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Structure of the Spherand* 6,12,18,24,30,36-Hexamethoxy-3,9,15,21,27,33-hexamethyl[0.$_6$]metacyclophane, $C_{48}H_{48}O_6$, and of Three Related Spherands and Spherand Complexes: $C_{48}H_{48}O_6.LiCl$, $C_{48}H_{48}O_6.NaSO_4CH_3.C_6H_5CH_3$ and $C_{42}H_{30}F_6.2CH_2Cl_2$

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Abstract

(I): $C_{48}H_{48}O_6$, $M_r = 720{\cdot}9$, rhombohedral, $R\overline{3}$, $a = 11{\cdot}697\,(3)$ Å, $\alpha = 114{\cdot}25\,(2)^\circ$, $V = 954\,(2)$ Å^3, $Z = 1$, $D_m = 1{\cdot}267\,(5)$, $D_x = 1{\cdot}255$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}54184$ Å, $\mu = 5{\cdot}7$ cm^{-1}, $F(000) = 384$, $T = 295$ K, $R = 0{\cdot}063$ for 1200 unique reflections with $I > \sigma(I)$. (II): $C_{48}H_{48}O_6.LiCl$, $M_r = 763{\cdot}3$, rhombohedral, $R\overline{3}$, $a = 11{\cdot}152\,(1)$ Å, $\alpha = 110{\cdot}60\,(1)^\circ$, $V = 1020{\cdot}5\,(5)$ Å^3, $Z = 1$, $D_m = 1{\cdot}235\,(5)$, $D_x = 1{\cdot}242$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}54184$ Å, $\mu = 11{\cdot}3$ cm^{-1}, $F(000) = 404$, $T = 295$ K, $R = 0{\cdot}050$ for 1150 unique reflections with $I > \sigma(I)$. (III): $C_{48}H_{48}O_6.NaSO_4CH_3.C_7H_8$, $M_r = 947{\cdot}1$, monoclinic, $P2/c$, $a = 11{\cdot}572\,(5)$, $b = 10{\cdot}467\,(5)$, $c = 22{\cdot}072\,(7)$ Å, $\beta = 108{\cdot}97\,(3)^\circ$, $V = 2528\,(4)$ Å^3, $Z = 2$, $D_m = 1{\cdot}227\,(5)$, $D_x =$

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* Nomenclature according to Vögtle & Neumann (1969, 1970). The three related compounds are: 6,12,18,24,30,36-hexamethoxy-3,9,15,21,27,33-hexamethyl[0.$_6$]metacyclophane–lithium chloride (1/1), $C_{48}H_{48}O_6.LiCl$; 6,12,18,24,30,36-hexamethoxy-3,9,15,21,27,33-hexamethyl[0.$_6$]metacyclophane–sodium methyl sulfate–toluene (1/1/1), $C_{48}H_{48}O_6.NaSO_4CH_3.C_7H_8$; 6,12,18,24,30,36-hexafluoro-3,9,15,21,27,33-hexamethyl[0.$_6$]metacyclophane–methylene chloride (1/2), $C_{42}H_{30}F_6.2CH_2Cl_2$.

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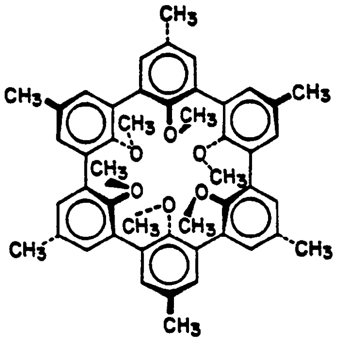
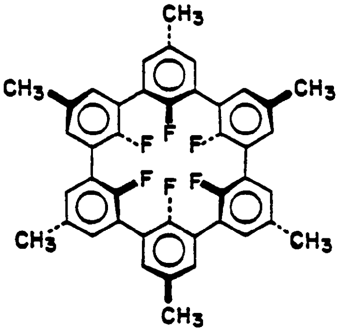
1·244 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 1·01 cm^{-1}, F(000) = 1004, T = 295 K, R = 0·103 for 2903 reflections with $F > 3\sigma(F)$. (IV): $C_{42}H_{30}F_6.2CH_2Cl_2$, M_r = 818·6, cubic, $Pa\bar{3}$, a = 15·621 (4) Å, V = 3812 (3) Å^3, Z = 4, D_x = 1·426 g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ = 3·2 cm^{-1}, F(000) = 1680, T = 295 K, R = 0·097 for 887 reflections with $F > 3\sigma(F)$. The structures of these novel hosts and host–guest complexes were determined by direct methods from diffractometer data and were refined by least squares. The methyl sulfate counterion in (III) and the solvent in (III) and in (IV) are disordered. Compound (I) is the prototype spherand, a macrocycle in which six 4-methylanisole units are joined in the 2- and 6-positions. The rings are tipped alternately up and down about 30° from the median plane of the molecule. The methoxy groups are in the center of the macrocycle, with their methyl groups directed alternately up and down relative to the median plane. Compound (I) is the strongest known binder of Li^+ and Na^+, and binds only these two ions. Compounds (II) and (III) are the lithium chloride and sodium methyl sulfate complexes of (I); (IV) is the analog of (I) in which the six methoxy groups have been replaced by F atoms. The uncomplexed hosts of (I) and (IV) and the host moieties in (II) and (III) are very similar structurally and have little conformational flexibility; there is essentially no reorganization of (I) upon complexation, quite in contrast to typical crown ethers and cryptands. The O atoms in the center of the molecule are arranged octahedrally; the cavity defined by them has a diameter between about 1·4 and 1·8 Å, scarcely large enough for a sodium ion. The aromatic rings and their attached atoms in these four molecules are deformed significantly from coplanarity, in a fashion consistent with the intramolecular overcrowding. (IV) is the flattest of these molecules, because the F atoms in the central cavity are effectively smaller than oxygen and have no attached methyl groups. The *overall* librational motion of the host molecules is small in each of these room-temperature structures. Although there is evidence of significant wagging of the methyl groups, and torsional motion about the C_{arom}—O bonds in (I), (II) and (III), the skeleton of linked aromatic rings in each of these four molecules is quite rigid, uncommonly so for such large molecules.

