	6	17	0.00	3.81	4.27	0.46		
1	4	13	10.10	14.51	10.09	-7.73	6.45	4	8	14	0.00	3.38	-1.22	-3.16	13	13	15	0.00	1.78	1.21	-1.21	11	6	17	0.00	3.24	3.11	0.13	
1	4	13	0.00	3.14	0.03	3.14	5	8	14	0.00	1.35	-1.47	0.48	14	13	15	0.00	0.43	-0.43	0.00	12	6	17	0.00	2.78	-2.44	1.33		
1	4	13	14.92	14.73	9.74	7.65	6	8	14	0.00	4.02	2.48	-3.16	15	13	15	0.00	3.29	6.37	-6.37	13	7	17	0.00	0.26	-0.21	0.55		
1	4	13	0.67	0.67	0.02	0.02	7	9	14	0.00	1.29	-0.64	-1.10	16	13	15	0.00	0.00	0.43	-0.43	14	7	17	0.00	3.28	1.77	2.74		
1	4	13	29.72	28.07	-28.07	0.00	8	9	14	0.00	1.36	0.00	0.00	17	13	15	0.00	0.00	0.43	-0.43	15	7	17	0.00	2.80	5.97	-5.60		
1	4	13	18.49	17.83	14.84	-9.87	9	9	14	0.00	6.58	6.13	-2.39	18	13	15	0.00	2.85	1.34	1.34	16	8	17	0.00	0.00	0.00	0.00		
1	4	13	0.00	6.01	-3.65	-8.77	3	9	14	11.74	11.74	5.74	-2.39	19	13	15	0.00	7.92	4.02	0.00	17	8	17	0.00	0.40	-0.48	0.00		
1	4	13	0.00	6.45	0.34	-6.46	4	9	14	0.00	3.41	1.16	3.20	20	13	15	0.00	3.95	-2.97	1.91	18	8	17	0.00	3.20	-2.38	-2.57		
1	4	13	10.42	9.97	2.29	9.71	5	9	14	0.00	4.02	3.87	-0.87	21	13	15	0.00	9.49	9.78	-9.78	19	8	17	0.00	0.42	-1.87	-0.90		
1	4	13	8.03	8.03	3.48	3.87	5	9	14	0.00	5.93	-5.74	0.40	5	14	15	0.00	1.94	-1.74	-0.89	20	8	17	0.00	3.80	4.41	4.30		
1	4	13	0.00	1.07	0.24	-3.84	6	9	14	0.00	4.78	2.21	2.21	6	14	15	0.00	2.05	3.30	-1.30	21	8	17	0.00	0.40	-0.83	0.88		
1	4	13	0.00	1.43	-1.46	0.71	7	10	14	0.00	1.21	-2.21	0.00	7	14	15	0.00	1.16	1.54	-2.92	22	8	17	0.00	0.65	0.00	-0.45		
1	4	13	26.47	23.58	0.00	23.46	8	10	14	0.00	2.67	-1.46	0.41	8	14	15	0.00	2.03	3.96	2.38	23	8	17	0.00	2.29	2.28	-0.14		
1	4	13	7.39	7.93	7.21	3.25	9	10	14	0.00	2.80	2.31	-1.98	9	14	15	0.00	1.97	1.54	-0.56	24	8	17	0.00	0.14	-0.08	0.63		
1	4	13	8.53	7.28	-7.24	-0.77	3	10	14	0.00	2.64	-2.21	-1.98	10	14	15	0.00	1.97	1.54	-0.56	25	8	17	0.00	0.87	-0.74	0.40		
1	4	13	3.90	6.45	0.34	-6.46	4	10	14	0.00	3.05	2.42	-1.66	11	14	15	0.00	1.21	-1.21	0.00	26	8	17	0.00	3.81	2.79	-2.60		
1	4	13	9.22	6.12	-0.85	6.06	5	10	14	8.72	8.72	4.05	0.00	12	14	15	12.84	1.21	6.62	13.61	27	8	17	0.00	0.02	-0.96	0.71		
1	4	13	7.36	7.36	0.00	0.00	6	11	14	0.00	5.14	2.45	0.00	13	14	15	0.00	3.28	-2.91	1.52	28	8	17	0.00	0.50	0.78	-0.67		
1	4	13	9.00	4.01	-1.13	-3.44	7	11	14	0.00	4.40	1.86	-1.92	14	14	15	0.00	1.13	1.35	-2.82	29	8	17	0.00	0.42	-1.87	-0.90		
1	4	13	0.00	1.17	-1.17	0.00	8	11	14	0.00	4.91	2.18	3.25	15	14	15	0.00	1.97	-1.96	-0.11	30	8	17	0.00	0.25	-0.00	-0.23		
1	4	13	8.18	14.73	14.63	-1.68	4	11	14	0.00	3.67	3.20	1.79	16	14	15	0.00	0.43	0.42	1.36	31	8	17	0.00	0.90	2.29	-2.18		
1	4	13	0.00	1.17	-1.17	0.00	5	11	14	0.00	4.59	3.74	-0.16	17	14	15	0.00	0.98	3.37	-3.36	32	8	17	0.00	0.17	1.63	1.82		
