# 471. *The Structure of Molecular Compounds. Part XII.* Molecular Compounds of Tri-o-thymotide.*

By D. Lawton and H. M. Powell.

Tri-*o*-thymotide forms molecular inclusion compounds with many substances such as alkanes and their derivatives including alkyl halides, alcohols, esters, ketones, ethers, and polymethylene dihalides. If the included molecule does not differ much from the " straight " chain type, the resulting compound belongs to one of two classes. A clathrate type, $2C_{33}H_{36}O_6,M$, is formed with included molecules, M, of greatest length less than 9·5 Å. Longer molecules are enclosed in a different channel-type structure of composition $C_{33}H_{36}O_6,xM$ where $x$, which need not be rational, diminishes with increasing length of the included molecule. Several ordered and disordered variations of the two structures have been found. Some of the channel structures give one-dimensional diffraction patterns, due to included molecules, superposed on the main single-crystal *X*-ray diffraction pattern. The unit-cell dimensions of the clathrate type increase slightly and in a regular manner to accommodate the larger included molecules. For the channel type the cell dimensions are more nearly constant but vary in a periodic way as the length of included molecules increases. These changes are explained. Each of the 50 compounds studied is a new example of spontaneous optical resolution.

In several sets of crystalline molecular compounds one component forms an enclosing structure around the other. For each series this structure has, with small variations, a fixed form maintained by strong bonding between its components. Thus in the β-quinol clathrates $3C_6H_4(OH)_2,M$ (where M = various small atoms or molecules),[1] and in the adducts of urea or thiourea with numerous aliphatic compounds [2] there are covalencies, hydrogen bonds, or other forms of strong interaction binding the atoms of the enclosing structure. The enclosable molecules are limited to those which can fit into the restricted spaces.

In some circumstances a number of different structures might be formed by a given enclosing component. Thus for the gas hydrates various forms of polyhedra of water molecules surrounding the hydrating molecules have been suggested.[3] Although water or a more complex molecule may in this way form several different enclosures the number will be limited by factors such as the positions of the hydrogen-bonded atoms and the number and direction of their links.

However, in certain instances van der Waals forces alone are sufficient to hold together the molecules of an enclosing structure. In such a case a greater adaptability to the shape of enclosed molecules is to be expected. The van der Waals equilibrium distances between neighbouring atoms vary more than the length of a given type of hydrogen bond, such as that between two phenolic hydroxyl groups. Also van der Waals attraction is not restricted, as is hydrogen bonding, either to particular atoms which have definite positions in the molecule or to special directions in space relative to the rest of the molecule. The interaction between enclosed and enclosing molecules is qualitatively similar to that between any two molecules of the enclosing structure. The arrangements of the cage-forming molecules may therefore be considerably influenced by their interaction with the enclosed component.

* Part XI, *J.*, 1956, 4855.

[1] Palin and Powell, *J.*, 1948, 815.
[2] Schlenk, *Annalen*, 1949, **565**, 204; 1951, **573**, 142.
[3] Von Stackelberg, *Naturwiss.*, 1949, **36**; Clausen, *J. Chem. Phys.*, 1951, **19**, 259, 662; Pauling and Marsh, *Proc. Nat. Acad. Sci.*, 1952, **38**, 112.

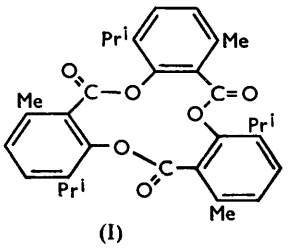
TABLE 1. *Adducts of tri-o-thymotide with unbranched molecules.*

| Included molecule (A) R·OH, where R = | | Calc. length of included molecule in extended form (Å) | Temp. | Dimensions of unit cell or pseudo-unit cell ($\psi$) (Å) *a* | *c* | Structure types apparent space-group | | Density (g./c.c. at 20°) | No. of included molecules per unit cell containing 6 tri-o-thymotide molecules † Calc. from cell dimensions and density | By chemical analysis (approx.) |
|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3$ | | 4·6 | 18° | (13·460 ± 0·001) * | (30·223 ± 0·005) * | Cavity | $P3_121$ | — | — | 3 |
| $C_2H_5$ | | 5·6 | 6 | — | 30·136 ± 0·004 | ,, | ,, | 1·1627 ± 0·0005 | 3·03 ± 0·05 | 3·7 |
| | | — | 7 | 13·440 ± 0·002 | — | | | | | |
| | | — | 18 | — | 30·155 ± 0·001 | | | | | |
| | | — | 19·5 | 13·455 ± 0·002 | — | | | | | |
| | | — | 37·5 | — | 30·189 ± 0·003 | — | | | | |
| | | — | 38·5 | 13·470 ± 0·002 | — | | | | | |
| $C_3H_7$ | | 6·9 | 18 | 13·515 ± 0·003 | 30·288 ± 0·004 | Cavity | $P3_121$ | 1·1606 ± 0·0005 | 2·98 ± 0·06 | 3·4 |
| $C_4H_9$ | | 8·1 | 18 | 13·617 ± 0·004 $\psi$ | 30·603 ± 0·004 | ,, | ,, | 1·1456 ± 0·0005 | 2·98 ± 0·05 | 3·5 |
| $C_5H_{11}$ | | 9·4 | 18 | 13·695 ± 0·006 | 30·742 ± 0·005 | ,, | ,, | 1·138 ± 0·002 | 2·9 ± 0·1 | — |
| $C_5H_{11}$ | | 9·4 | 18 | 14·310 ± 0·001 | 28·987 ± 0·002 | Channel | $P6_2$ | — | — | 2·4 |
| $C_6H_{13}$ | | 10·7 | 19·5 | 14·268 ± 0·001 | 29·159 ± 0·003 | ,, | ,, | 1·1238 ± 0·0005 | 3·02 ± 0·03 | 3·1 |
| $C_7H_{15}$ | | 11·9 | 18 | 14·31 ± 0·01 | 29·055 ± 0·006 | ,, | $P6_1$ | 1·1217 ± 0·0005 | 2·67 ± 0·06 | 2·4 |
| $C_8H_{17}$ | | 13·2 | 19 | 14·307 ± 0·002 | 29·033 ± 0·002 | ,, | ,, | 1·1184 ± 0·0005 | 2·28 ± 0·02 | 2·4 |
| $C_{10}H_{21}$ | | 15·7 | 18 | 14·2825 ± 0·0005 | 29·120 ± 0·002 | ,, | ,, | 1·1251 ± 0·0005 | 2·00 ± 0·01 | 2·9 |
| $C_{12}H_{25}$ | | 18·2 | 18 | 14·314 ± 0·001 | 29·012 ± 0·006 | ,, | ,, | 1·1231 ± 0·0005 | 1·68 ± 0·02 | — |
| $C_{16}H_{33}$ | | 23·2 | 18·5 | 14·302 ± 0·001 | 29·050 ± 0·002 | ,, | ,, | 1·1263 ± 0·0005 | 1·32 ± 0·01 | — |
| $C_{18}H_{37}$ | | 25·7 | 18 | 14·304 ± 0·001 | 29·060 ± 0·005 | ,, | ,, | 1·1263 ± 0·0005 | 1·19 ± 0·01 | — |
| (B) R·X | | | | | | | | | | |
| R | X | | | | | | | | | |
| $CH_3$ | Br | 5·9 | — | 13·467 ± 0·003 | 30·119 ± 0·005 | Cavity | $P3_121$ | — | — | 2·6 |
| $CH_3$ | I | 6·3 | — | 13·5 | 30·2 | ,, | ,, | 1·2597 ± 0·0006 | *ca.* 3 | — |
| $C_2H_5$ | Br | 6·8 | — | 13·540 ± 0·002 | 30·140 ± 0·002 | ,, | ,, | 1·2152 ± 0·0006 | 3·05 ± 0·02 | 3·0 |
| $C_2H_5$ | I | 7·1 | — | 13·564 ± 0·005 | 30·28 ± 0·01 | ,, | ,, | 1·250 ± 0·002 | 2·96 | 2·9 |
| $C_3H_7$ | Br (A) | 8·0 | — | 13·7 $\psi$ | — | ,, | ,, | — | — | — |
| $C_3H_7$ | Br (B) | 8·0 | — | 13·62 ± 0·01 × 2 | 30·49 ± 0·03 | ,, | ,, | 1·206 ± 0·001 | *ca.* 3 | — |
| $C_3H_7$ | I | 8·4 | — | 13·7 × 2 | 30·3 | ,, | ,, | 1·2368 ± 0·0005 | *ca.* 3 | 3·0 |
| $C_4H_9$ | Br | 9·3 | — | 13·8 × 2 | 30·4 | ,, | ,, | 1·1908 ± 0·0003 | *ca.* 3 | 2·7 |
| $C_4H_9$ | I | 9·6 | 18 | 14·252 ± 0·003 | 29·030 ± 0·005 | Channel | $P3_1$ | 1·207 ± 0·001 | 2·95 ± 0·03 | 2·4 |
| $C_5H_{11}$ | Br | 10·5 | 20·5 | 14·255 ± 0·001 | 29·137 ± 0·004 | ,, | ,, | 1·1747 ± 0·001 | 3·02 ± 0·03 | 2·6 |
| $C_5H_{11}$ | I | 10·9 | *ca.* 18 | 14·288 ± 0·003 | 29·127 ± 0·006 | ,, | ,, | 1·2155 ± 0·0005 | 3·03 ± 0·02 | 3·1 |
| $C_6H_{13}$ | Br | 11·8 | 19 | 14·309 ± 0·001 | 29·120 ± 0·004 | ,, | $P6_1$ | 1·1650 ± 0·006 | 2·74 ± 0·12 | 2·6 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $C_7H_{15}$ | Br | 13·0 | 16·5 | 14·323 ± 0·008 | 29·033 ± 0·003 | ,, | ,, | 1·1586 ± 0·0006 | 2·40 ± 0·04 | 2·5 |
| | | — | 31·5 | 14·348 ± 0·006 | 29·024 ± 0·004 | | | — | — | — |
| $C_7H_{15}$ | I | 13·4 | 18·5 | 14·321 ± 0·003 | 29·030 ± 0·005 | ,, | ,, | 1·1972 ± 0·0003 | 2·42 ± 0·02 | 2·1 |
| $C_8H_{17}$ | Br | 14·3 | 19 | 14·294 ± 0·008 | 29·034 ± 0·008 | ,, | ,, | 1·1584 ± 0·0008 | 2·14 ± 0·04 | 1·96 |
| $C_8H_{17}$ | I (A) | 14·7 | — | 14·3 | 29·0 | ,, | ,, | — | — | 2·2 |
| $C_8H_{17}$ | I (B) | 14·7 | 18 | 14·278 ± 0·003 $\psi$ | 29·024 ± 0·006 | ,, | ,, | 1·1791 ± 0·001 | 1·95 ± 0·02 | 2·1 |
| $C_{16}H_{33}$ | Br | 24·4 | 16·5 | 14·311 ± 0·003 | 29·039 ± 0·002 | ,, | ,, | 1·1555 ± 0·001 | 1·36 ± 0·02 | 1·5 |
| $C_{16}H_{33}$ | I | 24·7 | 19 | 14·306 ± 0·003 | 29·056 ± 0·009 | ,, | ,, | 1·1298 ± 0·004 | 0·95 ± 0·04 | 1·3 |
| $C_{18}H_{37}$ | Br | 26·9 | 18 | 14·322 ± 0·001 | 29·078 ± 0·002 | ,, | ,, | 1·1540 ± 0·001 | 1·26 ± 0·01 | — |
| $C_{18}H_{37}$ | I (A) | 27·2 | 20 | 14·320 ± 0·002 | 29·044 ± 0·008 | ,, | ,, | 1·1664 ± 0·001 | 1·19 ± 0·01 | — |
| $C_{18}H_{37}$ | I (B) | 27·2 | — | 14·35 ± 0·05 | 29·2 ± 0·1 | | ,, | 1·144 ± 0·001 | — | — |
| (C) $X\cdot[CH_2]_n\cdot X$ | | | | | | | | | | |
| $n$ | X | | | | | | | | | |
| 1 | Br | 7·0 | 21 | 13·537 ± 0·001 $\psi$ | 30·174 ± 0·004 | Cavity | $P3_121$ | 1·285 ± 0·004 | 3·07 ± 0·07 | 2·3 |
| 1 | I | 7·7 | — | 13·655 ± 0·005 | 30·33 ± 0·01 | ,, | ,, | 1·347 ± 0·001 | 2·99 ± 0·03 | 3 |
| 2 | Br | 8·3 | — | 13·7 | 30·3 | ,, | ,, | — | — | 2·6 |
| 3 | Br (A) | 9·5 | — | 13·9 ± 0·2 | 30·6 ± 0·3 | ,, | ,, | — | — | 1·2 |
| 3 | Br (B) | 9·5 | — | 13·79 ± 0·01 × 2 | 30·57 ± 0·02 | ,, | ,, | — | — | 3·1 |
| 6 | I | 14·0 | — | 14·2 | 29·2 | Channel | $P6_1$ | — | — | — |
| (D) ROR′ | | | | | | | | | | |
| R | R′ | | | | | | | | | |
| $C_2H_5$ | $C_2H_5$ | 8·9 | 18 | 13·623 ± 0·002 | 30·715 ± 0·010 | Cavity | $P3_121$ | 1·1408 ± 0·001 | 3·03 ± 0·04 | — |
| $CH_3$ | $C_4H_9$ | 10·1 | 19 | 14·232 ± 0·002 | 29·153 ± 0·002 | Channel | $P3_1$ | 1·117 ± 0·001 | 3·05 ± 0·05 | — |
| $C_2H_5$ | $C_4H_9$ | 11·4 | 18 | 14·252 ± 0·002 | 29·268 ± 0·002 | ,, | $P6_2$ | 1·1216 ± 0·0007 | 3·00 ± 0·03 | — |
| (E) $C_nH_{2n+2}$ | | | | | | | | | | |
| $C_5H_{12}$ | | 9·0 | — | 14·31 ± 0·05 | 29·05 ± 0·05 | Channel | $P6_1$ | — | — | — |
| $C_6H_{14}$ | | 10·3 | — | 14·31 ± 0·05 | 29·05 ± 0·05 | ,, | $P3_1$ | — | — | — |
| (F) | | | | | | | | | | |
| $I_2$ | | 7·0 | — | 13·33 ± 0·05 | 30·2 ± 0·3 | Cavity | $P3_121$ | 1·33 ± 0·01 | — | — |
| $Hg(C_2H_5)_2$ | | 9·8 | — | 14·17 ± 0·04 | 29·06 ± 0·08 | Channel | $P6_2$ | — | — | — |
| (G) | | | | | | | | | | |
| $C_2H_4I_2$. 90% of cavities vacant | | — | — | 13·35 | 30·12 | Cavity | $P3_121$ | 1·185 | — | — |

