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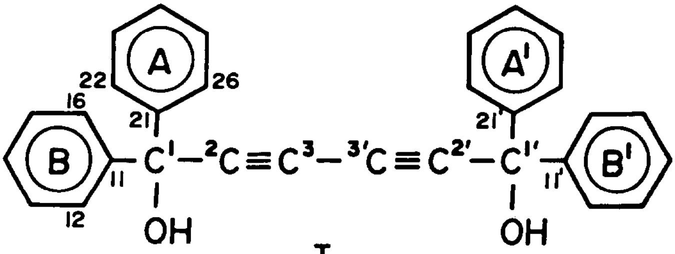
WHEEL-AND-AXLE DESIGN AS A SOURCE OF HOST-GUEST COMPOUNDS. THE CRYSTAL STRUCTURE OF THE 2:1 ACETONE:TETRAPHENYL-2,4-HEXADIYNE-1,6-DIOL COMPLEX

Fumio Toda*
Department of Chemistry, Faculty of Engineering, Ehime University, Matsuyama, Japan

Donald L. Ward and Harold Hart*
Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, USA

Abstract: The title diyne-diol crystallizes with an "open" structure containing channels, roughly parallel to the long axis of the host, in which the acetone is hydrogen bonded to the anti-oriented hydroxyl groups.

Some years ago one of us[1] reported that acetylenic diols such as I form crystalline complexes with a variety of small molecules. Diyne-diol I (as the host molecule) formed 1·2 complexes with over 20 different guests. The guests included a variety of ketones, amines, amides and a sulfoxide. The complexes had sharp melting points, and in each complex the normal ν_{O-H} at 3610 cm^{-1} for I was shifted to lower frequencies, suggesting H-bonding. Complexes without definite melting points were also formed with various halides (1:2; CCl_4, $CHCl_3$, CH_2Cl_2) and π-donors (1:1; alkenes, alkynes, arenes).



I

Since interest in the structures of host-guest complexes continues to be high,[2,3] and also because related complexes can be useful in resolving chiral tertiary acetylenic alcohols,[4] we decided to determine the crystal structures of some of these complexes. We report here the novel structure of the 2:1 acetone:I complex.

Figure 1 shows how two molecules of acetone and one molecule of I interact. The groups at the sp^3 carbons in I are staggered, with the hydroxyl groups (including the hydrogens)

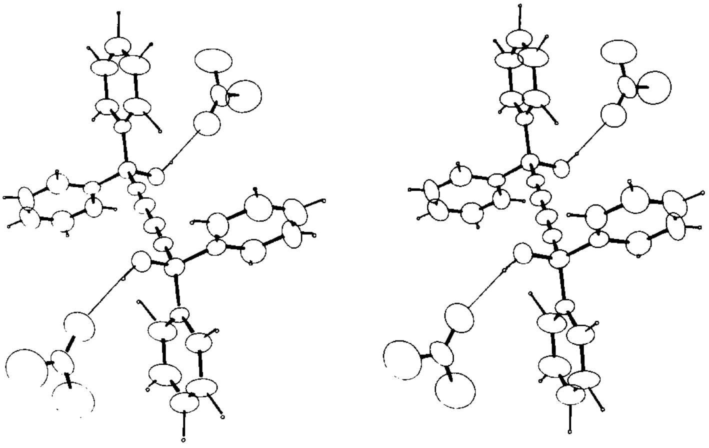


Figure 1. ORTEP stereodrawing of the 2:1 acetone:I complex. The thermal ellipsoids are drawn at the 50% probability level.

anti.[5] Each hydroxyl is hydrogen bonded to the carbonyl oxygen of an acetone molecule. As the ellipsoids in the figure show, the guest acetone molecules are less rigidly fixed in space (i.e., have greater thermal motion) than are the host diol molecules.

The arrangement of the phenyl groups in individual molecules of I is of some interest. Anti phenyls lie in parallel planes. One pair of phenyls (A,A') lie nearly in the same plane as is formed by C21-C1-C1'-C21', the dihedral angle between these planes being only 17°. The distance between the planes of phenyls A and A' is only 1.28 Å. On the other hand, the other set of anti phenyls (B,B') form an angle of 68° with the C11-C1-C1'-C11' plane; 5.76 Å separates the planes of these parallel phenyls. The two phenyls (A,B) attached to the same sp^3 carbon are nearly orthogonal (dihedral angle 81°).

Some of these structural features are more easily seen in the packing diagrams (Figures 2-4; see, for example, the two molecules at the left of Figure 2). These diagrams give views perpendicular to the three faces of the orthorhombic crystal. Figure 2 clearly shows the channels which penetrate the crystal and contain nothing but guest molecules (acetone). The channels roughly parallel the long six-carbon diacetylene axis. Figure 3 shows the zig-zag arrangement of the host main molecular axes, whereas Figure 4 shows another view of these axes with pendant phenyl and acetone moieties.

