70. *Molecular Complexes based on Derivatives of 4,4′-Dihydroxytriphenylmethane.*

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Numerous derivatives of 4,4′-dihydroxytriphenylmethane have been shown to give rise to molecular complexes, the enclosed compounds being held in long channels in the crystals. From the size of molecule which can be included, the channels are believed to be 6 Å or more in diameter. Heats of formation have been measured in a number of cases. Polymerisation of isoprene in several clathrate complexes by γ-radiation did not give rise to stereoregular polymers.

The formation and composition of some complexes between triphenylmethane derivatives and some aromatic compounds have been studied by Driver and his co-workers.[1,2] The one essential condition is that the triphenylmethane should have two hydroxyl groups in *para*-positions. A definite molecular ratio between the components was found in almost all cases, a situation normally associated with clathrate formation. On the basis of *X*-ray diffraction studies, Powell[3] has suggested that the triphenylmethane molecules form a layer-like structure whereby each hydroxyl group is hydrogen-bonded to hydroxyl groups from two other molecules; the substituent on the third phenyl group is " sterically linked " to the corresponding group in another molecule, *i.e.*, forms an interlocking assembly.

Under suitable conditions, it has been found possible to prepare channel complexes. Their formation and properties are described below.

Experimental

The 4,4′-dihydroxytriphenylmethanes were prepared as described by Driver,[1,2] the appropriate benzaldehyde being condensed with a slight excess of a phenol in the presence of acetic acid–sulphuric acid. After being washed free from acid, they were recrystallised from benzene, giving rise to the benzene complex. The unsolvated 4,4′-dihydroxytriphenylmethane was obtained by heating these complexes *in vacuo* to constant weight.

The annexed Table 1 lists the triphenylmethanes prepared and some of their properties. Channel complexes were formed by mixing the free compound with an excess of the other component in the presence of absolute methyl alcohol (*ca.* 5% based on the triphenylmethane). Complex-formation was usually complete in 24—48 hr., the extent of the inclusion being measured by *X*-ray powder photographs. The second components used were straight-chain,

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[1] Driver and Mok, *J.*, 1955, 3914.

[2] Driver and Lai, *J.*, 1958, 3219.

[3] Powell, personal communication.

TABLE 1. *Derivatives of 4,4′-dihydroxytriphenylmethane.*

Derivative	M. p.[a]	Benzene complex, m. p.[a]	Channel complex[b] M. p.	Channel complex[b] Included component (%)
3″-Nitro	162° (158·5 [1])	160° (72 [1])	ND[c]	—
2,2′-Dimethyl-3″-nitro	174 (171—172 [1])	89 (85—90 [1])	157—159°	6·4
3″-Amino	160—164 (168 [1])	110 (110 [1])	160—166	—
2″-Bromo	158 (156—157 [2])	100—120 (120 [2])	110—116	5·0
3″-Bromo-2,2′-dimethyl	218 (220—221 [2])	218 (216—218 [2])	197	8·5
4″-Bromo	125—126 (124—126 [2])	90 (98 [2])	ND	9·4
2″-Chloro[d]	166	103	134—138	10·5

[a] M. p. from the literature are given in parentheses. [b] All channel compounds formed by one triphenylmethane have the same m. p. [c] ND, complex formed but property not determined. [d] Found: Cl, 11·55. $C_{19}H_{15}ClO_2$ requires Cl, 11·4%.

branched-chain, or cyclic hydrocarbons. Complexes were also prepared by precipitation from chloroform solution by addition of the second component.

The heats of formation of some twenty complexes were calculated from vapour pressures measured in a modified dew-point apparatus.[4] The temperatures observed for the appearance and disappearance of a liquid film on a cooled ground-glass surface were within 0·5°. Dew-points for at least three different temperatures were obtained and when plotted as vapour pressure against reciprocal temperature were linear over a 30° range within the limits 15 80°. The heats of formation are given in Table 2.

TABLE 2. *Heats of formation of 4,4′-dihydroxytriphenylmethane complexes (in kcal./mole).*

Triphenylmethane	Benzene	Heptane	Octane	Decane	Oct-1-ene
2″-Bromo	8·1	7·6	8·0	9·0	6·9
3″-Bromo-2,2′-dimethyl	16·3	6·0	7·3	8·6	4·7
4″-Bromo	20·2	4·9	5·5	10·6	6·4
2″-Chloro	4·1	3·6	8·7	10·8	6·5

Isoprene complexes were formed in the same way. Polymerisation was accomplished in the presence of excess of isoprene by using γ-rays (cobalt 60) to a total dose of $1{\cdot}3 \times 10^{7}$/r. After the complex had been washed with isopentane to remove any externally formed polymer, the included polyisoprene was isolated by dissolving the triphenylmethane in acetone. At this dose, a conversion of *ca.* 10% was obtained.

