

# Inclusion Compounds

Volume 2

Structural Aspects of Inclusion Compounds  
formed by  
Organic Host Lattices



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Structural Aspects of Inclusion Compounds  
formed by  
Organic Host Lattices

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## PREFACE

In September 1980 the Institute of Physical Chemistry of the Polish Academy of Sciences hosted the First International Symposium on 'Clathrate Compounds and Molecular Inclusion Phenomena' at Jachranka, near Warsaw. At this timely meeting, the first devoted entirely to all types of inclusion behaviour, the unanimous opinion of the participants was that every effort should be made to draw together in print the various threads from which the rich tapestry of Inclusion Chemistry is currently being woven.

As a first step in this direction, the proceedings of the conference were published in special issues of the *Journal of Molecular Structure* (Volume 75, Number 1, 1981) and the *Polish Journal of Chemistry* (Volume 56, Number 2, 1982). However, to obtain a more global modern picture of Inclusion Chemistry it was apparent that an up-to-date Comprehensive Treatise would be necessary. In view of the rapid advances being made at present, it was clear that such a work could only be produced on an acceptable timescale, and with a sufficient depth of treatment of recent work, by inviting recognised international authorities to write on their own particular fields of interest. Accordingly, this was the plan chosen for the present work.

Earlier useful books, in English, have appeared on inclusion compounds over the years, each reflecting the state of knowledge at the time of publication, three being *Clathrate Inclusion Compounds*, Reinhold, 1962, by M. Hagen; *Non-Stoichiometric Compounds*, Academic Press, 1964, edited by L. Mandelcorn; and *Clathrate Compounds*, Chemical Publishing Company, 1970 by V. M. Bhatnagar. The most comprehensive of these is undoubtedly the book edited by L. Mandelcorn (1964) and in some ways the present treatise may be regarded as complementary to that work.

The editors note, with pleasure, the greatly increasing interest in inclusion phenomena, as evidenced by recent relevant publications on *specific* aspects of Inclusion Chemistry: *Cyclodextrin Chemistry*, by M. L. Bender and M. Komiyama, Springer-Verlag, 1977; *Host-Guest Complex Chemistry I and II*, edited by F. Vögtle, Springer-Verlag, 1981; *Ionophores and their Structures*, by M. Dobler, Wiley, 1981; *Cyclodextrins and their Inclusion Complexes*, by J. Szejtli, Akademiai Kiado, Budapest, 1982; and *Intercalation Chemistry*, edited by M. S. Whittingham and R. J. Jacobson, Academic Press, 1982. Also a new journal devoted to inclusion compounds *The Journal of Inclusion Phenomena* has been launched by Reidel.

We have great pleasure in dedicating these three volumes to Professor H. M. Powell, FRS, whose pioneering crystallographic work laid firm foundations for subsequent work in Inclusion Chemistry.

We wish to thank Professor Powell for kindly agreeing to write the important introductory chapter; and we are indebted also to all our other contributors for their help and participation in writing this book. We must also thank the staff of Academic Press for the efficient way in which the book has been produced.

The present volume is the second of a three volume series designed to provide comprehensive coverage of all aspects of inclusion compounds. Volume 1 is principally concerned with structural and design aspects of inclusion compounds formed by inorganic and organometallic host lattices, Volume 2 is concerned with similar aspects of inclusion compounds formed by organic host lattices, while Volume 3 concentrates on the physical properties and applications of inclusion systems.

January, 1983

J. L. Atwood  
J. E. D. Davies  
D. D. MacNicol

# Contents

List of Contributors . . . . .	v
Preface . . . . .	vii
Contents of Volumes 1 and 3 . . . . .	xiv

## Chapter 1. Structure and design of inclusion compounds: the clathrates of hydroquinone, phenol, Dianin's compound and related systems *D. D. MacNicol*

1. Introduction . . . . .	1
2. Hydroquinone . . . . .	2
2.1. $\beta$ -Hydroquinone Clathrates . . . . .	2
2.2. $\alpha$ -Hydroquinone and $\gamma$ -Hydroquinone . . . . .	8
3. Phenol and simple substituted phenols . . . . .	11
4. Dianin's compound and related molecules . . . . .	12
4.1. General considerations . . . . .	12
4.2. Crystal structures of the parent host and its thia-analogue . . . . .	13
4.3. Structural modifications of Dianin's compound . . . . .	17
4.4. Applications of Dianin's compound and its thia-analogue . . . . .	30
5. Other complex phenolic host molecules . . . . .	32
6. Concluding remarks . . . . .	40