The packing diagrams show the "open" nature of the molecular arrangement in the crystal. Nearest approaches are well beyond van der Waals radii. For example, the distance between a para hydrogen on one of the phenyl groups and the closest atoms on its nearest neighbor (acetylenic carbons C2, C3) ranges from 3.16 to 3.85 Å.

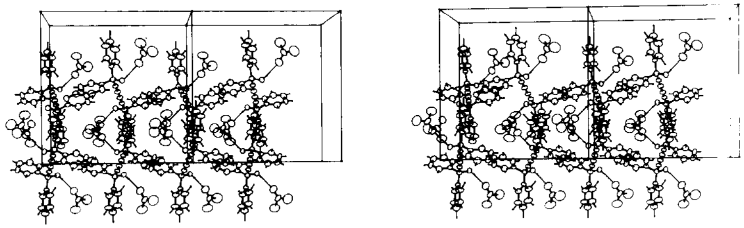


Figure 2. ORTEP stereodrawing of molecular packing. View is perpendicular to the c axis, and clearly shows channels occupied solely by acetone molecules.

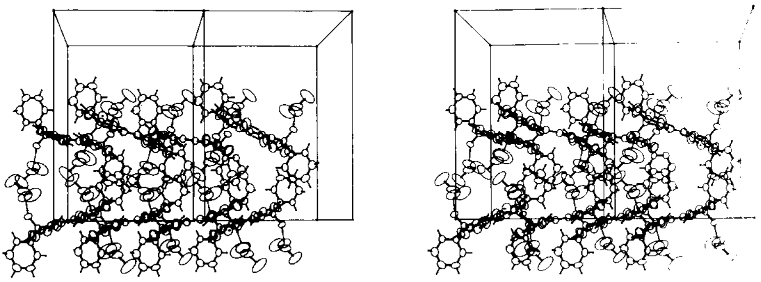


Figure 3. ORTEP stereodrawing of molecular packing (⊥ to b axis).

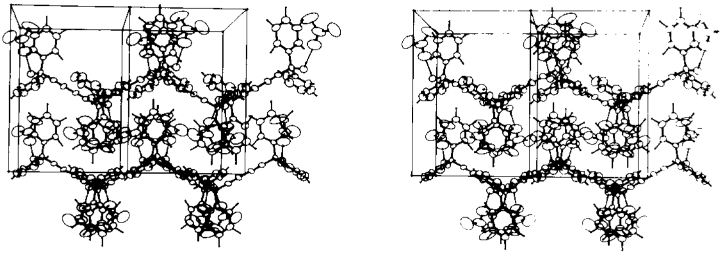


Figure 4. ORTEP stereodrawing of molecular packing (⊥ to a axis).

Compound I has a shape which may be likened to that of an axle with a wheel at either end. This shape does not appear to be conducive to close packing and may well contribute to the ease with which I forms so many host-guest compounds.[1] We have designed and are synthesizing other molecules with this shape to test this hypothesis.[6]

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References and Notes

1. F. Toda and K. Akagi, Tetrahedron Lett., 3695 (1968).
2. For a recent example and leading references, see J. A. Hyatt, E. N. Duesler, D. Y. Curtin and I. C. Paul, J. Org. Chem., **45**, 5074 (1980).
3. For a recent review, see D. D. MacNicol, J. J. McKenrick and D. R. Wilson, Chem. Soc. Rev., **7**, 65 (1978).
4. F. Toda and K. Tanaka, unpublished results.
5. An X-ray structure of the parent diol $HOCH_2$-C≡C-C≡C-CH_2OH has been reported: E. Hädicke, K. Penzien and H. W. Schnell, Angew. Chem. Int. Ed. Engl., **10**, 940 (1971). This substance was sensitive to X-rays and several crystals were used in succession for the intensity measurements. Although the resolution was not excellent and the substance readily polymerizes in the solid state, it was established that here too the substituents on the sp^3 carbons were staggered with the hydroxyls anti.
6. Crystals of I $(acetone)_2$ are orthorhombic; space group Pbca; a=16.009(6), b=16.200(6), c=11.516(4)Å; Z=4; M=472.59; ρ_c=1.045 g cm^{-3}. Intensity data were measured using MoKα radiation ($2\Theta_{max}$=50°) yielding 2665 total unique data and, based on I > 1σ(I), 1388 observed data. The final R value was 0.128. Bond distances and angles for the individual molecules were all well within normal ranges for comparable structures. Tables of the atomic coordinates, bond distances, bond angles, thermal parameters, all with standard deviation (4 pp) are available on request from the Director of the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, Great Britain. A copy of the structure factor table (11 pp) is deposited with the British Library, Lending Division.

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