proceeds *trans*, with inversion at the carbon carrying the chlorine atom.

The closest intermolecular contacts are made by the molecules shown in Fig. 3. The distances between O_3 of one molecule and C_5, C_{10} and C_{11} of the other are 3·44, 3·58 and 3·62 Å respectively. They can be regarded as normal, if we assume that the hydrogen atom of the hydroxyl group is not directed towards these atoms. Of C · · · C distances, only five are somewhat lower than 4·0 Å and they range from 3·68 to 3·87 Å. The shortest Br · · · C approach, shown in Fig. 3, is 3·78 Å. All other intermolecular distances are equal to or longer than the sum of the corresponding van der Waals radii.

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The Crystal Structure and Absolute Configuration of the Monoclinic Form of *d*-Methadone Hydrobromide

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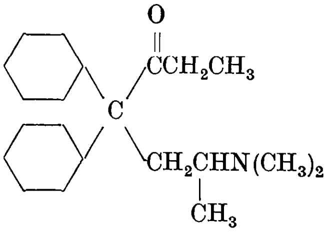
The crystal is monoclinic, probably $P2_1$, $a = 10{\cdot}69$, $b = 8{\cdot}74$, $c = 10{\cdot}74$ Å, $\beta = 94{\cdot}6°$, $Z = 2$. The structure determination, which was essentially three-dimensional, was begun by the heavy-atom method, and completed by means of differential syntheses. The absolute configuration of the molecule was determined by measuring the effect on two selected sets of reflexions of the imaginary part of the dispersion of copper radiation by the bromine atom.

Introduction

Methadone (Amidone, Dolophine, etc.) is a synthetic narcotic (Small, 1948; Attenburrow, Elks, Hems & Speyer, 1949; Baizer, 1953). It occurs in dextro- and laevo-rotatory isomers, the latter having by far the stronger analgesic properties. The structure determination was undertaken in order to assist investigations into the physiological properties of this compound by



establishing the absolute configuration of one of its isomers.

Experimental details

It has been found that crystals of *d*- or *l*-methadone hydrobromide grown from aqueous solution at room temperature may be either triclinic or monoclinic. It was decided to proceed with the structure determination of the monoclinic form, as it was felt that this would present the easier crystallographic problem. With an exception to be noted below, the *d*-isomer was used throughout the investigation.

The crystallographic data, obtained from precession photographs, and corrected for film shrinkage, are:

Monoclinic, probably $P2_1$

$$a = 10{\cdot}69 \pm 0{\cdot}03,\quad b = 8{\cdot}74 \pm 0{\cdot}02,\quad c = 10{\cdot}74 \pm 0{\cdot}03\ \text{Å}\,,$$
$$\beta = 94{\cdot}6 \pm 0{\cdot}2^\circ.$$

Also,

$$\varrho_o = 1{\cdot}32 \pm 0{\cdot}02\ \text{g.cm.}^{-3},\ \varrho_c = 1{\cdot}30 \pm 0{\cdot}01\ \text{g.cm.}^{-3}\ (Z=2),$$
$$\mu = 33\ \text{cm.}^{-1}\ (\text{Cu}\ K\alpha),\quad \mu = 25\ \text{cm.}^{-1}\ (\text{Mo}\ K\alpha)\,.$$

The crystal selected for examination was an elongated prism (very nearly a cylinder) of mean diameter 0·20 mm., and 1·7 mm. long. The long axis, coincident with b, was the only one suitable for rotation. Three-dimensional intensity data were collected on equi-inclination Weissenberg photographs of levels normal to b^* for values of $|k|$ up to 8. Data for the various levels were correlated by using a double layer-line screen to record simultaneously, on the two halves of the film, an equi-inclination photograph of the upper level, and an anti-equi-inclination photograph of the zero level (Hanson, 1958). A few reflexions on or near the b^* axis were not recorded on the Weissenberg photographs; some of these were obtained from precession photographs, using copper and molybdenum radiations. For the purpose of investigating the absolute configuration of the structure, an equi-inclination Weissenberg photograph for $|k| = 1$ was obtained by inclining the Weissenberg axis in the opposite sense to that used previously. It was thus possible to compare data for $(h1l)$ and $(h\bar{1}l)$.