DISCUSSION

Channel complexes were not obtained when the unsolvated triphenylmethane was recrystallised in presence of the second component: the former was too insoluble. However, addition of a trace of methyl alcohol brought about complex formation within 1—2 days at room temperature. Gas chromatography of the hydrocarbon after its release from the complex did not reveal any gross contamination by methyl alcohol, the maximum amount of which was 0·02%.

Molecules which gave rise to channel complexes were the n-alkanes, n-alkenes, and the branched molecules 2,2,4-trimethylpentane, di-isobutene, and squalane. All the triphenylmethanes used, except 3″-bromo-2,2′-dimethyl-4,4′-dihydroxytriphenylmethane, gave normal channel complexes with dipentene. From the known size of dipentene, it appears that the channels within the crystals were at least 6·5 Å in diameter (with the one exception mentioned). A slight increase in the diameters of the rings in the *X*-ray powder photograph of the dipentene complex of 3″-bromo-2,2′-dimethyl-4,4′-dihydroxytriphenylmethane presumably resulted from a distortion of the crystal lattice by the included molecule, indicating that the channels are probably *ca.* 6·0 Å in diameter.

Examination of the benzene complex, the channel complexes, and the free triphenylmethane by *X*-ray powder methods showed the presence of either two or three different crystal structures associated with each triphenylmethane. Only two crystal structures arose when the triphenylmethane and the complex were isomorphous, *e.g.*, for 4,4′-dihydroxy-3″-nitro- and 3″-amino-4,4′-dihydroxy-triphenylmethane.

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[4] Redlich, Gamble, Dunlop, and Millar, *J. Amer. Chem. Soc.*, 1950, **72**, 4153.

The complexes with benzene are of a different type from those with aliphatic compounds, having not only a different crystal structure but also a definite molecular composition. In the other complexes the weight ratio of the two components is constant irrespective of chain length of included component.

The benzene complexes of 4,4'-dihydroxy-2,2'-dimethyl-3''-nitro- and 3''-amino-4,4'-dihydroxy-2,2'-dimethyl-triphenylmethane were isomorphous. The channel complexes were also isomorphous although the free hosts had different crystal structures. That the channel compounds were isomorphous, and that the benzene complexes were isomorphous but that the free triphenylmethanes were not, was shown by *X*-ray powder photographs and was consistent with the infrared spectra.

2''-Chloro- and 2''-bromo-4,4'-dihydroxytriphenylmethane showed a similar tendency, as judged by the *X*-ray photographs, whereby the benzene complexes were isomorphous and the channel complexes were isomorphous although the free triphenylmethanes were not. The crystal relations were not confirmed in these two cases by infrared absorption spectroscopy but this was probably due to the very low stabilities of the complexes examined.

Some of these complexes were unstable, desolvation occurring very readily in the atmosphere. Measurement of the heats of formation (Table 2) confirmed this. The increase in heat of formation with increasing chain length shows few signs of being regular but is believed to be a genuine effect. From the accuracy of the measurements and from the reproducibility of the results, the heats of formation should be within ±0·5 kcal./mole. The irregular increase in heat of formation with chain length would be expected if the channel is irregular, *i.e.*, where interaction (steric effects) can occur between the substituent groups of the triphenylmethane that extend into the channels and the included components. This could occur without significant change in the *X*-ray powder photographs. Such a situation is different from that of the urea complexes where the host is arranged in a helix having six molecules of urea per turn,[5] the heats of formation there increasing fairly regularly.[4]

Polymerisation of isoprene was accomplished in three complexes, *i.e.*, those with 2''-chloro-4,4'-hydroxy-, 3''-bromo-4,4'-hydroxy-2,2'-dimethyl-, and 4''-bromo-4,4'-dihydroxy-triphenylmethane. Structure determination by infrared and near-infrared spectroscopy showed that the *cis*-1,4- to *trans*-1,4-ratio was *ca.* 1 : 9, very little different from that in emulsion-polymerisation. 1,2- and 3,4-Addition was reduced almost to zero. Apart from this there were no signs of steric factors affecting the polymerisation.

Urea complexes containing aliphatic esters have been examined by infrared spectroscopy, and considerable information obtained concerning the configuration of the included molecules.[6] Unfortunately, although aliphatic esters do interact with the 4,4'-dihydroxytriphenylmethanes the complexes are of a very different kind, probably involving hydrogen bonding between the ester and the phenolic hydroxyl groups.

The formation of complexes between 4,4'-dihydroxytriphenylmethanes and long-chain hydrocarbons, the inclusion also of branched and cyclic hydrocarbons, and the formation of polymers within the lattice indicate that long channels occur in the parent crystals. That these channels are discrete is indicated by the almost complete lack of 1,2- and 3,4-addition in the isoprene polymerisation. The channels are quite large but may have regular constrictions.

The structure determinations on the polyisoprenes were carried out by P. J. Corish. We thank Mr. H. M. Powell, F.R.S., for bringing the problem to our notice and for several discussions.

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[5] Smith, *Acta Cryst.*, 1952, **5**, 224.

[6] Barlow and Corish, *J.*, 1959, 1706.