## Chapter 2. Inclusion compounds of urea, thiourea and selenourea *K. Takemoto and N. Sonoda*

1. Inclusion compounds of urea . . . . .	47
1.1. Formation . . . . .	48
1.2. Composition . . . . .	50
1.3. Structure and properties . . . . .	51
1.4. Heats of formation . . . . .	55
2. Inclusion compounds of thiourea . . . . .	57
2.1. Formation . . . . .	57
2.2. Structure and properties . . . . .	60
3. Industrial applications of urea and thiourea inclusion compounds . . . . .	63
4. Inclusion compounds of selenourea . . . . .	63

## Chapter 3. Inclusion compounds of perhydrotriphenylene *M. Farina*

1. Introduction . . . . .	69
2. The preparation and composition of PHTP inclusion compounds . . . . .	71
3. Crystal structure of PHTP inclusion compounds . . . . .	74
4. Phase diagrams of binary systems forming inclusion compounds . . . . .	83
5. Inclusion compounds with long chain hydrocarbons . . . . .	89

## Chapter 4. Inclusion compounds of cyclotrimeratrylene and related hosts

### A. Collet

1. Introduction	97
2. Chemistry of cyclotrimeratrylene and related compounds	98
2.1. Synthesis of cyclotrimeratrylene	98
2.2. Preparation of analogues	102
2.3. Optically active derivatives	106
2.4. Geometry and conformational behaviour	107
3. Inclusion Compounds	111
3.1. Crystalline inclusion compounds	112
3.2. Molecular complexes	116

## Chapter 5. Structure and design of inclusion compounds: the hexa-hosts and symmetry considerations

### D. D. MacNicol

1. Introduction	123
2. The hexa-host analogy, hexa hosts and related systems	124
2.1. Nature of the concept	124
2.2. Synthesis of prospective hexa-hosts and initial observations	125
2.3. Crystal structure of the carbon tetrachloride inclusion compound of hexakis(phenylthio)benzene	134
2.4. Structure of the 1,4-dioxan inclusion compound of hexakis(benzylthiomethyl)benzene and systematic structural modification of the host	136
2.5. Effect of further inter-ring chain elongation and symmetrical removal of three hexa-host "legs"	140
2.6. Channel-type inclusion compound of hexakis( <i>p</i> - <i>t</i> -butylphenylthiomethyl)benzene with squalene as guest; conformational selection	143
2.7. Synthesis of the chiral hexa-host molecule hexakis( <i>R</i> - $\alpha$ -phenylethylsulphonylmethyl)benzene and the X-Ray crystal structure of its acetic acid inclusion compound	148
2.8. Nitrogen-based hexa-hosts and related aromatic molecules	150
2.9. Synthesis of hexakis(arylthio)benzenes and a hexaselenoether; X-ray crystal structure of the 1,4-dioxan inclusion compound of hexakis( $\beta$ -naphthylthio)benzene	155
2.10. Synthesis of the first hexakis(aryloxy)benzenes; the X-ray structures of an unsolvated system and of an acetonitrile inclusion compound	158
2.11. Synthesis of pentakis(phenylthio)pyridine and the unexpected formation of 1,3,4-tris(phenylthio)[1]benzothieno[3,2- <i>c</i> ]pyridine	160
2.12. First synthesis of octakis(arylthio)naphthalenes: X-ray study of the yellow and red forms of octakis(phenylthio)naphthalene	162
3. Design of hosts with trigonal symmetry: the third strategy	163
4. Concluding remarks	166



**Chapter 6. The trianthranilides: a new class of organic hosts** *W. D. Ollis and J. F. Stoddart*

1. Historical background . . . . .	169
2. Trianthranilides . . . . .	173
2.1. Trianthranilide synthesis . . . . .	173
2.2. Propeller and helical conformations of constitutionally symmetrical and unsymmetrical trianthranilides . . . . .	176
2.3. Solid state structures of the <i>N,N'</i> -dimethyl and <i>N,N'</i> -dibenzyl derivatives of trianthranilide . . . . .	179
2.4. Conformational behaviour of the constitutionally symmetrical and unsymmetrical trianthranilide derivatives in solution . . . . .	181
3. Triarylmethyltrianthranilides . . . . .	196
4. Inclusion compounds . . . . .	200
5. Conclusion . . . . .	203