* Product may be impure. The pure compound probably unobtainable. See text. † Given only when the constants are all known with sufficient accuracy.

Among compounds of this kind now discovered are the crystalline adducts of tri-*o*-thymotide (I) with a variety of substances. Wilson Baker, Gilbert, and Ollis [4] first showed the existence of such compounds. Two structures have already been recognised,[5] one containing benzene or chloroform and the other *n*-hexane. The two types although related in cell dimensions and in their symmetries are readily distinguishable. Many of the new adducts described in this paper have structures similar to one or other of them; some have structures which differ from both but have a structural relation to them, but in others no connection is apparent. This communication gives details only for those which are trigonal or hexagonal. These all resemble the two types mentioned but the symmetry relations prove to be complex and the two kinds cannot be contrasted simply by attributing to each a single space-group. For convenience they will be called the cavity and the channel type.



(I)

The cavity type includes adducts which resemble those of chloroform or benzene. They are trigonal and have $000l$ absent unless $l = 3n$. In general the *X*-ray reflection $hkil$ is not equal in intensity to $hki\bar{l}$, *i.e.*, oscillation photographs about the *c* axis are unsymmetrical above and below the zero layer-line, but those in which oscillation is about the *a* axis are symmetrical. The space-group is $P3_121$ (or enantiomorphous $P3_221$). The unit cell, referred to hexagonal axes, has *a* in the range 13·3—13·9 and *c* in the range 30·1—31·1 Å. This cell contains six molecules of tri-*o*-thymotide which by symmetry are all of the same enantiomorphous form. In nearly every case there are three molecules of the second component per unit cell; exceptionally a departure from the exact 2 : 1 ratio of tri-*o*-thymotide to the other component occurs.

The channel-type adducts are like that of *n*-hexane. The unit cells all have *a* about 14·3 and *c* about 29·0, *i.e.*, *a* is larger and *c* smaller than the corresponding dimension of the cavity type. On the basis of absent *X*-ray reflections they cannot all be attributed to the same space-group. Some, such as the *n*-pentyl alcohol adduct with $000l$ absent for $l \neq 3n$, appear to have space-group $P6_2$ (or enantiomorphous $P6_4$). For this space-group single-crystal oscillation photographs about the *c* axis should be symmetrical above and below the zero layer line, and should repeat every 60°. Close examination of the diffraction patterns shows that the *n*-pentyl iodide and some other adducts depart from this symmetry. Repetition occurs every 120° for oscillation about the *c* axis; oscillation photographs taken at 60° to each other have top and bottom interchanged. The effect is visible in only a few spots. Re-examination of the hexane adduct photographs, consequent on this observation, revealed similar but very faint effects. Differences of intensities of corresponding spots above and below the zero layer are slight, but that they are real symmetry effects is shown by the systematic alternations above and below the zero layer at 60° intervals. Accordingly for certain adducts the formal space-group will be $P3_1$ (or enantiomorphous $P3_2$). Since the effect in adducts of *n*-pentyl iodide and the molecules which contain a heavy atom is more marked than in *n*-hexane and other molecules which do not, it must be due to the included molecule. Others of these channel-type adducts with $000l$ absent when $l \neq 6n$ have space-group $P6_1$ (or enantiomorphous $P6_5$). Their oscillation photographs repeat accurately at 60° intervals around the *c* axis and are symmetrical about the zero layer.

Table 1(A) records constants for adducts with a series of *n*-alcohols. The second column gives the calculated maximum lengths required for packing each molecule into a space in the crystal. The molecule is assumed to have the normal form of aliphatic chain. Each carbon–carbon bond of length 1·54 Å is projected on a line passing through alternate carbon atoms and the projected length 1·256 Å is taken as the contribution to

[4] Baker, Gilbert, and Ollis, *J.*, 1952, 1443.
[5] Newman and Powell, *J.*, 1952, 3747.

the total distance between the centres of the terminal atoms. The method is extended to other molecules in the later Tables. Distances C–Cl = 1·76, C–Br = 1·91, C–I = 2·10, C–O = 1·43 and O–H = 0·96 Å are projected similarly; the C—O—C angle in ethers is taken as the tetrahedral; in diethylmercury the two C–Hg bonds are assumed to be collinear and of length 2·0 Å. In this way a projected length between terminal atom centres is derived. Normally hydrogen atoms are ignored but in the case of *n*-alcohols the projection of the O–H distance is included. To find the maximum packing length allowance is made for end-groups. For alkanes and halogen derivatives the van der Waals radii Cl = 1·80, Br = 1·95, I = 2·15 or $CH_3$ = 2·0 Å, are added to the projected lengths between terminal atom centres. For the alcohols a van der Waals radius of 1·2 Å is used for the hydroxyl-H atoms.

*Structural Type of Adduct and Dimensions of Included Molecule.*—Inclusion compounds of urea or β-quinol are not formed by molecules which have some dimension incompatible with the space available. With tri-*o*-thymotide similar critical dimensions are found but molecules are not divided by these limits into those which do and those which do not form molecular compounds; rather, the dimensions determine which of several structurally different types of molecular compound is formed. This communication excludes wide molecules so that here the length only is involved. As Table 1(A) shows, *n*-alcohols of length less than about 9·5 Å give the cavity-type adduct of simple and fixed molecular ratio $2C_{33}H_{36}O_6$,R·OH. Those of length greater than this form a series of channel-type adducts in which the molecular ratio, although definite for a given alcohol, may not be simple and varies from one to another.

The existence of one type of adduct with very long molecules is evidence for a structure containing extended channels. The compositions confirm this. The longer the chain included in the channel the greater the number of tri-*o*-thymotide molecules required to enclose it. Accordingly, in the Table where figures refer to channel-type unit cells of fixed tri-*o*-thymotide content, the number of included molecules diminishes as the molecular length increases. All molecules listed in Table 1(A) as included in the channel type have similar cross-sections but vary in length. That they fit in the channels without difficulty is apparent from the inclusion (Table 2) of branched molecules without marked changes in cell dimensions. Variation in length of the included molecule has only small effects on the width of the channel or the repeat distance along its structure. To a first approximation the enclosing structure is constant for all adducts of the longer *n*-alcohols. The minor variations, less than 0·2 Å, are considered below. *X*-Ray evidence shows that the channels are parallel to the *c*-axis.