1	4	13	0.00	0.73	0.33	-0.33	6	11	14	0.00	3.63	-1.47	3.53	18	14	15	0.00	3.22	4.05	0.00	33	8	17	0.00	3.72	6.07	-6.07		
1	4	13	0.00	3.61	-3.69	1.03	-3.55	7	12	14	0.00	1.48	-1.48	0.00	19	14	15	0.00	0.69	-6.98	-6.09	34	8	17	0.00	0.16	-0.16	0.00	
1	4	13	0.00	4.12	-3.34	3.34	-3.34	8	12	14	0.00	1.79	1.00	1.49	20	14	15	0.00	0.18	-0.98	-4.06	35	8	17	0.00	2.33	-3.03	0.00	
1	4	13	0.00	5.49	4.98	3.53	-3.52	9	12	14	0.00	0.00	-0.33	2.71	21	14	15	0.00	0.33	-0.16	-0.29	36	8	17	0.00	0.21	0.21	0.00	
1	4	13	0.00	7.11	0.00	7.11	0.00	10	12	14	0.00	4.00	-3.53	3.16	22	14	15	0.00	2.53	1.16	-0.29	37	8	17	0.00	0.95	-0.95	0.00	
1	4	13	0.00	4.88	-2.94	-2.94	2.94	11	12	14	0.00	4.96	-4.57	-1.92	23	14	15	0.00	2.05	-2.00	-0.47	38	8	17	0.00	1.88	0.86	-0.86	
1	4	13	0.00	7.28	3.29	3.69	-3.69	12	12	14	0.00	4.87	0.00	-4.87	24	14	15	0.00	0.05	-3.59	-2.82	39	8	17	0.00	0.90	7.99	-6.03	
1	4	13	0.00	4.62	-3.93	2.43	-2.43	13	13	14	0.00	1.02	0.30	-0.28	25	14	15	0.00	0.00	0.00	0.00	40	8	17	0.00	1.31	-0.75	-1.08	
1	4	13	0.00	4.04	3.88	-1.14	-3.13	14	13	14	0.00	2.22	1.89	-1.28	26	14	15	0.00	0.84	-1.57	-3.49	41	8	17	0.00	2.63	2.29	0.24	
1	4	13	0.00	4.38	-4.62	2.23	-2.23	15	13	14	0.00	4.84	-4.83	0.01	27	14	15	0.00	1.71	-1.38	-0.39	42	8	17	0.00	1.49	2.36	-2.36	
1	4	13	0.00	6.57	4.34	-4.34	0.00	16	14	14	0.00	0.31	-0.31	0.00	28	14	15	0.00	2.69	-2.90	0.71	43	8	17	0.00	0.96	-0.92	-2.75	
1	4	13	10.42	11.46	-2.01	11.28	17	14	14	0.00	1.11	-0.76	0.81	29	14	15	0.00	0.69	-0.70	-0.70	44	8	17	0.00	3.96	-3.98	0.00		
1	4	13	8.28	8.15	6.00	-5.62	18	14	14	0.00	4.83	-3.26	-2.86	30	14	15	0.00	1.16	0.99	0.99	45	8	17	0.00	0.73	0.85	-1.50		
1	4	13	8.28	8.15	6.00	-5.62	19	14	14	0.00	17.95	0.00	-17.95	31	14	15	0.00	4.36	3.81	3.06	46	8	17	0.00	2.33	-2.32	0.00		
1	4	13	8.28	8.15	6.00	-5.62	20	14	14	0.00	27.63	0.00	-27.63	32	14	15	0.00	1.63	0.00	0.00	47	8	17	0.00	5.99	6.29	-6.29		
1	4	13	0.00	2.42	0.88	-2.23	21	14	14	0.00	0.21	0.00	-0.21	33	14	15	0.00	0.37	0.37	-3.32	48	8	17	0.00	1.10	-1.10	-4.24		
1	4	13	0.00	3.46	-3.46	-0.62	-0.62	22	14	14	0.00	7.31	0.00	-7.31	34	14	15	0.00	11.31	1.64	-0.06	49	8	17	0.00	0.20	0.00	-0.42	
1	4	13	0.00	6.45	0.00	0.00	0.00	23	14	14	0.00	7.63	0.00	-7.63	35	14	15	0.00	0.00	1.13	1.64	2.66	50	8	17	0.00	2.91	-2.30	-1.78
1	4	13	0.00	5.59	-3.86	4.04	-4.04	24	14	14	0.00	2.37	0.00	-2.37	36	14	15	0.00	3.98	0.83	-3.89	51	8	17	0.00	0.23	0.23	0.00	
1	4	13	0.00	6.73	6.73	-0.74	-0.74	25	14	14	0.00	9.06	0.00	-9.06	37	14	15	0.00	7.50	0.00	0.00	52	8	17	0.00	0.09	-0.09	-0.10	
1	4	13	0.00	0.30	-0.25	0.17	-0.17	26	14	14	0.00	11.50	0.00	-11.50	38	14	15	0.00	6.40	-0.81	-3.79	53	8	17	0.00	2.65	-2.53		