**Chapter 7. Inclusion compounds of deoxycholeic acid** *E. Giglio*

1. Deoxycholic acid . . . . .	207
2. Choleic acids . . . . .	210
3. Structural investigations of choleic acids . . . . .	211
3.1. Introduction . . . . .	211
3.2. Orthorhombic crystals . . . . .	213
3.3. Tetragonal crystals . . . . .	220
3.4. Hexagonal crystals . . . . .	223
4. Stability of choleic acids by vapour pressure measurements . . . . .	225

**Chapter 8. Structural aspects of cyclodextrins and their inclusion complexes** *W. Saenger*

1. Introduction: general description of cyclodextrins . . . . .	231
2. General structural features of cyclodextrin molecules . . . . .	235
2.1. The glucose is a "rigid" unit . . . . .	235
2.2. The macrocyclic geometry is rather well defined . . . . .	237
2.3. The torsion angle index . . . . .	238
2.4. A ring of intramolecular hydrogen bonds . . . . .	238
2.5. Glycosyl torsion angles $\phi$ and $\psi$ are rather constant . . . . .	239
3. Two types of crystal structures: channels and cages . . . . .	240
3.1. Channel type structures . . . . .	240
3.2. Cage type structures in herringbone and brick arrangements . . . . .	240
3.3. What are the conditions for channel or cage type formation? . . . . .	242
4. The "empty" cages formed by hydrated cyclodextrins and the "induced-fit" type complex formation of $\alpha$ -cyclodextrin . . . . .	243
5. Order and disorder in the cage . . . . .	246
6. Channel type complexes are mostly disordered . . . . .	249
7. Linear polyiodide in $\alpha$ -CD channels as a model for the blue starch-iodine complex . . . . .	251
8. Hydrated cyclodextrins display circular and flip-flop hydrogen bonds . . . . .	253
9. Increasing the extent of the hydrophobic cavity by methylation: 2,6-tetradeca- <i>O</i> -methyl- $\beta$ -cyclodextrin . . . . .	255
10. Why study cyclodextrins? . . . . .	255

<b>Chapter 9. Complexes of crown ethers with molecular guests</b>	<b>I. Goldberg</b>
1. Introduction	261
2. Host-guest complexes of the macrocyclic 18-crown-6 system	264
2.1. Association with metal cations	264
2.2. Guests with $-\text{CH}_3$ and $>\text{CH}_2$ coordinating entities	265
2.3. Guests with uncharged $-\text{NH}_2$ coordinating entities	269
2.4. Coordination of metal-ligand assemblies	272
2.5. Guests with partially charged $-\text{NH}_2$ coordinating entities	276
2.6. Interaction with ammonium and alkylammonium substrates	278
2.7. Interaction with diazonium moieties	282
2.8. Conformational features, in relation to the free ligand	283
3. Inclusion of alkylammonium guests within crown ether hosts	285
3.1. Chiral and achiral complexes with penta- and hexaether macrocycles	285
3.2. Complexes with larger 24-crown-8 and 30-crown-10 derivatives	294
3.3. Compounds with nitrogen-containing hosts	297
3.4. Geometry of binding interactions	300
4. Other types of complexes with monocyclic hosts	302
4.1. Interaction of hydronium ions with crown ethers	302
4.2. Exclusive inclusion of water molecules	303
4.3. Encapsulated guanidinium and uronium cations	307
4.4. Intramolecular complexes	308
4.5. Complexes of hemispherands and spherands, ligands with sterically enforced cavities	311
5. Inclusion compounds of open-chain polyether ligands	317
5.1. Complexes of metal cations	317
5.2. Complexes with non-metal guests	327
6. Concluding remarks	330
 <b>Chapter 10. Cryptate complexes</b>	 <b>B. Dietrich</b>
1. Introduction	337
2. Macrobicyclic ligands—cryptates	338
2.1. Diaza-polyoxa macrobicycles	338
2.2. Structural modifications	347
3. Macrotricycles, macrotetracycles, mononuclear and dinuclear cryptates	357
3.1. Spheroidal macrotricycles	358
3.2. Cylindrical macrotricycles and macrotetracycles	360
4. Functionalized macrocycles	368
4.1. Chiral macrocycle derived from L-(+)-tartaric acid	369
4.2. Face-discriminated and side-discriminated macrocycles	372
5. Anion complexation	373
5.1. Introduction	376
5.2. Guanidinium containing anion receptors	377
5.3. Ammonium containing receptors	378
6. Cryptate applications	385
6.1. Applications of cation complexation	385
6.2. Cryptate associated anions	387
6.3. Applications of anion complexation	394