For the other type of adduct a critical length which cannot be exceeded by the included molecule suggests cavities of limited dimensions. As the size of included molecule varies there is, with one exception, no change from the ideal molecular ratio resulting from every cavity's being occupied by a single molecule. Variations up to nearly 1·0 Å in cell dimensions show that in this type the enclosing structure adapts itself to a greater extent to the dimensions of the enclosed molecule, even for the different *n*-alcohols. In β-quinol clathrates hydrogen bonds link the component molecules of the enclosing structure and the cavity can be altered to fit the shape of included molecule only by a process analogous to the stretching of a trellis. Distances between joints remain constant but the shape of the hole alters by increase in one diagonal and decrease in the other. The cell dimensions for pure β-quinol with all its cavities empty are the same as those for the clathrate if the enclosed molecule is small. They are determined by contacts between atoms of the quinol structure itself. A small molecule which is a little too long in one direction to be included in this structure will form a clathrate but, in so doing, causes *c* to increase and *a* to diminish by the trellis extension effect. The behaviour in tri-*o*-thymotide cavity-type adducts is different. Enlargement of the hole can take place in all directions. The available space cannot be completely filled in the methanol compound which has nearly the same cell dimensions as its ethanol analogue. This is confirmed by the observation of

TABLE 2. *Adducts of tri-o-thymotide with branched molecules.*

| Included molecule (A) CORR′ R | R′ | Calc. length of included molecule in extended form (Å) | Temp. | Dimensions of unit cell (Å) *a* | *c* | Structure type | Apparent space group | Density (g./c.c. at 20°) | No. of included molecules per unit cell containing 6 tri-*o*-thymotide molecules. † Calc. from cell dimensions and density |
|---|---|---|---|---|---|---|---|---|---|
| $CH_3$ | $CH_3$ | 6·5 | 20° | 13·470 ± 0·008 | 30·273 ± 0·010 | Cavity | $P3_121$ | 1·1689 ± 0·0003 | 3·06 ± 0·12 |
| $C_2H_5$ | $C_2H_5$ | 9·0 | 19 | 13·650 ± 0·003 | 31·064 ± 0·003 | ,, | ,, | 1·1359 ± 0·0007 | 3·00 ± 0·05 |
| A tetraketone * | | 49·2 | — | 14·337 ± 0·003 | 28·958 ± 0·005 | Channel | $P6_1$ | — | — |
| (B) R·$CO_2$R′ R | R′ | | | | | | | | |
| H | $n$-$C_3H_7$ | 9·5 | — | 13·55 ± 0·05 | 30·5 ± 0·3 | Cavity | $P3_121$ | 1·157 ± 0·001 | — |
| $n$-$C_{12}H_{25}$ | $CH_3$ | 20·2 | — | 14·278 ± 0·001 | 29·093 ± 0·005 | Channel | $P6_1$ | 1·1293 ± 0·0008 | — |
| (C) $CH_3$·CHRX R | X | | | | | | | | |
| $C_2H_5$ | Br | 8·0 | — | 13·63 ± 0·05 | 30·45 ± 0·1 | Cavity | $P3_121$ | 1·1945 ± 0·0007 | — |
| $C_6H_{13}$ | OH | 11·9 | — | 14·24 ± 0·1 | 29·09 ± 0·1 | Channel | $P6_1$ | — | — |
| $C_6H_{13}$ | Br (A) | 13·0 | — | 14·2 ± 0·2 | 29·1 ± 0·2 | ,, | ,, | 1·193 ± 0·0007 | — |
| $C_6H_{13}$ | Br (B) | 13·0 | — | 14·426 ± 0·003 | 28·911 ± 0·003 | ,, | ,, | — | — |

* $CH_3$·$[CH_2]_7$·CO·$CH_2$·CO·$[CH_2]_7$·CO·$CH_2$·CO·$[CH_2]_7$·$CH_3$. † Given only when the constants are all known with sufficient accuracy.

TABLE 3. *Some diffraction effects due to molecules included in the channel structure.*

| Included molecule | Approx. length calc. for molecule in extended form (Å) | Spacing calc. from one-dimensional layer streaks (Å) | Assumed orders of observed streaks (*c*-axis oscillation) | No. of included molecules per unit cell Ideal, calc. from spacing of third column | Calc. from unit cell weight |
|---|---|---|---|---|---|
| *n*-Butyl iodide | 9·6 | — | None obs. | — | — |
| *n*-Pentyl bromide (A) | 10·5 | 8·8 | 1, 2 | 3·3 | — |
| ,, (B) | 10·5 | 9·6 | † 1, 2 | 3·0 | 3·02 ± 0·03 |
| *n*-Pentyl iodide | 10·9 | — | None obs. | — | — |
| *n*-Hexyl bromide | 11·7 | 11 | 2 | 2·6 | 2·74 ± 0·12 |
| *n*-Heptyl bromide | 13·1 | 12 | 3 | 2·4 | 2·40 ± 0·04 |
| *n*-Heptyl iodide | 13·4 | 12·5 | 2, 3 | 2·3 | 2·40 ± 0·02 |
| *n*-Octyl bromide | 14·3 | 13·5 | 2, 3 | 2·1 | 2·14 ± 0·04 |
| *n*-Octyl iodide (A) | 14·7 | 14·5 | * 2, 4 | 2·0 | 1·95 ± 0·02 |
| ,, (B) | 14·7 | — | § None obs. | — | — |
| *n*-Hexadecyl bromide | 24·4 | 24 | 3, 4, 5, 6, 7 | 1·2 | 1·36 ± 0·02 |
| *n*-Hexadecyl iodide | 24·7 | 24 | 4, 6, 7 | 1·2 | 0·95 ± 0·04 |
| *n*-Octadecyl bromide | 26·9 | 26 | 1, 2, 3, 4, 5 | 1·1 | 1·26 ± 0·01 |
| *n*-Octadecyl iodide (A) | 27·2 | 27 | 2, 3, 4, 5, 6, 7, 8 | 1·1 | 1·19 ± 0·01 |
| ,, (B) | 27·2 | — | None obs. | — | — |
| 2-Bromo-octane | 13·1 | 12 × 2 | ‖ 1, 2, 3, 4, 6 | 2·4 | 2·49 ± 0·02 |
| Hexamethylene di-iodide | 14·0 | 12·5 | ‡ 1, 2, 3 | 2·3 | — |
| Diethyl mercury | 9·8 | 9·7 | † 1, 3 | 3·0 | — |
| Methoxybutane | 10·1 | 9·7 | † 1 | 3·0 | 3·03 ± 0·05 |
| Ethoxybutane | 11·4 | 9·7 | † 1 | 3·0 | 3·03 ± 0·04 |

(A) (B) indicate that two crystalline forms are found. * Coincident with 4th and 8th sharp layers. † Coincident with 3rd, 3rd and 6th, or 3rd and 9th sharp layers. ‡ Also streaks corresponding to 3·5 Å. § Additional sharp spots on 4th and 8th layers. ‖ Molecules presumed paired, head-to-head.

approximately the same values for crystals of tri-*o*-thymotide which have been obtained in a trigonal form with most of the cavities unoccupied. As the length of the included molecule increases beyond that of ethanol the cavity is steadily enlarged. Both *a* and *c* increase; there is no factor analogous to the hydrogen bonding of quinol to link an increase in one with a diminution in the other. The enclosing molecules merely move further apart. Although the length of the included molecule is varied considerably the unit-cell dimensions do not change by more than 1·0 Å between the smallest and the largest member of the series. Evidently there is in the unexpanded structure a space nearly sufficient to hold the largest of the molecules shown as giving the cavity-type adduct. To accommodate a molecule lengthened by a further $CH_2$ group would require a relatively big increase of about 1·5 Å in at least one lattice dimension which might, by creating space other than that needed for the larger molecule itself, lead to instability. Lengthening the molecule beyond a certain limit in fact results in formation of the channel structure.

The methanol adduct appears anomalous. The cell dimensions given in Table 1 are slightly greater than those of the ethanol analogue. Sometimes methanol solutions deposit unsolvated tri-*o*-thymotide and occasionally a different adduct of monoclinic form has been obtained. Attempts to prepare the trigonal cavity-type adduct by crystallisation of the pure unsolvated tri-*o*-thymotide from pure methanol failed. The adduct could be obtained from ordinary laboratory methanol on seeding with a little of the acetone adduct and the cell dimensions given are derived from a crystal of this origin. It is thought that a little acetone or other impurity must be included. This will account for cell dimensions larger than those expected. In view of this circumstance an accurate determination of molecular ratio is impossible for this adduct, and no density is recorded.

The critical limit of length is estimated from the behaviour of *n*-pentyl alcohol. In some crystallisations this acts as a short molecule forming a cavity-type adduct which, however, has cell dimensions close to the largest observed in the series. When left in the mother-liquor at room temperature these crystals change into the orthorhombic form of pure tri-*o*-thymotide. In other crystallisations the solution deposits crystals of the channel-type appropriate to a long-molecule adduct. It appears therefore that the greatest length of the *n*-pentyl alcohol molecule is very close to the critical limit for a short molecule.

The existence of this limit has been confirmed by examination of adducts with molecules other than *n*-alcohols. In Table 1, parts B—F give constants for other unbranched molecules. The included molecules of Table 2 have a single atom or methyl group branching from the main chain. Alkyl halides, polymethylene dihalides, esters, ketones, and ethers are found among the molecules of length not greater than 9·5 Å, which form cavity-type adducts. Channel-type adducts have been made with molecules of all these types with lengths greater than 9·5 Å. That *n*-pentyl bromide behaves as a long molecule agrees with the conclusion that *n*-pentyl alcohol, slightly smaller, is just on the limit.

The unit-cell dimensions for both the cavity- and the channel-type adducts formed by this variety of molecule have, within a few hundredths of an Ångström unit, the same limits of variation as the corresponding *n*-alcohol adducts. Even if it contains one of the branched molecules of Table 2, the channel-type varies much less than the cavity-type containing unbranched molecules.

Space requirements alone do not exclude short molecules from the channel type, but no very short molecule has been found to enter this structure. For molecules with greatest dimension near the limit, behaviour varies and seems to indicate difficulty in formation of the cavity structure. In one instance, that of *n*-pentane, the only adduct found is of channel type although the cavity form is expected. Sometimes one or more crystalline forms can be obtained in addition to the cavity-type adduct. These may, but do not always, include a channel form. Thus *n*-butyl bromide gives the cavity form only, whereas from solutions of tri-*o*-thymotide in *n*-butyl iodide three different adducts have been obtained, cavity and channel forms, and a third type which has not been examined

in detail. Trimethylene dibromide gives as a second form an orthorhombic compound $2C_{33}H_{36}O_6,Br\cdot[CH_2]_3\cdot Br$ of a type so far found with this molecule only. Some diethyl ether solutions deposit orthorhombic crystals of an adduct. These rapidly lose ether on exposure to air, and are metastable with respect to the cavity-type.

