Allenes as Clathrate Hosts: Formation of a New Channel Network

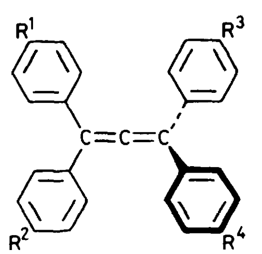
Edwin Weber,*[a] Wilhelm Seichter,[a] and Israel Goldberg[b]

[a] *Institut für Organische Chemie und Biochemie der Universität Bonn, Gerhard-Domagk-Strasse 1, D-5300 Bonn-1, Federal Republic of Germany*
[b] *School of Chemistry, Sackler Faculty of Exact Sciences, Tel-Aviv University, 69978 Ramat-Aviv, Israel*

The tetra-aryl-allenes (**1d**) and (**2**) are representatives of a new host design, acting *via* formation of crystal channels and selective guest inclusion.

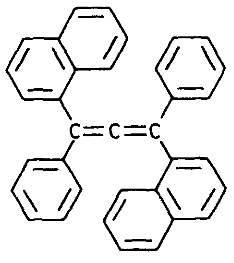
The rigid backbone and clear molecular shape of allenes[1] would appear to make them particularly suitable as clathrates.[2,3] Substitution of an allene by bulky non-flexible groups should prevent close packing in the crystal and hence lead to clathrate formation.[4,5] On that account we have synthesized a series of tetra-aryl- [(**1**) and (**2**)] and bridged tetra-aryl-allenes [(**3**)—(**5**)] and investigated their potential clathrate behaviour.

Compound (**1d**) shows interesting inclusion properties upon crystallization from various solvents including alicyclic compounds (*e.g.* cyclopentane, methylcyclopentane, cyclohex-

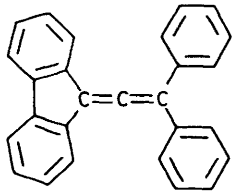


(1)

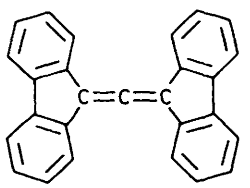
a; $R^1 = R^2 = R^3 = R^4 = H$
b; $R^1 = Br$, $R^2 = R^3 = R^4 = H$
c; $R^1 = R^3 = Br$, $R^2 = R^4 = H$
d; $R^1 = R^2 = R^3 = R^4 = Bu^t$
e; $R^1 = R^2 = R^3 = R^4 = MeO$



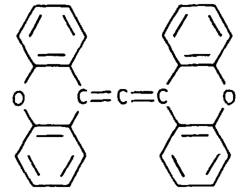
(2)



(3)



(4)



(5)

ane, methylcyclohexane, cycloheptane), cycloalkenes (*e.g.* cyclohexene, cycloheptene), aromatic compounds (*e.g.* benzene, PhMe, *o*-, *m*-, *p*-xylene, PhBu^t, PhBr, mesitylene), heterocycles (*e.g.* tetrahydrofuran, 1,3-dioxolane, 1,4-dioxane, piperidine, morpholine), cyclic ketones (*e.g.* cyclopentanone, 3-methylcyclopentanone, cyclohexanone), and cyclohexaneamine; all the inclusion compounds are of 1:1 stoicheiometry. Notwithstanding this broad clathrate capability, high inclusion selectivity is also demonstrated by this host. A few results from solvent competition experiments are summarized in Table 1. They reveal (**1d**) as a specific agent for the separation of constitutional isomers (entry 1), of homologues (entries 2 and 3), and of compounds having different degrees of saturation (entry 4), as well as of chemically different species (entry 5). Inclusion of aliphatic compounds has not been observed; thus use of the host (**1d**) allows separation of aliphatic from alicyclic or aromatic compounds.[4]

The allene (**2**) also behaves as a host molecule, but is less efficient since the only inclusion compound obtained is a 1:1 clathrate with benzene. Remarkably, all the other allenes [(**1a**—**c** and **e**), and (**3**)—(**5**)] gave solvent-free crystals under the same experimental conditions.

Thus inclusion compound formation is strongly influenced by the bulk of the substituents; furthermore, linking two of the aryl groups [as in (**3**)—(**5**)] does not induce host properties.

Table 1. Preference of guest binding of (**1d**) from two-component solvent mixtures.

Entry	Recrystallization solvent (equimolar mixture of components I/II)	Inclusion compound stoicheiometric ratio (host : I : II)[a]
1	Cyclohexane/methylcyclopentane	1:1:0
2	Benzene/toluene	1:0:1
3	1,3-Dioxolane/1,4-dioxane	1:1:0
4	Cyclohexane/benzene	1:1:0
5	Benzene/pyridine	1:1:0

[a] Determined by n.m.r. integration.

The strict 1:1 stoicheiometry along with the similarity of the guest molecules in size and shape (mean molecular length around 6 Å,[4] all cyclic), suggests a relatively invariant host lattice and raises questions about its structure.

In view of this we have investigated the structures of three inclusion compounds by *X*-ray diffraction, those of (**1d**) with toluene, cyclohexene, and cyclohexane.† The structural principles are the same in the three inclusion compounds, showing a unique channel network of host molecules. The continuous channels are occupied by the three guest species. Figure 1, which illustrates the structure of (**1d**)·PhMe, is representative of the general construction.

In the (**1d**)·PhMe clathrate, the channels have a nearly rectangular shape of van der Waals dimensions 4.0 × 6.5 Å, giving a good fit to the thickness and width of the guest ring. The channel walls are not entirely uniform, but contain dents around the methyl groups of the slightly tilted toluene molecule.