**Chapter 11. Inclusion compounds formed by other host lattices***J. E. D. Davies, P. Finocchiaro and F. H. Herbstein*

1. Introduction	407
2. Organic host lattices	408
2.1. Trimesic acid (TMA)	408
2.2. Substituted methanes and ethanes	418
2.3. Cyclophanes	421
2.4. BSX and HMX	427
2.5. 4,4'-Dinitrobiphenyl	430
2.6. <i>N</i> -( <i>p</i> -Tolyl)tetrachlorophthalimide	430
2.7. Other organic host lattices	431
3. Inorganic and organometallic host lattices	439
3.1. Cyanide and thiocyanate complexes	439
3.2. Other inorganic and organometallic host lattices	445
Author index	455
Subject index	481

# 1 • STRUCTURE AND DESIGN OF INCLUSION COMPOUNDS: THE CLATHRATES OF HYDROQUINONE, PHENOL, DIANIN'S COMPOUND AND RELATED SYSTEMS

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1.	Introduction	1
2.	Hydroquinone	2
3.	Phenol and simple substituted phenols	11
4.	Dianin's compound and related molecules	12
5.	Other complex phenolic host molecules	32
6.	Concluding remarks.	40

## 1. Introduction

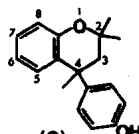
Host molecules possessing at least one phenolic hydroxyl group have played a vital role in the development of the chemistry of crystalline multimolecular inclusion compounds. Viewing this fascinating area in historical perspective one may identify as important landmarks the early *chance* discoveries of key host molecules such as hydroquinone (1), phenol (2), and Dianin's compound (3); the subsequent X-ray elucidation of the crystal structures of adducts of these hosts; and, comparatively recently, the successful *design* of new host molecules belonging to the phenolic class. A number of reviews have appeared,<sup>1-26</sup> and the principal aims of the present chapter are to



(1)



(2)



(3)

cover recent structural work on phenolic hosts and to describe in some detail the successful synthesis of new hosts by structural modification of a known host, Dianin's compound (3). Other important aspects of the key phenolic class of host molecule are discussed in detail elsewhere, as indicated: infrared and Raman studies (Volume 3, Chapter 2), thermodynamic considerations (Volume 3, Chapter 1), and dielectric and magnetic resonance investigations (Volume 3, Chapter 3). In the present chapter some practical applications are mentioned, and a brief survey of less-studied phenolic hosts is also given. The successful synthesis of new host molecules with no *direct* structural relationship to any known host, based on the recognition of the importance of the (OH...O) hydrogen-bonded hexameric unit found in many phenolic host lattices, represents a significant step forward in host design, and this is considered separately in Volume 2, Chapter 5.