In urea adducts the enclosed molecule must have a minimum length in order that the van der Waals interaction shall be sufficient to retain it. As may be expected the minimum is not a fixed length but depends on the nature of the included molecule. Thus acetone, butyric acid, and hexan-1-ol, although of different lengths, are the shortest molecules of their homologous series which form urea adducts.[2] For the tri-*o*-thymotide channel adducts any consideration of a lower length limit must take into account the possibility of the alternative cavity structure. If a molecule below the upper limit of size for the cavity type does not form a channel adduct, it may be for reasons analogous to those applicable in the urea adducts, or simply that the cavity-type adduct is more stable. Whichever explanation holds, a lower limit of length required for formation of the channel type is not fixed geometrically like the upper limit for the cavity type, and if it existed, would not necessarily have the same value as this upper limit.

The relative stabilities of the three tri-*o*-thymotide structures may be roughly compared by means of the closeness of molecular packing. Approximate values for the space in the crystal per molecule of tri-*o*-thymotide present, are 750 Å$^3$ in the racemic unsolvated form, 790 Å$^3$ in the cavity-type unsolvated crystal, and 851 Å$^3$ in the most closely packed channel structure. The channel type does not appear to be formed without included molecules. Presumably it is too open. The cavity type, so far as the tri-*o*-thymotide molecules are concerned, is more densely packed and is usually formed in preference to the channel type unless the length of included molecule forbids. It may be obtained with nearly all cavities empty but this form is metastable with respect to the still more closely packed orthorhombic unsolvated form.

*Symmetry and Molecular Arrangement in Channel-type Adducts.*—Results recorded in Tables 1 and 2 have led to general conclusions concerning the crystal structures of the two types of adduct, in particular the nature of the spaces available for the included molecule. These conclusions do not require or imply detailed information about the atomic arrangements. The rule concerning maximum length of included molecule in the cavity type can be applied empirically, but any structural details obtainable should help to explain it. Those given below concern the positions of molecules and spaces rather than of individual atoms. A complete determination of atomic parameters, although feasible, would be very lengthy owing to the general complexity of the structures, and the large number of parameters. A favourable circumstance is the occurrence of so many related structures and freedom to substitute heavy atoms for phase determination. Against this, however, must be set the combination of a three-fold or six-fold screw axis with non-centrosymmetry. As will appear also, heavy atoms introduced in the included molecules do not necessarily go into the structure in an ordered manner, and thus may complicate rather than simplify the phase problem.

Channel-type structures will be considered first. The unit cells of those with space group $P6_1$ (or $P6_5$) always have considerably less than six included molecules although there is no position of less than six-fold multiplicity in this space-group. There is evidence that the packing of tri-*o*-thymotide molecules leaves an array of channels parallel to the *c* axis and that in these the other molecules are enclosed in their extended chain forms with greatest lengths parallel to the channels. The conformity of some of the structures as a whole with space-group symmetry $P6_1$ may therefore be illusory. From their dimensions alone it follows that many of the included molecules must occupy positions in the unit cell which do not have a constant parameter at least along the *c* axis. Consequent disorder effects mentioned below as more readily detectable when the included molecule contains a heavy atom may, in the absence of a heavy atom, usually be so weak as to escape observation. It is convenient therefore to consider first the arrangement of the tri-*o*-thymotide

molecules alone, and to use space-group terms which strictly do not apply to a disordered structure as a whole.

For the channel-type adducts with *n*-alcohols and *n*-alkyl halides the unit-cell dimensions, which vary little with included substance, indicate an unchanging assembly of tri-*o*-thymotide molecules. This is confirmed by the intensities of the *X*-ray reflections. Provided the included molecules contain no heavy atoms, little change is observed in the intensities of 0*kil* reflections when one molecule is substituted for another. A large number of atoms of the structure as a whole must therefore remain in the same position. This would be the case if the six tri-*o*-thymotide molecules preserved a constant arrangement in accordance with $P6_1$ (or $P6_5$) on a six-fold spiral. Pure tri-*o*-thymotide has not been obtained directly in the channel form but a partial indirect realisation supports the view that this six-fold spiral is the arrangement in all structures of this type. For the adduct with diethylmercury, approximate molecular length $= c/3$, the absent spectra 000*l* when $l \neq 3n$ and the intensity relations indicate space-group $P6_2$ (or enantiomorphous $P6_4$). Under the influence of *X*-rays, or more slowly without, the crystals darken through decomposition of the diethylmercury. Simultaneously the weak reflections 000*l* where $l = 3$, 9, or 15 disappear. The space-group then appears to be $P6_1$. The crystal still gives the characteristic single crystal pattern of sharp *X*-ray reflections though there is some breaking up of spots in the high orders and powder lines of decomposition products are superposed. This shows that the tri-*o*-thymotide spiral alone results in the absence of 000*l* for $l \neq 6n$. Included diethylmercury molecules repeat at intervals of $c/3$ with or without relative rotation about this axis. The two components of the combined structure have in common the condition for the absence of 000*l* where $l \neq 3n$. Complete or partial decomposition of included molecules destroys the regularity which produces thirding. Evidently such decomposition can take place to an appreciable degree without collapse of the enclosing structure. The channel adducts formally belonging to $P3_1$ (or $P3_2$) significantly contain only molecules which, having extended lengths fairly close to $c/3$, could give similar thirded structures. The few adducts which formally belong to $P6_2$ must therefore have a structure very similar to those in $P6_1$. As mentioned, the *n*-hexane adduct ($P3_1$) gives a diffraction pattern which differs very little from that expected for $P6_2$ to which it was at first supposed to belong. If the structure in fact has a symmetry $P6_2$ the $6_1$ spiral would have to be modified by displacement of molecules parallel to *c*. In view of the closeness of cell dimensions and similarities in the intensities of *X*-ray reflections, such a change seems unlikely and those crystals which appear to have space-group $P6_2$ or $P3_1$ are therefore considered to have the $6_1$ spiral. It may be that differences in intensities of *hkil* and *hki*$\bar{l}$ reflections are too small for observation or are obscured by twinning on (0001).

In the space-group $P6_1$ the six tri-*o*-thymotide molecules must lie in general positions forming a six-fold spiral. There are no special positions. The exact form of the tri-*o*-thymotide molecule is not known. It is not planar but is folded so that there is no significant empty space in the middle of the central twelve-membered ring. This conclusion is based on the construction of scale models which show that it has roughly the form of a discus, somewhat distorted from the circular and with protuberances, particularly due to the three *iso*propyl groups. That the molecule may not have the three-fold axis suggested by the formula appears from the infrared absorption spectra of orthorhombic unsolvated tri-*o*-thymotide and of the acetone adduct. Examined in the form of Nujol mulls both give evidence that one of the three carbonyl groups of the tri-*o*-thymotide molecule differs from the other two. The spectra of the two materials can be distinguished only by effects due to the carbonyl group of the acetone. Packing considerations show that the tri-*o*-thymotide molecules can be arranged with the flat of the discus approximately parallel to the spiral axis, but not perpendicular to it.

The structure therefore consists of tri-*o*-thymotide molecules spirally arranged around channels parallel to the *c* axis (Fig. 1). The other molecules are enclosed, in their extended

chain forms, with their greatest lengths parallel to the channels. The packing lengths of the extended forms of the molecules of hexadecyl bromide, 24 Å, and octadecyl alcohol, 26 Å, are considerably greater than the *a* dimension, 14·3 Å, of the unit cell. For a completely ordered structure it could be concluded that these molecules must have their lengths far from parallel to *a*, but when channels are postulated the argument is inapplicable. The tetraketone included in Table 2 has a molecular length of 49 Å. To contain such a molecule, longer than any line across a single unit cell, the channels must continue into adjacent cells and therefore extend throughout the whole crystal. Cell dimensions provide evidence for the direction of the channels only when branched molecules are considered. For the adduct formed by 2-bromo-octane, *a* is greater by 0·1 Å, and *c* is less by 0·12 Å than the corresponding dimensions for the *n*-heptyl bromide adduct. To accommodate the greater width of the molecules the channels must have opened out, and they are thus shown to be parallel to the *c* axis. This spreading out of the tri-*o*-thymotide molecules incidentally makes possible a unit-cell contraction in the *c* direction.

Since the branched molecule requires only a slight increase in channel cross-section there must be more than enough space for the straight-chain molecules. This would allow them to have various orientations in the channels and so to preserve the apparent 6-fold symmetry.

Although the space-group symmetry is $P6_1$ the number of channels per unit cell is not necessarily a multiple of six. The extension of the channels parallel to *c* reduces the symmetry problem to that of the corresponding plane group P6. In this the general position remains 6-fold but there are special positions of 3-fold, 2-fold, and 1-fold multiplicity. There is strong evidence for a single channel per unit cell.

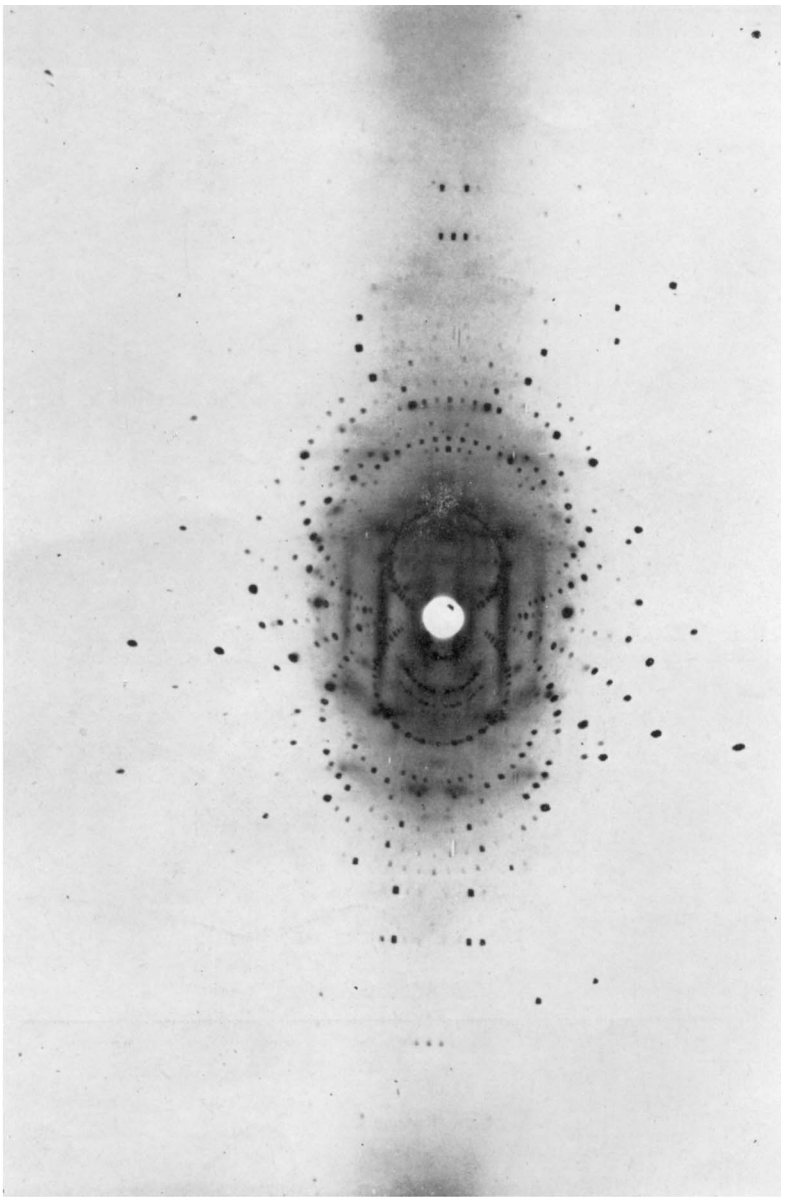
For some adducts such as that of *n*-pentyl iodide there are three molecules, each of length approximately *c*/3, per unit cell. If the molecules were in separate channels a greater number could be included. As soon as the included molecule has more than one-third of the length of the *c* axis, less than three molecules are included per unit cell. They must therefore be placed one on top of the other in a single channel centred on the origin.