In the collection of intensity data the stronger reflexions were recorded by integrating techniques, and photometered. The rest were recorded without integration, and estimated visually. Appropriate Lorentz-polarization factors were applied (Cochran, 1948; Kartha, 1952), and where applicable corrections were made for distortion of upper-level reflexions (Phillips, 1954). No corrections were made for absorption although this could have been done by treating the crystal as a cylinder of radius 0·1 mm. ($\mu R = 0{\cdot}33$). It is felt that errors due to absorption are small, and that their main result should be slightly erroneous temperature and scale factors. The total number of reflexions observed was 1926. The number theoretically observable with copper radiation is about 2337, and of these about 2159 have k indices equal to or less than 8. Finally, in order to provide further data for confirming the absolute configuration, some precession photographs were obtained (with molybdenum radiation) for a comparable crystal of the *l*-isomer.

Structure determination

All computations required for the procedures described in this section were carried out on FERUT, using the programmes described by Ahmed (1957).

The position of the bromine atom was obvious from inspection of the weighted $(h0l)$ reciprocal-lattice section. The fringes associated with the bromine–bromine vector were well-defined, and indicated reliable signs for most of the reflexions in the zone. A b-axis Fourier projection resolved more than half of the atoms, and suggested plausible positions for the rest. The phases of the general (hkl) reflexions were next assumed to be those of the bromine contribution, and a three-dimensional Fourier synthesis was computed. The origin was of course so chosen that the phase of the bromine contribution was everywhere real. Reflexions for which the bromine contribution was small were not considered. The resultant synthesis was centrosymmetrical, and approximated to a superposition of the actual structure and one related to it by a centre of symmetry. With some assistance from the b-axis projection, it was possible to assign tentative positions to all the atoms, although there was a possible second choice for three of them. Structure factors were computed at this stage, and the agreement residual ($R = \Sigma|F_o - F_c|/\Sigma|F_o|$) was found to be 19·3%. The scattering factor curves used were those of McWeeny (1951) for carbon, nitrogen, and oxygen, and that of Thomas & Umeda (1957) for bromine. The temperature factor was assumed to 2·35 Å^2; this value was subsequently modified to 2·85 Å^2. The three atomic positions which might have been in error were confirmed by computing the Fourier synthesis of one small region of the unit cell. A differential synthesis was computed for the remaining atoms. These syntheses were used to modify the atomic positions and structure-factor calculations indicated that the agreement residual at this stage was 14·3% for all reflexions and 14·7% for $(h0l)$ reflexions.

A second differential synthesis, computed this time for F_c as well as F_o, suggested the atomic positions in Table 1. For the light atoms, the average shifts suggested by the F_c synthesis, in the x, y, and z directions, were 0·0086, 0·0088, and 0·0096 Å. The maximum shifts were 0·0273, 0·0182, and 0·0302 Å. The shifts in the y direction are certainly not greater than those in the x and z directions, and it appears therefore that the finite summation error due to neglect of terms for which k exceeds 8 is negligible for this structure.

Observed and calculated peak electron densities are also listed in Table 1. The agreement is reasonable, but the comparison suggests (and this is confirmed by

Table 1. *Atomic positions*

	x/a	y/b	z/c	ϱ_o e.Å^{-3}	ϱ_c e.Å^{-3}
Br	0·9197	0·2500	0·1082	79·9	82·7
O	0·5840	0·4169	0·0838	13·3	13·2
N	0·8091	0·7296	−0·0040	11·1	10·7
C_1	0·5900	0·1342	0·2179	8·0	8·4
C_2	0·5577	0·2911	0·2809	8·0	8·7
C_3	0·5893	0·4330	0·1961	9·2	9·0
C_4	0·6131	0·5892	0·2579	9·7	8·8
C_5	0·6556	0·7074	0·1628	9·3	8·7
C_6	0·7956	0·6862	0·1338	9·2	8·9
C_7	0·8879	0·7963	0·2086	8·5	8·8
C_8	0·7583	0·6111	−0·0936	8·2	8·8
C_9	0·7622	0·8807	−0·0496	8·2	8·9
C_{10}	0·4774	0·6313	0·2919	9·7	8·8
C_{11}	0·3913	0·6962	0·2019	8·6	8·5
C_{12}	0·2645	0·7180	0·2272	8·7	8·9
C_{13}	0·2265	0·6748	0·3456	8·7	9·0
C_{14}	0·3111	0·6107	0·4326	8·5	8·7
C_{15}	0·4369	0·5821	0·4089	9·2	9·0
C_{16}	0·7104	0·5891	0·3732	9·4	9·0
C_{17}	0·7083	0·6997	0·4620	9·3	9·2
C_{18}	0·8059	0·7104	0·5584	8·9	8·8
C_{19}	0·9010	0·6023	0·5665	8·4	9·1
C_{20}	0·9033	0·4910	0·4781	8·7	9·0
C_{21}	0·8055	0·4816	0·3836	9·1	8·7

a comparison of observed and calculated principal curvatures, not listed) that the thermal motions of individual atoms increase somewhat with distance from the centre of gravity of the molecule. The structure factors of the $(h0l)$ zone were calculated for the positions in Table 1. The agreement residual was found to be 13·5%, a slight improvement over the previous value, for this zone, of 14·7%. It seems reasonable to assume that a corresponding improvement for all the data would have been apparent if three-dimensional calculations had been carried out.

