Tetrahedron Letters No. 52, pp 4711 - 4712, 1975. Pergamon Press. Printed in Great Britain.

A STUDY OF THE ROLE OF HYDROGEN BONDING IN CLATHRATE FORMATION

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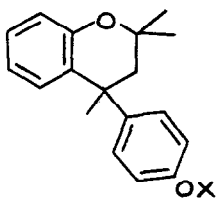
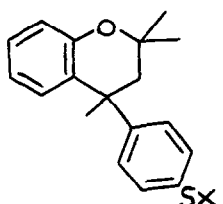
(Received in UK 27 October 1975; accepted for publication 13 November 1975)

A key feature of the clathrates formed by Dianin's compound[1] and related systems,[2] and also those formed by hydroquinone[3] and phenol,[4] is the linking of the OH groups of six molecules by a network of hydrogen bonds such that the oxygen atoms form a hexagon. We now report the first evidence that the OH function is almost certainly not unique in its ability to form this type of geometrical grouping in inclusion compounds.



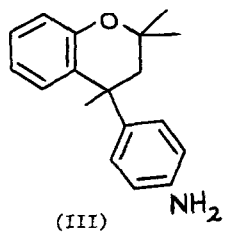
(Ia); X = H

(Ib); X = $-C(=S)-NMe_2$



(IIa); X = H

(IIb); X = $-C(=O)-NMe_2$



(III)

4-*p*-Mercaptophenyl-2,2,4-trimethylchroman (IIa), which corresponds to replacement of the OH group of Dianin's compound (Ia) by the SH function, was prepared[5] by thermal rearrangement (1.5 hr. at 270°C) of the aryl N,N-dimethylthioncarbamate (Ib) to give (IIb) which on hydrolysis yielded the required thiol (IIa) which gave unsolvated crystals, m.p. 134.5-135° (sealed tube), from cyclohexane. Structure (IIa) was confirmed by microanalysis, m/e 284 (M^+), i.r. (KBr disc, unsolvated material), ν(S-H) 2546 cm^{-1}, $\Delta\nu_{\frac{1}{2}}^{a}$ *ca* 12 cm^{-1}, and ^1H n.m.r. ($CDCl_3$) τ 9.06, 8.64, 8.32 (each 3H, s, Me), 7.80 (2H, AB, δ_{AB} 0.27 p.p.m., J 14 Hz, methylene), 6.6 (1H, s, SH), and 2.7-3.3 (8H, complex, arom. H).

The above crystals were found to be orthorhombic, space group $P2_12_12_1$ with *Z* = 4, showing that spontaneous resolution had occurred. In contrast, recrystallisation of the thiol (IIa) from carbon tetrachloride, gave crystals of the CCl_4 clathrate of (IIa) which were trigonal with space group $R\bar{3}$ (or R3) for which a host:guest ratio of 3:1 was found by microanalysis for chlorine. Solvent is lost from these crystals on standing. These crystals have lattice constants, referred to a hexagonal unit cell containing 18 molecules of (IIa), *a* = 26.898 (44) Å, and *c* = 12.022 (30) Å. Comparison with clathrates formed by Dianin's compound[1] (Ia) indicates a significant increase in the *c* dimension consistent with the longer C-S bond. The i.r. (crystals lightly ground, nujol mull) displays a broad ν(S-H) band, 2506 cm^{-1}, $\Delta\nu_{\frac{1}{2}}^{a}$ *ca* 70 cm^{-1}, whose position is compatible[6] with unusually strong SH...S hydrogen bonding; this may arise from a "supported hydrogen bond" effect.[7] The role of CCl_4 in consolidating

this structure may reflect efficient host-guest packing: an X-ray analysis of this clathrate is underway.

The amine (III), prepared[8,9] from (Ia), had spectroscopic properties and microanalysis in accord with its formulated structure. Spontaneous resolution occurs (space group $P2_12_12_1$, with $Z = 4$) when the amine (III) is recrystallised from ethanol, there being no solvent included. In the related case of resolved Dianin's compound, for which centrosymmetric packing is not possible, crystallisation also occurs without inclusion of solvent.[10]

Acknowledgement. We wish to thank the S.R.C. for support of this work.

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