## 2. Hydroquinone

### 2.1. $\beta$ -Hydroquinone clathrates

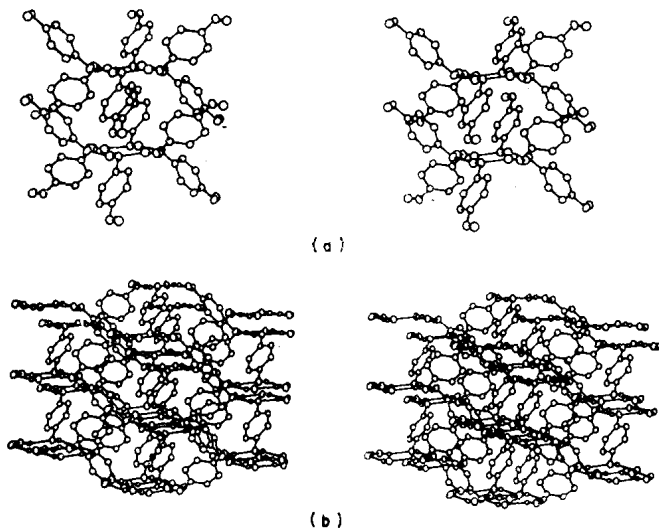
The history of adducts of hydroquinone, or quinol (1), already reviewed,<sup>1</sup> dates back into the nineteenth century: in 1849 Wöhler<sup>27</sup> found  $\text{H}_2\text{S}$  to be trapped by 1, then, ten years later, Clemm<sup>28</sup> found  $\text{SO}_2$  to be similarly retained; and in 1886 Mylius,<sup>29</sup> discovering the inclusion of carbon monoxide by 1, made the very shrewd observation that perhaps the molecules of hydroquinone were somehow able to lock the volatile component into position without chemically combining with it. It was not until the 1940s, however, that the pioneering X-ray studies of Powell and coworkers<sup>30,31a,32-34</sup> firmly established the true cage, or clathrate,<sup>35</sup> nature of these intriguing systems. In fact, hydroquinone can exist in three crystal modifications designated  $\alpha$ ,  $\beta$ , and  $\gamma$  forms, the  $\alpha$ -form being the stable form at room temperature. The monoclinic  $\gamma$ -form is produced by sublimation or by rapid evaporation of a solution of 1 in ether. The  $\beta$ -form is the most versatile, however, and the classical studies of Powell and colleagues<sup>30,31a,32-35</sup> established that three crystallographically distinguishable kinds of  $\beta$ -hydroquinone clathrate host lattice, now termed<sup>36</sup> Types I-III, can exist, all having

Table 1. Selected crystal data for  $\beta$ -hydroquinone clathrates and other forms of 1

Designation	Space group	Lattice parameters <sup>a</sup>	Guest	Hexamer dimensions (O...O)	Ref.
$\beta$ -form (Type I)	R $\bar{3}$	$a = 16.613(3)$ , $c = 5.4746(5)$ Å, $Z = 9$	None	2.678 (3) Å	37
$\beta$ -form (Type I)	R $\bar{3}$	$a = 16.616(3)$ , $c = 5.489(1)$ Å, $Z = 9$ (host)	H <sub>2</sub> S	2.696 (1) Å	41
$\beta$ -form (Type II)	R3	$a = 16.31(5)$ , $c = 5.821(1)$ Å, $Z = 9$ (host)	SO <sub>2</sub>	2.727 (6) Å, 2.733(6) Å	31(b)
$\beta$ -form (Type II)	R3	$a = 16.621(2)$ , $c = 5.562(1)$ Å, $Z = 9$ (host)	MeOH	2.653(5) Å, 2.779(5) Å	45
$\beta$ -form (Type II)	R3	$a = 16.650(1)$ , $c = 5.453(1)$ Å, $Z = 9$ (hpsl)	HCl	2.61 (1) Å, 2.77 (1) Å <sup>b</sup>	47
$\beta$ -form (Type II)	R3	$a = 15.946(2)$ , $c = 6.348(2)$ , $Z = 9$ (host)	CH <sub>3</sub> CN	2.779 (6) Å, 2.800 (6) Å	43
$\beta$ -form (Type III)	P3	$a = 16.003(2)$ , $c = 6.245(2)$ , $Z = 9$ (host)	CH <sub>3</sub> CN	2.778 Å <sup>c</sup> (mean)	43
$\alpha$ -form	R $\bar{3}$	$a = 38.46(2)$ , $c = 5.650(3)$ Å, $Z = 54$	None	2.677 (3) Å <sub>d</sub>	49
$\alpha$ -form	R $\bar{3}$	$a = 38.529$ , $c = 5.66$ Å, $Z = 54$ (host)	SO <sub>2</sub>		50
$\gamma$ -form	P2 <sub>1</sub> /c	$a = 8.07$ , $b = 5.20$ , $c = 13.20$ Å, $\beta = 107^\circ$ , $Z = 4$		<sup>e</sup>	52

<sup>a</sup> For R $\bar{3}$  and R3, the values of  $a$  and  $c$  given are referred to a hexagonal unit cell ( $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ ).<sup>b</sup> X-ray values.<sup>c</sup> Individual values for the three independent [OH]<sub>6</sub> rings are 2.792, 2.788, 2.785, 2.782, 2.745, 2.773 Å (e.s.d. 0.006 Å in each case).<sup>d</sup> Not available.<sup>e</sup> No hexamers present in structure, see Fig. 6(b).