Finally, a difference synthesis of the $(h0l)$ zone was computed. Apart from the region of the bromine atom, the difference map has no important features; there is one small negative region of about −1 e.Å^{-2}, a few peaks exceeding 1 e.Å^{-2}, and two of about 2 e.Å^{-2}. (Peak electron densities for carbon atoms in the corresponding F_o synthesis are about 9·0 e.Å^{-2}.) Many of the peaks can be roughly correlated with plausible hydrogen positions. The bromine position is surrounded by a symmetrical array of peaks and troughs characteristic of anisotropic thermal motion (Lipson & Cochran, 1953). The extreme electron densities are approximately +3 e.Å^{-2} and −3 e.Å^{-2}; the direction of maximum projected thermal motion makes angles of 62° and 33° with the positive directions of the *a* and *c* axes. To a first approximation the extreme values of B for the bromine atom, in this projection, would be 2·4 and 3·2 Å^2.

It seems clear that further refinement of the structure would require the assumption of different temperature factors for all atoms considered, and an anisotropic temperature factor for the bromine atom. The refinement would be practicable, but tedious, and probably not justified by the expected modest improvement in the accuracy of the result.

Reliability of the structure

It is believed that the structure defined in Table 1 is essentially correct. In support of this proposition, there is the agreement between observed and calculated peak electron densities, the absence of significant features in the *b*-axis difference map, and the plausibility of the structure itself. However, the final test for the correctness of any structure is the individual agreement between observed and calculated structure amplitudes. Three-dimensional structure-factor calculations were not undertaken for the final structure; the comparison had therefore to be made for the penultimate stage of refinement, with the understanding that the agreement for the ultimate stage would have been slightly better. It seems undesirable to publish the complete data (although these are available from the authors on request), and a summary may suffice. Table 2 gives the numbers of reflexions corresponding to specified categories of agreement; in order that the effect of the last stage of refinement may be estimated, parallel data are given for the $(h0l)$ zone in the last two stages of refinement. Structure factors were not calculated for unobserved reflexions, hence the summary applies only to observed reflexions. Values of F_o range from 2·4 to 97·2.

The 54 reflexions in categories (3) and (4) (for which the disagreement may be considered significant) form

Table 2. *Agreement summary*

	Number of reflexions		
Category	$(h0l)$ zone penultimate stage (R = 14·7%)	$(h0l)$ zone ultimate stage (R = 13·5%)	(hkl) penultimate stage (R = 14·3%)
1 ($\lvert\Delta F\rvert \le 2{\cdot}4$ *or* $\lvert\Delta F\rvert \le 0{\cdot}2F_o$)	186	194	1449
2 ($\lvert\Delta F\rvert \le 4{\cdot}8$ *or* $\lvert\Delta F\rvert \le 0{\cdot}4F_o$)	53	51	424
3 ($\lvert\Delta F\rvert \le 7{\cdot}2$ *or* $\lvert\Delta F\rvert \le 0{\cdot}6F_o$)	14	9	50
4 ($\lvert\Delta F\rvert \le 8{\cdot}4$)	2	1	4

$\Delta F = F_o - F_c$.
The smallest value of F_o is 2·4.

Each category includes all reflexions which meet the specified conditions, and which have not been previously included. For example, a reflexion in category 2 satisfies either (or both) of the conditions $\lvert\Delta F\rvert \le 4{\cdot}8$ and $\lvert\Delta F\rvert \le 0{\cdot}4F_o$, but does not satisfy either of the corresponding conditions for category 1.

less than 3% of the total number observed. None of these reflexions is very strong; F_o for the strongest is 19·2, and for 37 of them, is less than 10·0. The number of such reflexions in the ($h0l$) zone is appreciably reduced by the last stage of refinement, and it seems likely that a similar reduction would have been observed for the general reflexions if all structure factors had been calculated at this stage.

Any remaining significant discrepancies might be attributable to the use of a single, isotropic temperature factor or the unconsidered effects of hydrogen atoms, of which there are 58 in the unit cell. In any case, it is felt that the individual agreement is satisfactory, and that the essential correctness of the structure is beyond reasonable doubt.