angles are 1.2° for tetrahedral C–C–C bonds. Table 5 indicates the bond distances arranged in groups of similar type and their average values. As seen in the table, the C–C single bond distances vary from 1.487 \AA [C(16)–C(17)] to 1.622 \AA [C(8)–C(9)], but a mean value for the twenty-three C–C bonds found in the molecule is 1.547 \AA , which is not significantly different from the normal value. It is not certain whether the variation in the bond distances represents a real feature. The short distance of the C(16)–C(17) bond (1.487 \AA) may be attributed partly to the shortening caused by the angular oscillations of the C(17) atom around a centre near the C(16) atom. It is not conceivable that the original enmein derivative [C(16)=C(17) double bond] has mixed with the sample (dihydroenmein derivative, C(16)–C(17) single bond), since there was no such indication in the ultraviolet absorption spectrum and no region was found in electron density distribution suggesting another position for or any disordering of the C(17) atom.

As for the stereochemical structure of acetyl-bromoacetyldihydroenmein, the following points are now well established:

- Conformation of the ring *A* is of a chair form.
- Conformation of the ring *C* is of a boat form.
- The juncture between the ring *A* and the five-membered ring which has a hemiacetal moiety is in a *cis*-fusion and the bond C(10)–C(18) is axially oriented from the ring *A*.
- The five-membered hemiacetal ring is puckered at the C(5) atom. The four atoms C(10), C(18), O(6) and C(6) form a plane with a maximum deviation

of 0.08 \AA , and the C(5) atom deviates from this plane by 0.63 \AA .

- The C(14) of the [3,2,1]bicyclo-octane system is at the opposite side of C(18) and the methyl group of C(17) is *trans* to the bridge carbon atom C(14).
- The O(1) of the six-membered lactone ring has an equatorial configuration.
- The acetoxy group at C(3) is oriented axially in the ring *A*.
- The two acetyl groups C(21), C(22), O(2), O(7) and C(23), C(24), O(3), O(8) have both a planar configuration. The maximum deviations from the planes are about 0.03 \AA . The bromine atom lies about 1.89 \AA out of the latter plane.