In the clathrates of (**1d**) with cyclohexene and cyclohexane the cross-sections of the channels around the included guests have similar van der Waals dimensions (4.2 × 6.5 Å). However, in between the two neighbouring guests along the channels the opening narrows from 6.5 to about 3.4 Å, thus forming a partial enclosure around each guest. This may explain why the inclusion compounds of cyclohexene and cyclohexane are more stable.

---

† *Crystal data:* (**1d**)·C_7H_8 ($C_{43}H_{54}{\cdot}C_7H_8$), $M = 660.42$, triclinic, space group $P\bar{1}$, $a = 12.614(1)$, $b = 12.621(4)$, $c = 14.317(2)$ Å, $\alpha = 82.12(2)$, $\beta = 74.87(1)$, $\gamma = 72.29(1)°$, $Z = 2$, $D_c = 1.056$ g cm^{-3}; (**1d**)·C_6H_{10} ($C_{43}H_{54}{\cdot}C_6H_{10}$), $M = 650.43$, triclinic, space group $P\bar{1}$, $a = 12.395(6)$, $b = 12.835(7)$, $c = 15.372(3)$ Å, $\alpha = 101.84(4)$, $\beta = 95.95(4)$, $\gamma = 113.57(3)°$, $Z = 2$, $D_c = 1.014$ g cm^{-3}; (**1d**)·C_6H_{12} ($C_{43}H_{54}{\cdot}C_6H_{12}$), $M = 652.54$, triclinic, space group $P\bar{1}$, $a = 12.367(9)$, $b = 12.719(3)$, $c = 15.228(3)$ Å, $\alpha = 101.85(2)$, $\beta = 96.55(4)$, $\gamma = 112.60(3)°$, $Z = 2$, $D_c = 1.032$ g cm^{-3}.

Intensity data were measured to $2\theta_{max} = 46°$ with a CAD4 diffractometer, using Mo-K_α ($\lambda = 0.7107$ Å) radiation. Structures were partially disordered, with a rotational disorder of the Bu^t groups and a translational/conformational disorder of the guest species. This disorder could not be defined sufficiently well during the crystallographic least-squares refinement; geometric constraints were applied, however, to the disordered fragments to avoid unreliable distortions of the covalent parameters. The various refinements converged only at $R = 0.12$ (for 1996 reflections above the intensity threshold of 3σ out of 4797 unique data above zero), $R = 0.13$ (for 2013 out of 4726 reflections), and $R = 0.14$ (for 1895 out of 4728 reflections) for (**1d**) with toluene, cyclohexene, and cyclohexane, respectively.

The atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

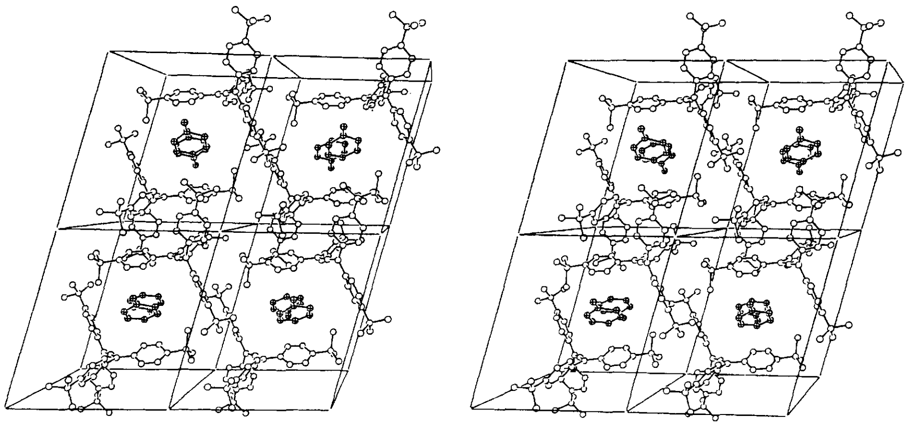


Figure 1. Stereoscopic representation of the (**1d**)·PhMe clathrate viewed down the channel axis. Host and guest atoms are specified by empty and cross-marked circles, respectively.

The shortest C–C distances of the guests from the channel walls (3.8 Å) show the absence of any specific host–guest interaction. The geometry of the host conforms to the expected values.[6]

In view of the general properties of allenes,[1] and since channel inclusions are advantageous for solid-matrix reactions,[3] the design for hosts outlined here has great potential. Other uses with appropriately substituted allenes, including chiral recognition,[2] are readily envisaged.

E. W. acknowledges financial support from Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Received, 29th May 1987; Com. 730

References

1 S. R. Landor, 'The Chemistry of the Allenes,' Academic Press, London, 1982, vols. 1—3.

2 E. Weber, 'Molecular Inclusion and Molecular Recognition—Clathrates I,' *Top. Curr. Chem.*, vol. 140, Springer-Verlag, Berlin-Heidelberg, 1987.

3 J. L. Atwood, J. E. D. Davies, and D. D. MacNicol, 'Inclusion Compounds,' Academic Press, London, 1984, vols. 1—3.

4 *Cf.* E. Weber, J. Ahrendt, M. Czugler, and I. Csöregh, *Angew. Chem.*, 1986, **98**, 719; *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 746.

5 *Cf.* H. Hart, L.-T. Lin, and D. L. Ward, *J. Am. Chem. Soc.*, 1984, **106**, 4043.

6 H. Irngartinger and W. Götzmann, *Angew. Chem.*, 1986, **98**, 359; *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 340.