The absolute configuration

Peterson has shown (1955) that the absolute configuration of optically active bromine derivatives may often be established (by the methods of Bijvoet, Peerdeman & van Bommel (1951), Trommel & Bijvoet (1954) and Peerdeman & Bijvoet (1956)) without the aid of special target materials. Violations of Friedel's law were therefore sought during the collection of intensity data. For the space group $P2_1$ the only polar axis is b, and the appropriate inequality can be given as $I_{hkl}/I_{h\bar{k}l} \neq 1$ ($I_{hkl}/I_{\bar{h}k\bar{l}} = 1$). It was found that for the sets of reflexions (210) and (11$\bar{2}$), the ratio of intensities was nearly two. The intensities were obtained by photometry of integrated spots, and are believed to be in error by not more than 10%.

For the reliable measurement of the effect of dispersion, the difference between the intensities of a set of reflexions should of course be as large as possible, and therefore the bromine contribution to the structure factor should be large also. Moreover, the intensities themselves should be low, in order to reduce the effect of errors of measurement; it follows that the light-atom contribution to the structure factor should almost cancel the bromine contribution. It is clear then that the interpretation of dispersion effects requires fairly reliable structure-factor calculations, since a small error in, say, the light-atom contribution will cause a proportionately much greater error in the complete structure factor. For a given accuracy of atomic position, therefore, it is better if the indices of the reflexions considered are low; it is fortunate that the sets (210) and (11$\bar{2}$) are satisfactory in this respect.

Appropriate structure factors were calculated, using, for the bromine atom $f = f_o + \Delta f' + i\Delta f''$, where f_o is the scattering factor used previously, and $\Delta f' = -0·9$ e.Å^{-2}; $\Delta f'' = 1·6$ e.Å^{-2} (Dauben & Templeton, 1955). For this calculation, an attempt was made to estimate the hydrogen contribution. Where possible, the hydrogen atoms were assumed to be in plausible positions, and were given the scattering factor predicted by McWeeny (1951). Methyl groups were given a scattering factor appropriate to a freely-rotating group (Cruickshank, 1955). The estimate of the hydrogen contribution was certainly not very accurate. It was small, however, and could safely have been neglected. Observed and calculated data are given in Table 3.

Table 3. *Calculated and observed structure factors*

	A_c	B_c	F_c	F_o
(210)	−5·5	15·1	16·0	18·7
(2$\bar{1}$0)	5·5	10·2	11·5	14·2
(11$\bar{2}$)	−5·4	12·2	13·4	17·1
(1$\bar{1}\bar{2}$)	5·4	6·7	8·6	12·6

The agreement seems to be satisfactory, and it is concluded that the atomic positions in Table 1 correspond to a right-handed set of axes.

As a further check on the absolute configuration, the intensities of the (210) set of reflexions were compared on precession photographs of the ($hk0$) zones of both the original crystal and a comparable crystal of the l-isomer. Molybdenum radiation was used, so that for bromine $\Delta f' = -0·3$ e.Å^{-2}, $\Delta f'' = 2·7$ e.Å^{-2} (Dauben & Templeton, 1955). Observed and calculated intensity ratios are compared in Table 4. The observed values are based on visual estimates,

Table 4. *Ratio* $I_{210}/I_{2\bar{1}0}$ (Mo $K\alpha$)

Isomer	Obs.	Calc.
d	3	3·4
l	⅓	1/3·4

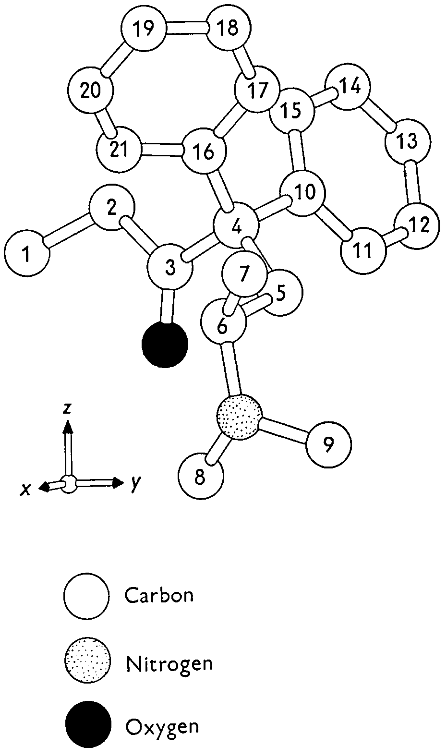


Fig. 1. The d-methadone molecule, as it occurs in the monoclinic form of the bromine derivative. The orientation triplet is composed of 1 Å vectors, in the directions of the principal axes.

and no great accuracy is claimed for them. However, the difference in intensities is considerably greater than for copper, and accuracy of measurement is not so important. It should be noted that the intensity ratio is inverted for the *l*-isomer.