In Figs. 5 and 6 are shown two views of the structure, along the *a* and *c* axes. Intermolecular interatomic distances less than 3.5 \AA are also shown. It must be pointed out that the rather close approaches of the molecules, 2.97 and 3.08 \AA from the carbonyl oxygen atom O(5) to C(23) and to C(24), are found in the structure. Bolton (1964) has shown that very close interactions between a carbonyl oxygen atom and a carbon atom are often found in structures which satisfy the following conditions: (a) Several carbonyl groups associated in a planar ring molecule. (b) Insufficient protons for complete hydrogen bonding between all electronegative atoms in or attached to the ring. The closest C...O distances thus found were 2.77 \AA in parabanic acid, 2.85 \AA in chloranil, 2.90 \AA in barbituric acid, 2.79 \AA in alloxan and 2.85 \AA in triketoindane. Although the approach of 2.97 \AA found in the present structure is not so short as in the examples shown by

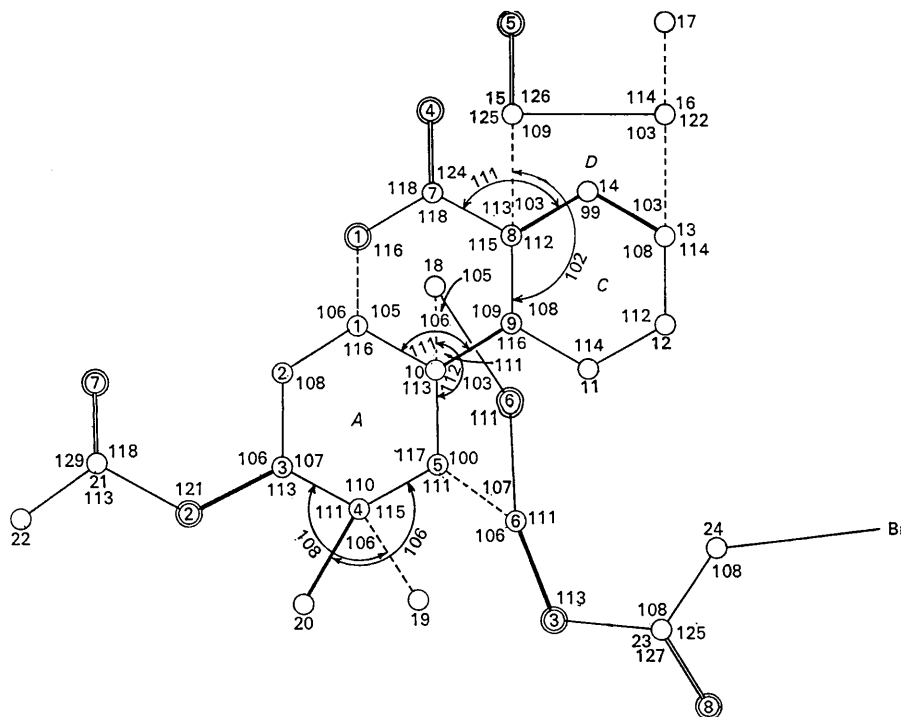


Fig. 4. Bond angles of the molecule.