the same general formula  $3\text{C}_6\text{H}_4(\text{OH})_2 \cdot x\text{G}$ , where G represents the encaged guest molecule and  $x$  is a site occupancy factor between zero and one. Table 1 gives representative crystal data, mainly selected from recent sources, for  $\beta$ -hydroquinone, as well as for the  $\alpha$ - and  $\gamma$ -modifications. (The crystal structures of the  $\alpha$ - and  $\gamma$ -forms are discussed below.) As indicated in Table 1, the unsolvated  $\beta$ -form and the corresponding  $\text{H}_2\text{S}$  clathrate correspond to the Type I situation for 1, and in such cases cavities having  $\bar{3}$  ( $\text{C}_{3i}$ ) symmetry are present. Figure 1a shows a stereoview of such a centrosymmetric cage of the unsolvated form. As can be seen the top and bottom of the void are formed by hexagons of hydrogen-bonded oxygen atoms; an ordered arrangement of hydrogen atoms is apparent in the  $[\text{OH}]_6$  rings and host molecules point alternately above and below the mean plane of the (nearly planar) six oxygen atoms. The hexameric units forming the ceiling and floor of a given cage, as may be seen from Fig. 1b, belong to two identical, but displaced, three-dimensional interlocking networks first defined for the "empty" form by Powell and Riesz.<sup>38</sup> The remarkably low packing coefficient,<sup>39</sup> 0.62 (or 0.59 excluding the hydrogen atoms involved in hydrogen bonding<sup>37</sup>) may be compared with the normal range, 0.65–0.77, for most organic molecular crystals, and demonstrates the realization of an "open" structure with unfilled cavities stabilized by an extended system of



**Fig. 1.** Stereoviews illustrating (a) the construction of a single cage in the unsolvated form of  $\beta$ -hydroquinone and (b) more extended portions of the two identical, but displaced, three-dimensional networks from which cages are constructed. (Both drawn from data of ref. 37.)

hydrogen bonds. In recent X-ray work on the  $\text{H}_2\text{S}$  clathrate, undertaken to define accurately a Type I clathrate, Mak and coworkers<sup>40,41</sup> have found that the  $\text{H}_2\text{S}$  guest molecule, situated in an approximately spherical cavity of mean free diameter *c.* 4.8 Å, undergoes pronounced thermal motion, particularly in the direction of the centres of the  $[\text{OH}]_6$  rings, that is, along the *c*-axis of the crystal. In this centrosymmetric clathrate<sup>42</sup> the results are consistent with rotational disorder of the guest molecule.

In Type II clathrates, such as those formed by 1 with  $\text{SO}_2$ , MeOH, HCl, or  $\text{CH}_3\text{NC}$ , a lowering of space group symmetry from  $R\bar{3}$  to  $R3$  is found, and guest accommodation is provided in cages which are still trigonal, though no longer centrosymmetric. For the relatively long guest molecule methyl isocyanide the cage length, corresponding to the *c*-spacing (Table 1), is markedly increased compared with the Type I systems already discussed (see below). Figure 2 illustrates the alignment of the  $\text{CH}_3\text{NC}$  along the

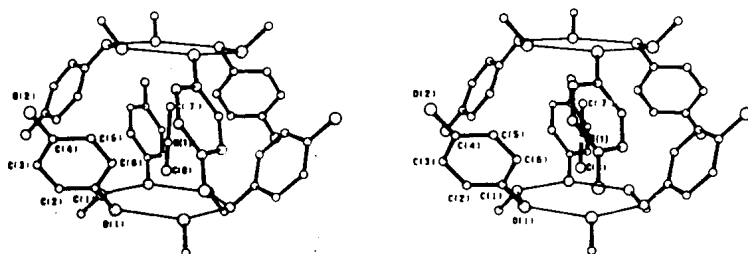


Fig. 2. A stereo-drawing showing a  $\text{CH}_3\text{NC}$  guest molecule trapped inside a cage in the structure of hydroquinone (1). For clarity all hydrogen atoms have been omitted. (Reproduced, by permission, from ref. 43.)