*X-Ray Diffraction due to Material included in the Channels.*—Direct *X*-ray evidence supports the channel structure. Diffraction patterns obtained from crystals oscillating about the symmetry axis in certain instances show more or less continuous streaks parallel to the layer lines of sharp reflections that correspond to the unit cell. Such effects which have been observed with other crystals [6] are due to diffraction by a part of the structure which behaves as a one-dimensional diffraction grating for *X*-rays. Even on long exposures they are usually not observable for the tri-*o*-thymotide adducts unless the included molecule contains a heavy atom. A one-dimensional grating gives its layer-line diffraction effect without the oscillation needed for a three-dimensional crystal grating. The Plate shows a diffraction pattern obtained with a stationary crystal of the 2-bromo-octane adduct. Copper radiation filtered through nickel foil was used. The *c*-axis was vertical but, without oscillation, only a few of the sharp reflections on the normal layer-lines have appeared. For these few the corresponding planes happened to be in the reflecting positions for the characteristic radiation. Continuous horizontal lines also due to diffraction of the $K_\alpha$ radiation may be seen without the confusion of ordinary layer-lines, together with other diffraction effects, chiefly a Laue pattern formed by diffraction of the white component of the imperfectly filtered radiation. A number of diffuse reflections may be seen on vertical row-lines. They correspond in position to Bragg reflections. The crystal was, however, not in a position to give the Bragg reflections and the diffuse spots observed are due to imperfections, either static or dynamic, of the lattice.

Table 3 records streaks parallel to the layer lines observed in diffraction patterns obtained by the normal technique with single crystals oscillating about the *c* axis. For the different members of the series of channel adducts, the intermediate streaks vary in

[6] Borchert and Dietrich, *Heidelberger Beitr. Mineral.*, 1952, **3**, 124.

**X**-*Ray diffraction pattern given by stationary crystal of* 2-*bromo-octane adduct. The axis of the cylindrical film, to which the c-axis of the crystal was parallel, is here horizontal.*



[*To face p.* 2348.

FIG. 1. *Schematic representation of spiral arrangement of molecules forming the channels. Each molecule denoted by a line; the nearby figures indicate relative displacements of molecules in fractions of c axis length. Vertical screw axes are indicated by* $6_1$, $3_1$, *and* $2_1$.

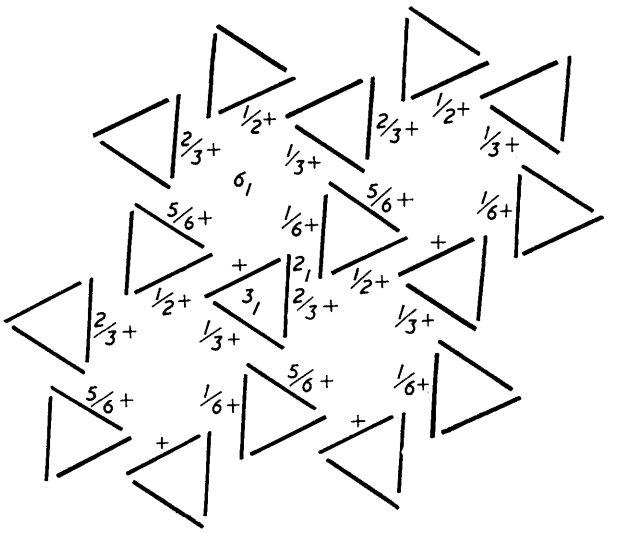
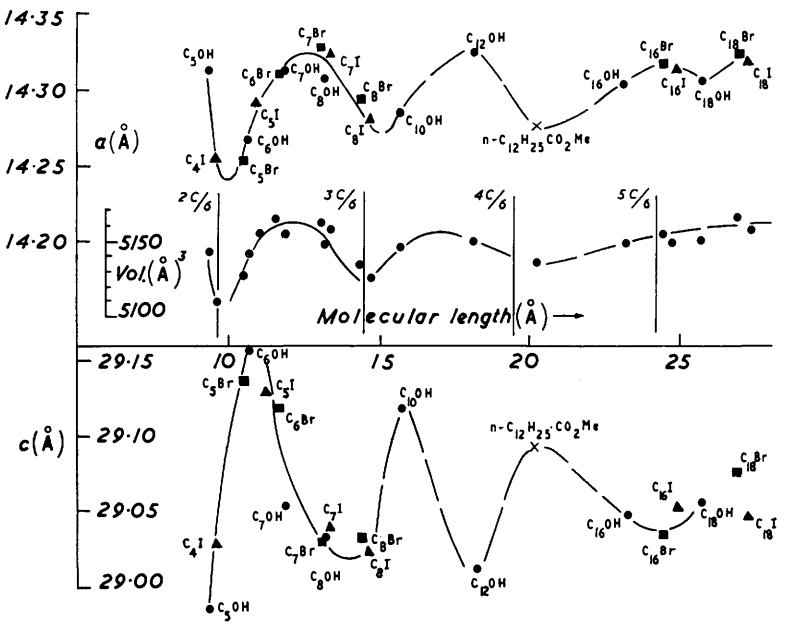



FIG. 2. *Variation of cell dimensions and volume with length of included molecule in channel. In the plots of a and c, alcohols shown by circles, bromides as squares, and iodides as triangles.*



position according to the length of the included molecule, being related to its repeat distance in the channel. There is no relation other than accidental between this distance and the *c* dimension of the unit cell. Certain included molecules have a packing length which is a simple fraction of *c*. In such a case there is a common unit translational repeat distance parallel to *c* and these adducts either do not show streaks or have them coincident with the layer-lines of sharp spots.

For the hexamethylene di-iodide adduct three streaks are observed which correspond to the first three layer-lines of a structure with repeat distance 12·5 Å. This is very close to the expected packing length of hexamethylene di-iodide and may therefore be taken as the repeat distance of the molecules included in the channels. The smallest *c* dimension divisible by both 29 and 12·5 Å (approximately) is 87 Å. For a pattern of this repeat distance the observed streaks would be the 7th, 14th, and 21st layer-lines. A fourth and rather sharp streak corresponds to a spacing of 3·5 Å and may be indexed as the 25th layer for the 87 Å spacing. The first three observed layers are strong because they correspond to the repeat distance 12·5 Å between similar iodine atoms of successive molecules. The fourth streak is sharp and prominent because the 3·5 Å spacing corresponds to the distance parallel to *c* between the iodine at the end of one molecule and its near neighbour, an iodine of the next molecule. On the basis of the included molecule length 12·5 Å this streak has to be assigned a fractional order $3\frac{4}{7}$ or about $3\frac{1}{2}$. For the other included molecules simple orders may be readily assigned to the observed layer streaks and consistent one-dimensional lattice spacings calculated. In Table 3 the lengths of a series of alkyl halides and a few other molecules are compared with the calculated spacings. Some of the streaks are difficult to observe accurately and the agreement is considered good for most of the long molecules. The change in spacing for each $-CH_2-$ group is approximately as expected. The maximum length has been calculated in all cases and generally this is slightly larger than the observed spacing. Any difference may be explained by the way in which the end-groups fit together. The spacing calculated for the *n*-pentyl bromide adduct is, however, considerably less than the packing length. For such short molecules the calculated length is likely to differ from the repeat distance. Since the channels are broader than is necessary to hold the *n*-halides, a short chain, the axis of which has been assumed parallel to the *c*-axis for purpose of calculating the repeat length, may in fact be inclined to *c*. A comparison of the *n*-pentyl bromide and the *n*-hexyl bromide streaks shows an increase in the packing length of 2·4 Å as a result of the addition of a single $CH_2$ group. With all allowance for experimental inaccuracy, this is far beyond the projected length 1·256 Å or even the maximum 1·54 Å which could occur if an extra C–C bond had been added, without any other change, to the atoms as they are placed in the *n*-pentyl bromide adduct. The over-all lengths of the higher members of the series evidently require them to be nearly parallel to *c*. Successive removal of many $CH_2$ groups may permit only a small variation in inclination of molecular length to the channel axis but, at some stage, one such removal may result in a very large change in inclination. An extreme case would be that of *n*-alkanes in a channel of such width that ethane could just lie broadside on. Evidently the large change occurs because *n*-pentyl bromide is short enough to be noticeably tilted across the channel whereas *n*-hexyl bromide is nearly parallel to it. An even greater change of inclination would be expected if *n*-butyl bromide could be substituted for *n*-pentyl bromide. With this may be connected the change to cavity type which occurs when the attempt is made.

*Ideal Compositions of Channel-type Adducts.*—The one-dimensional layer line spacing may be used to calculate what may be called an ideal composition of the adduct. Divided into the corresponding value of the *c*-dimension given in Table 1 or 2, it should give a maximum number of molecules that can be fitted into the single channel of the unit cell containing six tri-*o*-thymotide molecules. The resulting figures are compared in Table 3 with the number of included molecules estimated from the unit cell weight. The general agreement shows that in most cases the channels are filled. A value from cell weight

lower than the " ideal " could be explained by unoccupied spaces in the channels. The " ideal " value should never be the lower of the two by an amount exceeding possible errors of measurement, which are mainly in the " ideal " compositions derived from faint and diffuse streaks and may amount to a few per cent. The Table shows that his requirement is satisfied except possibly for the hexadecyl bromide and the octadecyl bromide adduct.