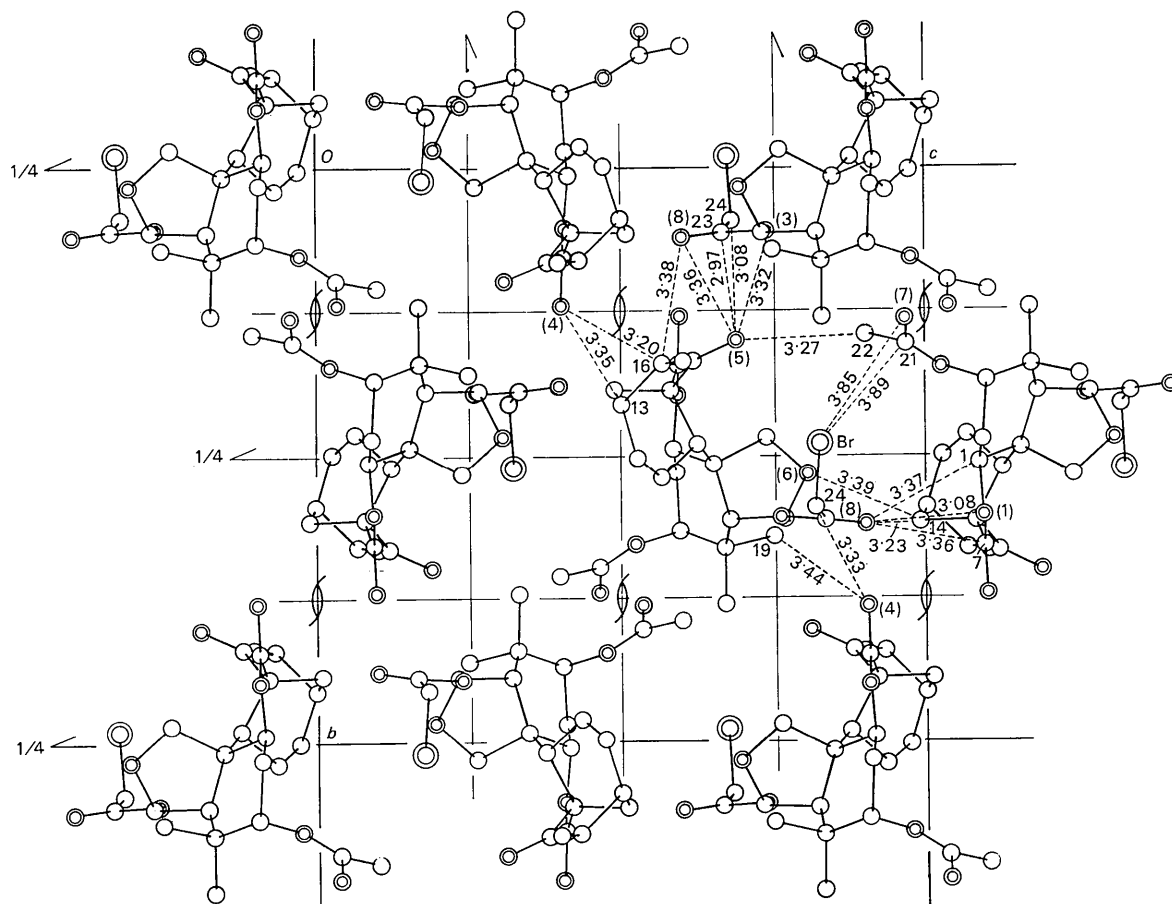


Fig. 5. Projection of the structure along the a axis. The numbering of the atoms is as in Fig. 2. Numbers in parentheses indicate oxygen atoms. The intermolecular interatomic distances less than 3.5 \AA , and less than 4 \AA in the case of those related to bromine, are shown.

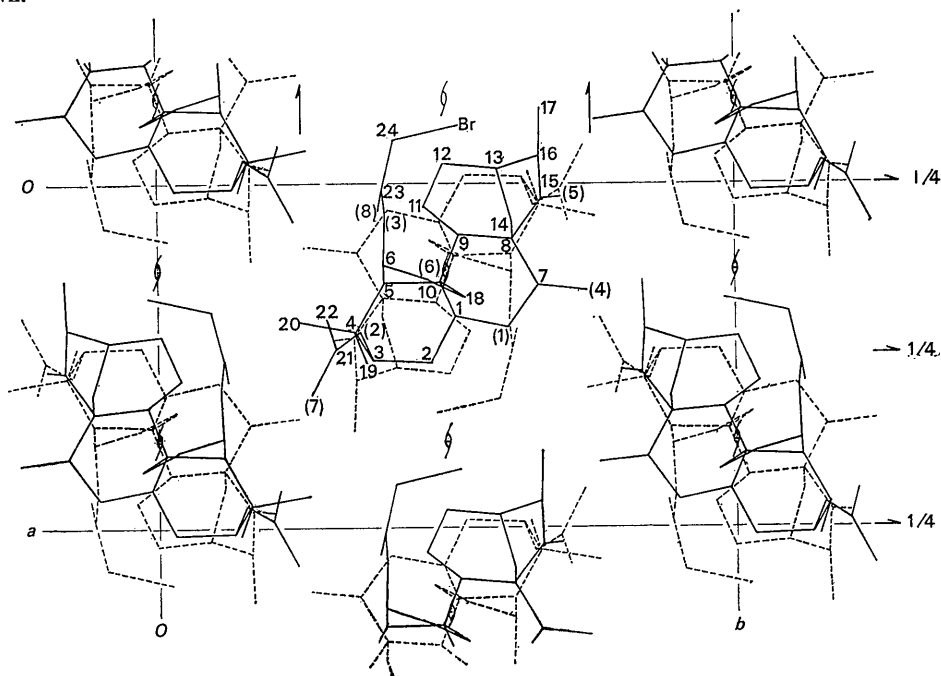


Fig. 6. Projection of the structure along the c axis.