*c*-axis in its Type II clathrate.<sup>43</sup> Interesting new information has recently become available on the Type II MeOH clathrate, a system previously studied by Palin and Powell<sup>44</sup> using two-dimensional X-ray data. Mak,<sup>45</sup> employing diffractometer data, has found that the encaged MeOH molecule is located in three preferred orientations related by three-fold rotation about the *c*-axis, one such orientation being shown in Fig. 3. In each orientation, the C—O bond is tilted by  $35^\circ$  from *c* to facilitate interaction of the hydroxyl group with three phenolic oxygen atoms of the adjacent  $[\text{OH}]_6$  ring. The inclination of  $35^\circ$  found above is in excellent agreement with the values of  $32^\circ$  below 100 K and  $40^\circ$  at 300 K deduced from recent dielectric studies.<sup>46</sup> In the MeOH clathrate, host-guest interaction is reflected in unequal  $\text{OH}\cdots\text{O}$  hydrogen bonds in the  $[\text{OH}]_6$  ring (Table 1); and, interestingly, this feature, a marked hydrogen bond length alternation, has also been found by Boeyens and Pretorius<sup>42</sup> in an X-ray and neutron diffraction study of the HCl clathrate



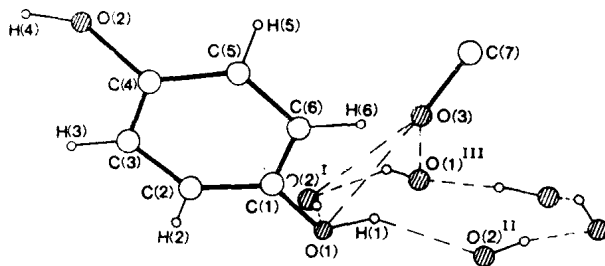


Fig. 3. Host-guest interactions in the methanol clathrate of hydroquinone (1). The O(3)-C(7) bond of the CH<sub>3</sub>OH guest molecule is inclined at an angle of 35° to the c-axis of the crystal. (Reproduced, by permission, from ref. 45.)

of 1. In this latter study the lowering of symmetry to R3 has been attributed to a large number of weak OH...Cl-H...OH interactions which orient the HCl molecule in its cage, the location of the guest being described as lying preferentially on the surface of a cone, with its generator inclined by 33° to *c* and its apex at the Cl position. The reasonable conclusion has been reached<sup>45</sup> that formation of Type II  $\beta$ -hydroquinone clathrates is favoured by guest molecules of appropriate sizes which can interact appreciably with specific sites in the walls of a clathration cavity. Very recent work<sup>31b</sup> has established that the SO<sub>2</sub> clathrate is also of Type II, and a weak interaction has been observed between the SO<sub>2</sub> molecule, through one of its oxygen atoms, and the [OH]<sub>6</sub> ring of the hydroquinone framework. In the acetonitrile clathrate of 1, the only authenticated Type III system, a further lowering of symmetry from the rhombohedral lattice (R3) of Type II leads to a trigonal lattice, space group P3. There are now three distinct types of trigonal clathrate cavity and all these have the shape of prolate spheroids.<sup>36,43</sup> The three symmetry-independent acetonitrile molecules fit snugly inside these cavities, with, as previously suggested,<sup>33</sup> one guest molecule aligned in the opposite sense to the other two, see Fig. 4. Figure 5 shows electron density sections through the guest molecules; although molecule *c*, in the opposite orientation from molecules *a* and *b*, appears to be displaced from its "idealized" position along the *z*-axis, the disposition of this molecule with respect to the top [OH]<sub>6</sub> ring of its cage is virtually the same as that of the other molecules with respect to their bottom rings.<sup>43</sup> In the markedly unstable CH<sub>3</sub>CN and CH<sub>3</sub>NC clathrates, which rapidly lose the guest in air,<sup>43</sup> the mean O...O hydrogen bond lengths, 2.778 Å and 2.790 Å respectively, are significantly longer than the corresponding distances of 2.696 Å, 2.69 Å, and 2.716 Å found in the relatively stable<sup>48</sup> H<sub>2</sub>S, HCl and MeOH  $\beta$ -hydroquinone clathrates. (There are problems in assigning an e.s.d. to the mean of quantities which are known to be unequal, Table 1.) It is intriguing