The channel-type adducts as a group are distinguished from those of the cavity type in having an ideal ratio of included molecule to tri-*o*-thymotide which varies with molecular length. For each adduct the ratio of molecules is in practice definite although it may not be simple. However, even if any departures from ideal molecular ratios are ignored, the two types cannot be contrasted as stoicheiometric and non-stoicheiometric, since some of the channel adducts have rational compositions. As far as the compositions alone are concerned it is more appropriate, in this type of molecular compound, to distinguish rational and irrational. Non-stoicheiometry implies disorder, and varying displacement of included molecules relative to a fixed part of the channel is the form of disorder here associated with an irrational composition. However, varying displacements in different channels are possible when the molecular length accidentally requires a simple ratio, so that this simple ratio does not seem in principle different from any other relation. The channels diminish in length with increase of temperature but the effective lengths of enclosed molecules will increase. Structurally it would therefore be possible for the ratio to vary slightly with the temperature of preparation. The effect is beyond the limits of the present measurements, but the possibility makes the description " stoicheiometric " unsuitable.

*Order and Disorder in the Channels.*—The *X*-ray diffraction effects show at least two kinds of channel adduct according to the degree of order. Constant spacing of the included molecules in the channel gives rise to a one-dimensional grating effect if the structure is disordered in certain other ways. Where the length of included molecule requires displacements along the channel it seems unlikely that the molecules in one channel could restrict the positions of those in any other. The individual one-dimensional gratings are kept parallel and equally spaced by the channels but their molecules do not form a three-dimensional lattice. This will account for the observed streaks. When the length of included molecule is rationally related to the *c* dimension a more regular arrangement could occur, each included molecule being displaced a similar distance along the channel relative to an origin of the unit cell. Since the channels have a six-fold spiral structure such regularity might be expected when the length of included molecule is a multiple of $c/6$, *i.e.* $n \times 4{\cdot}84$ Å. The case of $n = 1$ does not arise because such a short molecule will form a cavity-type adduct, but the list of included molecules contains several examples where the molecular length is approximately a higher multiple of 4·84 Å. The small variations of the nearly constant unit-cell dimensions provide evidence for the more regular arrangement. Plotted in Fig. 2 they show a periodic variation of both *a* and *c* with length of included molecule. As *c* increases, *a* diminishes, so that roughly the top and bottom curves of Fig. 2 are mirror images in a plane between then. The minima in *c*, and the corresponding maxima in *a*, are separated from each other at intervals which are near to multiples of 4·84 Å along the molecular length axis. Also they occur at molecular lengths which are themselves not very different from $n \times 4{\cdot}84$ Å where *n* is 2, 3, 4, or 5. For consistency, the maximum molecular lengths, as calculated above from atomic dimensions, have been used in the graph. As has been shown, these, especially for the shorter molecules, are rather larger than the effective lengths and the points as plotted should perhaps be displaced by an uncertain and variable amount, never likely to be much more than 1 Å, to the left. This brings most of the minima in *a* and the maxima in *c* closer to positions at $n \times c/6$ on the horizontal axis.

These unit-cell dimensions are determined by the way in which the component molecules fit together. Regular repetition of included molecules, always with similar

surroundings, may result in a slightly different, and, it would be expected, closer packing of the tri-*o*-thymotide components than is attainable when arbitrary displacements of included molecules along the channels must be allowed.

The middle curve of Fig. 2 shows the volumes of the unit cell plotted against the same scale of molecular lengths. The overall result of the opposed changes in $a$ and $c$ is to produce minima in the cell volume for lengths of included molecule which are close to $n \times c/6$. All the curves of Fig. 2 have to be drawn from relatively few points except in the region 9—16 Å. The positions of the maxima in $c$ do not exactly coincide with those of minima in $a$, or either of these with the minima in volume. Even if there were no difficulty in tracing the curves or uncertainty in the absolute scale for molecular length, there would be no reason why they should. In the absence of finer structural detail which might explain everything, the idea that an improved packing of the structure takes place for molecules of lengths which are multiples of the spiral component $c/6$ is based on the periodicity common to all three curves and the occurrence of minima in $a$ and in the volume at molecular lengths somewhere near to $n \times 4{\cdot}84$ Å, rather than on any exact coincidence. A slightly closer fit of the molecules forming the channel may be imagined. This may be illustrated by a set of ball-ended rods enclosed between extended corrugated sheets. As the length of rod, imagined to lie across the corrugations, steadily increases, the separation between the sheets will vary periodically, with minima when all the ball-ends lie in hollows. Any such manner of packing included material so that its protuberances have the same periodicity as the indentations of its surroundings, should lead to similar effects.

The increase in $a$ produced by inclusion of a branched molecule may be greater than the periodic variations. Points plotted in Fig. 2 therefore refer to unbranched molecules. The sole exception is methyl laurate which may be considered only slightly branched. The values, included because others were not available in that region, fit well with the general trend of the curves.

Since, when close fitting occurs, $a$ decreases, the tri-*o*-thymotide molecules are drawn together in two dimensions and the spaces between them are diminished. The increase in $c$ is regarded as consequential, the tri-*o*-thymotide neighbours projecting into these spaces from the direction of the third dimension being forced outwards. For the shortest molecules, of length about 10 Å, the cell volume varies by about 1% between the closest and loosest packing. As the length of molecule increases there will be a smaller proportion of places in the channel where the ends make a closer fit. The oscillations in the curves for cell dimensions and cell volume therefore diminish in amplitude, tending on the right towards limiting values appropriate to an indefinitely extended polymethylene chain. The volumes seem to approach a limit which is not less than any value for a shorter molecule. Similarly the limiting value for $a$ is about equal to the maximum values reached in the intermediate positions where the included molecules do not make their closest fitting, *i.e.*, as the proportion of close-fitting places becomes less the minimum in $a$ rises, but the maximum is unchanged. This behaviour is consistent with the idea that widening of the channels is the primary effect. The consequential change does not require the limiting value of $c$ to be the same as the lowest of its minima.

Between molecular lengths of $9\frac{1}{2}$ and 15 Å the curves of Fig. 2 can be traced without use of the results for alcohols. The values for the alcohols fit the curve well in this region and this suggests that the molecular lengths used are approximately correct, and that the channels contain single molecules. If they contained hydrogen-bonded double molecules, the points plotted in the Figure for alcohols would have to be displaced to positions somewhat less than double the molecular length shown. It may be seen that such changes would destroy the regularities which the forms of the curves strongly suggest are based on a structural reality.

When displacements along the channel are constant other structural regularities are possible. If all the included molecules also have orientations which are either the same or related by the $6_1$ screw axis the structure as a whole forms a three-dimensional lattice

which will give no one-dimensional layer-line streaks. When the orientations are unrelated to each other or are related but irregular in sequence the structure is disordered even though the length of included molecule is commensurable with the channel *c* spacing. Irregularities could be connected with the sequence in any one channel or with the relation between one channel or region of the crystal and others. These disordered structures should give various diffraction effects including layer-line streaks. Among adducts formed by molecules of these special lengths there appear to be examples of both ordered and disordered forms.

The *n*-pentyl bromide adduct has three included molecules, of effective length about *c*/3, per unit cell. Only the faintest layer-line streaks have been observed, some heavily exposed oscillation photographs showing no signs of disorder. For one specimen the streaks give the expected *c*/3 (9·6 Å) spacing in the channels but for another the spacing is different (8·8 Å). Two explanations are possible for the faintness of streaks. There may be only a few disordered molecules or the disorientation may be obscured because the bromine atoms contribute only to the sharp normal reflexions. Being a terminal substituent and fairly large, each bromine may fit the channel in the same way and provide an anchor so that only the rest of the molecule can vary in its orientation. In that case the effect of disorder among the lighter atoms would be no stronger than for the *n*-alcohol series where, in practice, it cannot be observed. It is less likely that such anchors can be placed in line parallel to *c* when they have varying displacements relative to their surroundings, and in this case the halogen atoms will contribute to the disorder streaks. The adduct of *n*-butyl iodide with a unit-cell volume very close to the first minimum in Fig. 2 gives no streaks. Probably the effective length of the molecule is a little less than *c*/3. The general behaviour that molecules are packed as closely as possible in the channels according to their length may break down when the included molecule has a length very nearly equal to *c*/3. On this view, which is supported by the compositions, the *n*-butyl iodide molecules leave some channel space unoccupied, and thus achieve a periodicity simply related to that of the surroundings. The *n*-pentyl iodide adduct also gives no layer-line streaks, although the effective molecular length is expected to be slighty greater than *c*/3. In this case it may be necessary for the molecule to adapt its orientation, conformation, or inclination to the channel length to attain a periodicity commensurable with *c*. Adaptation of either the slightly longer or slightly shorter molecule to channel periodicity is accompanied by a more complete order of the whole structure. This is shown, not only by the absence of layer-line streaks, but also by the appearance of the sharp reflections 000*l*, where $l = 3n$, which cause the formal space-group to be $P3_1$. The second form of *n*-pentyl bromide for which the streaks give a spacing of 8·8 Å indicates that although molecules of approximately the right length may adapt in this way to the channel periodicity, they sometimes behave otherwise.

Two adducts are formed by *n*-octyl iodide which has a molecular length approximately *c*/2. One (B) shows no disorder effects and the other (A) has streaks coincident with the 4th and the 8th *c* layer-lines. To reconcile the positions of the streaks with the molecular length it is necesary to take them as the 2nd and the 4th order. The extinction of odd-order layers may be attributed to the presence of channels containing molecules in certain positions and an equal number of channels with molecules similarly placed except for a relative displacement of half the molecular length, *i.e.*, $\pm c/4$. Form (B) shows the complication that additional sharp reflexions, occurring instead of streaks on the 4th and the 8th *c* layers, can be indexed on the basis of a hexagonal cell of seven times the normal *a*-dimension. That extra reflexions are unobserved for all except the 4*n*th layers may be attributed in this form also to the presence of included molecules in two or more positions with relative displacements of *c*/4. If there is no disorder these must be in different channels and, strictly, an even number of filled channels is required for complete interference to be possible when $l \neq 4n$. The unit cell has 49 channels and the effect of the odd one might be slight among so many. It is possible, however, to devise structures

consistent with the space-group in which $(6n + 1)$ channels ($n = 0,1,2 \ldots$) are unoccupied. They have an even number of filled channels per unit cell, and some such structure may be necessary to account for the 7-fold enlargement of $a$. Presumably the disordered form (A) has similar filling of channels with $c/4$ relative displacements but lacks regularity of sequence in neighbouring channels. Octadecyl iodide forms a disordered structure (A) with streaks corresponding to a spacing of 27 Å. An ordered form (B) has no streaks and presumably the molecules are adapted so that they repeat regularly at the slightly greater distance 29 Å of the $c$ dimension. The lower density of the (B) form is in agreement with there being some empty space. Adducts of diethylmercury, methoxybutane, and ethoxybutane all give streaks coincident with sharp layers. The molecular lengths, 9·8, 10·1, and 11·4 Å respectively, are close to $c/3$ or, in the case of ethoxybutane, must be adapted to it, but there is disorder similar to that in form (A) of the *n*-octyl iodide adduct.