Bolton, it is still significantly shorter than the expected minimum value of 3.1 Å corresponding to the sum of the minimum van der Waals contacts. It is to be noted that the present structure has no planar ring system, but an electronegative bromine atom is attached to the carbon atom C(24).

All the other packing distances seem to correspond to normal van der Waals separations.

As seen in Fig. 6, the gross feature of the crystal structure may be described as follows. The molecules are arranged in parallel chains along the twofold screw axes parallel to *c*. Within a chain the molecules are associated with each other head to tail, mainly through the van der Waals interactions involving the bromine and oxygen atoms O(8), O(6) and O(5) (Fig. 5). The chains are held together in the structure, as illustrated in Fig. 6, by the usual van der Waals forces and the C...O interactions described above.

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The Crystal Structure of Anhydrous Nitrates and their Complexes.

II. The 1:1 Copper(II) Nitrate-Nitromethane Complex*

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(Received 28 April 1965)

The structure of the complex $\text{Cu}(\text{NO}_3)_2 \cdot \text{CH}_3\text{NO}_2$ has been determined by two-dimensional Fourier methods. There are four molecules of complex in each orthorhombic unit cell of space group *Pnma* and dimensions $a = 12.41 \pm 0.04$, $b = 8.30 \pm 0.03$, $c = 7.08 \pm 0.03$ Å. Each copper atom has tetragonal pyramidal [4+1] coordination and the square bases of the pyramids are linked diagonally, through bridging nitrate groups at each corner, into corrugated sheets. The Cu-O distances within these sheets are all close to 1.95 Å and the fifth bond of length 2.31 Å to each copper atom is from an oxygen atom of the unidentate nitromethane. Adjacent corrugated sheets are held together in the *x* direction by van der Waals forces. The structure is compared with that of the α form of anhydrous copper(II) nitrate itself.

Experimental

Anhydrous copper(II) nitrate, prepared as described by Addison & Hathaway (1958), was dissolved in freshly distilled nitromethane at 60°C until a saturated

- #### References
- BERGHUIS, J., HAANAPPEL, IJ. M., POTTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
 BIJVOET, J. M., PEERDEMAN, A. F. & VAN BOMMEL, A. J. (1951). *Nature, Lond.* **168**, 271.
 BOLTON, W. (1964). *Nature, Lond.* **201**, 987.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS, A Fortran Crystallographic Least-squares Program*. Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.
 DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.
 IITAKA, Y. & NATSUME, M. (1964). *Tetrahedron Letters*, No. 20,1257.
 IKEDA, T. & KANATOMO, S. (1958). *J. Pharm. Soc. Japan*, **78**, 1128.
 KANATOMO, S. (1958). *Chem. Pharm. Bull. Japan*, **6**, 680.
 KANATOMO, S. (1961). *J. Pharm. Soc. Japan*, **81**, 1049, 1437.
 KUBOTA, T., MATSUURA, T., TSUTSUI, T. & NAYA, K. (1961). *Bull. Chem. Soc. Japan*, **34**, 1737.
 KUBOTA, T., MATSUURA, T., TSUTSUI, T. & NAYA, K. (1963). *J. Chem. Soc. Japan*, **84**, 353.
 KUBOTA, T., MATSUURA, T., TSUTSUI, T., UYEO, S., TAKAHASHI, M., IRIE, H., NUMATA, A., FUJITA, T., OKAMOTO, T., NATSUME, M., KAWAZOE, Y., SHUDO, K., IKEDA, T., TOMOEDA, M., KANATOMO, S., KOSUGE, T. & ADACHI, K. (1964). *Tetrahedron Letters*, No. 20,1243.
 NAYA, K. (1958). *J. Chem. Soc. Japan*, **79**, 885.
 TAKAHASHI, K., FUJITA, M. & KOYAMA, Y. (1958). *J. Pharm. Soc. Japan*, **78**, 699.
 TAKAHASHI, K., FUJITA, M. & KOYAMA, Y. (1960). *J. Pharm. Soc. Japan*, **80**, 594, 696.
 THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.

solution was obtained. Blue-green crystals of the complex were deposited on standing and analysis for the copper content confirmed the 1:1 composition. The crystals were deliquescent so, for X-ray studies, they were mounted in thin-walled Pyrex capillaries in a dry box.

Oscillation and equi-inclination Weissenberg photographs showed that the crystals were orthorhombic and

* Part I, Wallwork & Addison, 1965.