Discussion of the structure

A projection of a single molecule along a convenient direction is shown in Fig. 1. The absolute configuration is that of the *d*-isomer. The bromine atom, which is not shown, lies near the apex of the pyramid formed by the nitrogen atom and its neighbours. It is 3·22 Å from N, and 3·70 and 3·62 Å from C_8 and C_9, respectively. With these exceptions, the nearest approach of the bromine atom to any light atom is 3·96 Å. (Hydrogen atoms are not considered in this discussion.) The nearest approach of light atoms in adjacent molecules is 3·50 Å. It must be emphasized that the configuration shown has been established only for the monoclinic form of the bromine derivative; it could conceivably differ in other circumstances.

Table 5. *Bond lengths (mean* $\sigma(l)$ *=* 0·03 Å)

Bond	Length	Bond	Length
Aromatic	*1·40* Å	Single	*1·54* Å
C–C	—	C–C	—
C_{10}–C_{11}	1·400 Å	C_1–C_2	1·579 Å
C_{11}–C_{12}	1·417	C_2–C_3	1·590
C_{12}–C_{13}	1·417	C_3–C_4	1·529
C_{13}–C_{14}	1·368	C_4–C_5	1·546
C_{14}–C_{15}	1·410	C_5–C_6	1·565
C_{15}–C_{10}	1·428	C_6–C_7	1·556
C_{16}–C_{17}	1·359	C_4–C_{10}	1·567
C_{17}–C_{18}	1·414	C_4–C_{16}	1·552
C_{18}–C_{19}	1·382		
C_{19}–C_{20}	1·366	Single	*1·47* Å
C_{20}–C_{21}	1·401	C –N	—
C_{21}–C_{16}	1·382	C_6–N	1·545 Å
		C_8–N	1·486
Double	*1·20* Å	C_9–N	1·481
C=O	—		
C_3–O	1·212 Å		

Table 6. *Bond angles (mean* $\sigma(\theta)$ *=* 1·6°)

Angle	Value	Angle	Value
Planar	*120°*	Tetrahedral	*109·5°*
C_{10}–C_{11}–C_{12}	120·7°	C_1–C_2–C_3	111·7°
C_{11}–C_{12}–C_{13}	118·9	C_3–C_4–C_5	111·0
C_{12}–C_{13}–C_{14}	120·1	C_4–C_5–C_6	112·9
C_{13}–C_{14}–C_{15}	122·5	C_5–C_6–C_7	113·6*
C_{14}–C_{15}–C_{10}	117·7	C_5–C_6–N	109·1
C_{15}–C_{10}–C_{11}	120·0	C_7–C_6–N	103·8*
C_4–C_{10}–C_{11}	120·3	C_3–C_4–C_{10}	100·7*
C_4 –C_{10}–C_{15}	119·2	C_3–C_4–C_{16}	115·1*
C_{16}–C_{17}–C_{18}	120·5	C_5–C_4–C_{10}	108·8
C_{17}–C_{18}–C_{19}	119·9	C_{10}–C_4–C_{16}	112·8
C_{18}–C_{19}–C_{20}	119·8	C_5–C_4–C_{16}	108·3
C_{19}–C_{20}–C_{21}	119·5		
C_{20}–C_{21}–C_{16}	121·4	Pyramidal	*113°*
C_{21}–C_{16}–C_{17}	118·1	C_6–N–C_8	113·1°
C_4 –C_{16}–C_{17}	120·8	C_6–N–C_9	118·7*
C_4 –C_{16}–C_{21}	120·4	C_8–N–C_9	108·1*
C_2 –C_3 –C_4	119·0		
C_4 –C_3 –O	121·8		
C_2 –C_3 –O	119·0		

* Value significantly different from expected.

The mean standard deviations of coordinates, calculated by Cruickshank's method (Lipson & Cochran, 1953) are 0·0021 Å for bromine, and 0·021 Å for light atoms. The mean standard deviations of bond lengths and angles were approximately estimated to be 0·03 Å and 1·6°, respectively. Bond lengths and angles for the structure and, for comparison, the expected values, are given in Tables 5 and 6. Of the bond lengths, little can be said; none is, by the criterion of Cruickshank (Lipson & Cochran, 1953), significantly different from the expected value. This is true also of the bond angles in planar configuration. For the other configurations, however, some differences are much greater than $2{\cdot}33\sigma(\theta)$, and must therefore be considered significant. It seems likely that there is considerable steric force within the molecule, and that this is most readily balanced by the distortion of some angles.

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