*Cavity-type Structures.*—In the cavity-type adducts molecules of tri-*o*-thymotide are arranged in trigonal ($3_1$) spirals, the two spirals passing through a unit cell ($a = 13{\cdot}5$ Å) being related to each other by a two-fold symmetry axis parallel to $a$. The cell dimensions are readily distinguishable from those of the channel adducts in which the molecules may be regarded (Fig. 1) as lying on $3_1$ spirals related by a two-fold screw axis parallel to $c$, but are sufficiently similar to them to suggest related arrangement of tri-*o*-thymotide molecules in the two structures. However, the spaces for the included molecules in the cavity-type adducts are not merely smaller forms of the hexagonal channel. They differ in character and position. That they are not continuous channels is shown by the existence of an upper limit of length of included molecule. The volume in the crystals per tri-*o*-thymotide molecule suggests about half as much space available for inclusion as in the channel type. Since in certain cases a small increase in the width of a molecule due to the replacement of one substituent by another results in the cavity-type adduct's not being formed, it is concluded that the cavities are limited crosswise and may be considered as roughly cigar-shaped. The unit cell contains three included molecules which formally could occupy either of the special positions $x0\frac{5}{6}$ or $x0\frac{1}{6}$. Both these require the molecule to have a two-fold symmetry axis. A number of the included molecules have this symmetry but many do not. Some therefore cannot be arranged in accordance with strict space-group symmetry and this limits the validity of any arguments designed to locate the cavities by symmetry considerations. Some evidence is provided by the iodine adduct. Its crystals are pleochroic, transmitting red light when the electric vector is perpendicular to $c$ and yellow light when it is parallel. The length of the iodine molecule, and hence, it is assumed, the length of the cavity, is therefore not parallel to $c$. Though not necessarily perpendicular to $c$ it is inclined at a considerable angle to it. Structural investigations of the methylene iodide adduct in which the iodine atoms may be located because of their high scattering factor show that the line joining centres of the two iodine atoms lies at right angles to the $a$ axis and is inclined at about 16° to a plane parallel to (0001). The over-all contact length for this direction of the molecule is 7·7 Å. This is greater than the permitted width of the molecule and may be expected to lie approximately in the direction of the cigar length.

The cavity-type adducts of the *n*-alcohols are shown in Table 1 as having space-group $P3_121$ with $a$ and $c$ approximately 13·5 and 30·5 Å respectively. The other adducts of this kind in Tables 1 and 2 have a similar $c$-dimension, but those formed by halogen-substituted alkanes often have the $a$-dimension doubled. In the Tables this is recorded as 13·5 (approx.) × 2. The structure may be ordered, giving sharp reflexions, on the whole weaker than the rest, corresponding to the doubled $a$-dimension, or it may be disordered. For both kinds, as for those without doubled $a$, oscillation photographs show repetition every 120° around the $c$-axis and in general the intensity of $hkil$ is not equal to that of $hki\bar{l}$. The only systematic absence is that of $000l$ when $l \neq 3n$. The equality in intensities of reflexions $hki0$ and $khi0$ shown, for example, by the symmetry in oscillation photographs taken around the $a$-axis establishes the presence of the two-fold symmetry

axis. The space-group remains $P3_121$ in spite of the doubling of *a*. The disordered structures do not show sharp spots corresponding to doubling of *a* but give streaks along the direction of $a^*$ in the reciprocal lattice. In the ordered structures presumably the included molecules have alternative orientations in regular sequence along *a*. The streaks could be explained by an irregular sequence. Unit cells with doubled *a* dimension are given by the adducts of *n*-propyl bromide (B), *n*-propyl iodide, *n*-butyl bromide, and trimethylene dibromide (B). Disordered forms are given by *n*-propyl bromide (A), *n*-butyl alcohol, ethylene dichloride, and ethylene dibromide. Of the two forms given by *n*-propyl bromide the more ordered was obtained by slower crystallisation, but it is not known whether this is accidental or not.

*Optical Resolution.*—Crystallisation of each trigonal or hexagonal compound constitutes a new example of spontaneous optical resolution similar to that already shown experimentally for the *n*-hexane and the benzene adduct. Some of the unit cells contain six molecules of tri-*o*-thymotide, just enough to occupy one set of space-group positions which are equivalent, and the crystal therefore must contain tri-*o*-thymotide molecules of one configuration only. The resolution has been confirmed polarimetrically for adducts with *sec.*-butyl bromide and 2-bromo-octane. Those compounds with cell dimensions multiples of the simpler values could show varying degrees of optical resolution. The *n*-octyl iodide adduct for which *a* is multiplied seven times contains 49 separate sets of six equivalent molecules. According to space-group symmetry each set of six should have the same configuration, but different sets could be different. Similarly the trigonal adducts such as that with propyl bromide which have doubled *a* dimensions contain four separate sets of six equivalent tri-*o*-thymotide molecules. By measurement of the optical rotatory power of a solution prepared from a single crystal of this adduct, it was found, however, that the resolution was as complete as in the benzene adduct. The crystal contains only one enantiomorphous form of tri-*o*-thymotide molecule and multiplication of cell dimensions is therefore not to be explained by alternations or other sequences of *dextro*- and *lævo*-kinds.

*General Conclusions.*—Tri-*o*-thymotide has thus been shown to form a hexagonal or trigonal adduct with each of fifty or more substances of varying chemical character all of which have molecules of restricted width. The rules concerning permissible dimensions being known, it is expected that hundreds of other molecules will behave similarly. In particular a large number of long molecules should form the channel type of adduct. An upper limitation of length means that fewer will form the cavity type in which smaller molecules are enclosed as in clathrates. The molecules must also not be too small. One of the enclosable substances, methyl bromide, is a gas at room temperature. Its cavity-type compound decomposes more readily than the others, some of which do not readily lose weight when heated to 100° above the normal boiling point of the included substance. Comparative smallness of the included molecule makes its imprisonment less effective. Attempts to prepare adducts containing yet smaller gas molecules such as argon or carbon dioxide have so far proved unsuccessful.

The results for the whole series have a bearing on a general principle of organic crystal chemistry. The difficulty in finding rules analogous to those applicable for inorganic chemistry is that sufficiently small variations of the structural components cannot usually be made. The effect of varying atomic or ionic radius in simple compounds may be examined by gradual changes, but when naphthalene is compared with benzene, or when two isomers are compared, there are such differences of crystal structure that little information is obtained concerning the factors which influence stability.

In the absence of special complications such as hydrogen-bonding, the molecules in organic crystals pack closely. Not only do neighbouring atoms or groups maintain roughly constant van der Waals equilibrium distances, but also they seem to achieve this in ways that leave no great empty spaces. Kitaigorodski [7] has expressed this by calculating from appropriate atomic radii the volumes proper to certain molecules and comparing them

[7] Kitaigorodski, " Organischeskaya Kristallokhimiya," Acad. Sci., U.S.S.R., Moscow, 1955.

with the volume required for one molecule as calculated from unit-cell dimensions. The result, the packing coefficient of the molecule in the crystal, varies for certain classes of organic compound between 0·6 and 0·8.

Strictly, this coefficient cannot be compared with that for packing of equal spheres. Its value ought to be compared with those for all possible structures of the same substance and, as with spheres, it is probable that many different structures with the same packing coefficient could be devised. That the structure adopted is the closest of all possible packings of the particular assumed molecular shape is improbable in view of the complex nature of molecular interaction, but as a rough guide the close-packing principle may be accepted. In the present work it has been possible to examine the effects of small variations which leave the general character of the structure unchanged. The tendency to close packing is revealed in the minimum of unit cell volume which occurs in the channel-type of adduct whenever possible, but the structure is still formed when less closely packed. Similarly some cavity-type adducts must be less than closest packed since diminution in proper volume of included molecules on substitution of a lower for a higher member of a homologous series is not accompanied by an equal decrease in unit-cell volume.

## Experimental

*Preparation of Tri-o-thymotide.*—Mixtures of tri-*o*-thymotide and di-*o*-thymotide prepared by the method of Wilson Baker, Gilbert, and Ollis [4] were purified by extraction with acetone in a Soxhlet apparatus. In two further extractions, the yield of acetone adduct from the previous stage was used as the starting material. The resulting acetone adduct was twice recrystallised from methanol. The product, which in addition to unsolvated material might contain the methanol adduct, was either heated under reduced pressure or kept at 130° for 24 hr. It was then recrystallised from fractionally distilled *iso*octane in the orthorhombic unsolvated form.

*Preparation of Adducts.*—Whenever possible the second component material was of " AnalaR " grade. All were further purified by appropriate standard methods. One or two were specimens purified in other laboratories for research purposes. The *n*-pentane was a specimen of purity suitable for mass-spectrometer calibration.

Usually tri-*o*-thymotide was dissolved in the other component heated to a suitable temperature. The solution on cooling deposited a crystalline adduct. In a few cases the nature of the product appeared to depend on the rate of cooling, a more ordered form of adduct resulting from the slower cooling. A few adducts were made by evaporation of solutions at room temperature. Sometimes the crystalline form deposited was metastable and a second form gradually replaced it. When the other component was a solid it was dissolved together with tri-*o*-thymotide in 2 : 2 : 4-trimethylpentane or 2 : 3-dimethylpentane, which do not form adducts. Cooling the solution caused the adduct to crystallise.

*Analysis (Chemical).*—For many of the compounds carbon and hydrogen percentages are of little value in fixing the ratio of tri-*o*-thymotide to the other component; they are more sensitive mainly when they are not necessary, *i.e.*, when there is a large proportion of halogen. Whenever possible the analysis is based on halogen or active hydrogen which gives a direct determination of the amount of included substance. However, the proportion of active hydrogen is very small and the results will be affected by occluded solvent or moisture, either of which exaggerates the solvent content. Comparatively large amounts of material, 30 mg., were used for active-hydrogen determinations in view of the very small percentage present. A further general difficulty for all chemical methods of analysis arises from decomposition of some adducts and uncertainty concerning methods of drying. For the higher-alcohol adducts prepared by dissolving tri-*o*-thymotide and the alcohol in an indifferent solvent, it seems to be impossible to wash away surplus alcohol without causing decomposition. Although chemical analysis, where its accuracy permits, confirms the compositions given, it is generally unable to provide the finer details required to establish the nature of these molecular compounds. For the alkyl halide cavity-type adducts, apart from that of methyl bromide which is subject to decomposition, a fairly constant value of three molecules per unit cell is found. In these the proportion of halogen is highest and the results are therefore among the more reliable. They agree with the molecular ratio determined from unit-cell weight. For the channel-type adducts chemical analysis shows that in general the molecular proportion of an included substance is

less the longer its molecules, but the ratio can be determined only roughly in this way. Even in the favourable case of the *n*-pentyl bromide adduct the calculated bromine content changes only from 6·6 to 6·4% when the number of molecules is changed from 3 to 2·9 for each six tri-*o*-thymotide molecules.

Table 4 shows the observed percentages of carbon, hydrogen, halogen, and active hydrogen, as appropriate. Compounds are listed in the same order as in Tables 1 and 2. When no analysis is given the existence of the compound is regarded as established by the *X*-ray investigation. For the cavity-type compounds calculated percentages are based on the composition $2C_{33}H_{36}O_6$,M (M = included molecule). For channel-type adducts calculated percentages are based on the molecular ratios, determined from the unit cell weight as listed in Tables 1 and 2.

TABLE 4.

| Included molecule | C (%) Found | C (%) Calc. | H (%) Found | H (%) Calc. | Active H or Halogen (%) Found | Active H or Halogen (%) Calc. |
|---|---|---|---|---|---|---|
| $CH_3$·OH | 74·1 | 73·7 | 6·9 | 7·0 | 0·09 | 0·1 |
| $C_2H_5$·OH | 73·9 | 74·0 | 6·9 | 6·9 | 0·11 | 0·09 |
| $C_3H_7$·OH | 74·5 | 74·2 | 7·3 | 7·2 | 0·10 | 0·09 |
| $C_4H_9$·OH | 74·5 | 74·9 | 7·2 | 7·3 | 0·10 | 0·09 |
| $C_6H_{13}$·OH | — | — | — | — | 0·09 | 0·09 |
| $C_7H_{15}$·OH | — | — | — | — | 0·07 | 0·08 |
| $C_8H_{17}$·OH | — | — | — | — | 0·07 | 0·07 |
| $C_{10}H_{21}$·OH | — | — | — | — | 0·08 | 0·06 |
| $CH_3Br$ | 70·0 | 69·9 | 6·2 | 6·6 | 6·1 | 6·9 |
| $CH_3I$ | 67·4 | 67·1 | 6·5 | 6·3 | 9·9 | 10·6 |
| $C_2H_5Br$ | 70·4 | 70·0 | 7·1 | 6·7 | 6·9 | 6·9 |
| $C_2H_5I$ | 68·6 | 67·3 | 6·2 | 6·4 | 10·0 | 10·5 |
| $C_3H_7Br$ | 70·8 | 69·2 | 6·7 | 6·8 | 6·9 | 6·8 |
| $C_3H_7I$ | 68·3 | 67·5 | 6·6 | 6·5 | 10·3 | 10·3 |
| $C_4H_9Br$ | 70·5 | 70·4 | 6·7 | 6·8 | 6·1 | 6·7 |
| $C_4H_9I$ | 68·4 | 67·7 | 6·8 | 6·6 | 9·7 | 10·2 |
| $C_5H_{11}Br$ | 70·7 | 70·6 | 7·1 | 6·9 | 5·9 | 7·3 |
| $C_5H_{11}I$ | 68·1 | 67·8 | 6·8 | 6·7 | 10·3 | 10·4 |
| $C_6H_{13}Br$ | 71·3 | 71·1 | 7·1 | 7·0 | 5·8 | 6·0 |
| $C_7H_{15}Br$ | 72·0 | 71·6 | 7·4 | 6·9 | 5·5 | 5·3 |
| $C_7H_{15}I$ | 70·1 | 70·6 | 7·0 | 6·6 | 7·3 | 9·0 |
| $C_8H_{17}Br$ | 72·5 | 72·1 | 6·6 | 7·1 | 4·4 | 4·8 |
| $C_8H_{13}I$ (A) | 71·0 | 70·5 | 6·8 | 6·5 | 7·4 | 6·8 |
| $C_8H_{13}I$ (B) | 70·4 | 70·5 | 7·2 | 6·5 | 7·3 | 6·8 |
| $C_{16}H_{33}Br$ | 73·6 | 73·6 | 7·3 | 6·4 | 3·3 | 3·1 |
| $C_{16}H_{33}I$ | 73·0 | 73·0 | 7·3 | 7·1 | 4·5 | 3·4 |
| $C_{18}H_{37}Br$ | — | — | — | — | 2·0 | 2·8 |
| $X\cdot[CH_2]_n\cdot X$ *n* X | | | | | | |
| 1 Br | 66·1 | 65·4 | 6·3 | 6·1 | 13·8 | 13·0 |
| 1 I | 61·6 | 60·7 | 5·76 | 5·6 | 19·2 | 19·2 |
| 2 Br | 65·8 | 65·6 | 6·2 | 6·2 | 14·0 | 12·8 |
| 3 Br (A) | 70·9 | 65·8 | 6·4 | 6·2 | 5·8 | 12·7 |
| 3 Br (B) | 66·2 | 65·8 | 6·5 | 6·2 | 13·2 | 12·7 |
| $Hg(C_2H_5)_2$ | 63·4 | 63·9 | 6·4 | 6·3 | — | — |
| 2-Bromo-octane | 71·4 | 71·7 | 7·5 | 7·1 | 5·0 | 5·5 |

*Analysis (by Unit-cell Weight).*—For a number of adducts the unit-cell weight has been determined accurately. There are 6 molecules of tri-*o*-thymotide of known weight in the cell and the weight of the remainder is determinable. The stated limits of error for molecular ratios are derived from the errors in cell dimensions and densities. Constancy of molecular ratio for the cavity-type, and the consistent relation to molecular length in the channel-type, confirm that this method is much more accurate than chemical analysis.

*Determination of Unit-cell Dimensions.*—Since owing to the large cell dimensions it would be impossible to index powder photographs, accurate cell dimensions had to be determined by single-crystal methods. Imperfection of the crystals results in vanishingly small intensities of reflexion of Cu radiation at high angles, and accordingly chromium radiation ($\lambda K\alpha_1 = 2{\cdot}2896$, $\lambda K\alpha_2 = 2{\cdot}2935$ Å) was used. The longer wavelength also makes for more certain indexing. A Unicam oscillation camera was used with film mounted according to Straumanis's method. Oscillation about the *c*-axis does not require an estimate of the axial ratio *c*/*a*, but there were no reflexions suitable for accurate extrapolation in either the cavity- or the channel-type crystals.

Oscillation about the *a*-axis was sometimes employed but usually both *a* and *c* were obtained from photographs made by oscillation about [210]. By suitable selection of oscillation ranges photographs symmetrical to right and left were obtained, and the points of entrance and exit of *X*-ray beam could be determined. Films were measured on a universal instrument of the Cambridge Instrument Company. Values of the Bragg *d*-spacings for a series of high-angle reflexions were extrapolated against $\sin^2\theta$ for values of $\theta$ above 70°. Some cell constants were obtained from Weissenberg films calibrated with the lines of metallic palladium. The palladium specimen was one used by Hume-Rothery and Hellawell [8] who determined its lattice constant as 3·8908 Å. Apart from the accurate cell dimensions needed to establish the rules of composition in the two main series of the adducts a number of approximate cell constants, derived from oscillation photographs taken with Cu-$K_\alpha$ or Cr-$K_\alpha$ radiation, are recorded in Table 1 in order to show the type of adduct formed by molecules of different lengths. For these no temperature is given.

*Density Measurements.*—Gradient columns were made with aqueous solutions of sodium bromide and calibrated with drops of xylene–bromobenzene mixtures. Densities of the mixtures were determined in a pyknometer. A column method is dictated by the small quantities of material available and the possible decomposition of some adducts. It has the advantage of showing by the sharpness of the layers formed in the column that in nearly all cases, the compositions are definite. In several instances it revealed a mixed product of two different crystalline forms which separated into two layers in the column. Thus both densities could be determined. Freshly prepared material was dried at the pump. If it was an adduct of a high-boiling substance it was washed with light petroleum to remove any adhering second component. A small quantity was powdered and covered with solution similar to that in the column, sometimes with the addition of a little wetting agent. It was kept in a vacuum-desiccator for ¼ hr., then washed into the column below the surface. Sharp layers of powder were obtained with some scattered fragments above consisting of less dense material presumably containing air. Positions of the calibrating drops and the position and spread of the layers were read with a cathetometer. An accuracy better than 1 : 1000 was usually obtained for the density.

In a few instances no density is recorded because a sharp layer could not be obtained in the density gradient column, or because little more than a single crystal of an adduct had been obtained and attempted repetition of the preparation gave a different crystalline form.

*Molecular Weights.*—The unit-cell weights are expressed in terms of O = 16·000 and are based on the unit-cell dimensions and the densities given in the Tables. Densities were measured at 20° and most cell constants within a degree or two of that temperature. Cell dimensions measured over a range of temperature for the ethanol and heptyl bromide adducts give the following changes (Å) of lattice constant for one degree rise of temperature: ethanol adduct, +0·001 (*a*), +0·0017 (*c*); heptyl bromide adduct, +0·0017 (*a*), −0·0006 (*c*). Where necessary, cell dimensions were corrected to 20° on the supposition that the two sets of values given above would hold for other crystals of the cavity and the channel type respectively. The value of Avogadro's number appropriate to cell dimensions in Ångström units was taken as $0{\cdot}60236 \times 10^{24}$. This is the value derived, after allowance for the conversion into the chemical scale of atomic weights, from a 1955 adjustment [9] of atomic constants and agrees with that obtained by Batuecas [10] from diamond. The weight of six molecules of tri-*o*-thymotide based on C = 12·01 and H = 1·008 is 3171·7 and for a typical case, that of the propan-1-ol adduct, the total cell weight is 3350·8. It is the difference, 179·1, divided by the molecular weight of propanol which gives the number of included molecules per unit cell and the accuracy of this result depends on that of the total cell weight. To show the kind of deviation from rational formula that may occur in the channel compounds it is necessary to estimate this difference to within 1—2%, *i.e.*, about 3 units of weight. Hence the total cell weights have been determined to approximately one part in a thousand. Atomic weights of comparable accuracy have to be used as may be seen in the example.

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