Introduction

Spherands are synthetic hosts designed to undergo at most minimal conformational reorganization upon complexation (Cram, Kaneda, Helgeson & Lein, 1979; Cram, Kaneda, Helgeson, Brown, Knobler, Maverick & Trueblood, 1985). A structural formula is given (see scheme below) for the host (I) and the host of (IV); (II) and (III) are the Li^+ and Na^+ complexes of (I). Systematic names are extremely complex, so we have used instead the nomenclature suggested by Vögtle & Neumann (1969, 1970). The present structural studies establish that indeed for the prototype spherand (I), a cyclic hexamer of a 2,6-disubstituted 4-methylanisole unit, there is essentially no reorganization upon complexation.



(I)



Host of (IV)

Some of the present results have been reported in preliminary form (Trueblood, Knobler, Maverick, Helgeson, Brown & Cram, 1981; Cram & Trueblood, 1981; Cram, Brown, Taguchi, Feigel, Maverick & Trueblood, 1984; Cram *et al.*, 1985).

Experimental

Most of the relevant experimental information is summarized in the *Abstract* or in Table 1. All crystals were grown by slow evaporation from the indicated solvents.*

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* A cubic crystalline modification of (II), which we denote (II*a*), was also found, with a = 21·981 Å at 115 K, $Pn\bar{3}n$, Z = 8, V = 10620 Å^3, D_m = 1·051 (3) g cm^{-3} at 296 K, D_x = 0·955 g cm^{-3} at 115 K for M_r = 763·3 (the formula weight of the complex, excluding any solvent). Small cubic crystals were obtained from methanol–water. Intensity data were collected with Cu $K\alpha$ radiation at 115 K and although the host was readily found and quite plausibly refined (in a position with $\bar{3}$ symmetry), there was disordered solvent or some other complication present, and when we found the form of (II) reported in the *Abstract*, we did not study the structure of this cubic form further.

Table 1. *Crystal, data-collection and refinement information*

All measured densities (see *Abstract*) were determined by flotation; all diffractometer measurements were made on a Syntex $P\bar{1}$ with graphite-monochromatized radiation, Cu $K\alpha$ for (I) and (II), and Mo $K\alpha$ for (III) and (IV); all lattice parameters were determined by least-squares fit of 15 centered reflections in the indicated ranges of 2θ; the maximum average deviation of a standard reflection during data collection for any structure was less than 2%, and for most it was well under 1%.

	(I)	(II)	(III)	(IV)
Solvent[a]	MC–T	MC–T	MC–T	THF–MC
Crystal dimensions (mm)	0·15 × 0·33 × 0·42	0·10 × 0·10 × 0·50	0·30 × 0·19 × 0·50	0·35 × 0·40 × 0·50
2θ range (°) (for lattice parameters)	74–84	75–100	22–26	30–36
Maximum $\sin\theta/\lambda$ (Å^{-1})	0·634	0·634	0·595	0·595
Range of h	0 to 13	−13 to 13	0 to 13	0 to 18
k	−14 to 11	−13 to 11	0 to 12	0 to 18
l	−12 to 11	−12 to 14	−24 to 24	0 to 18
Scan rate (° 2θ min^{-1})	2·0	2·0	2·0	12·0
Background scan	Yes	Yes	Yes	No
Systematic absences	None	None	$h0l$, $l = 2n + 1$	$0kl$, $k = 2n + 1$
No. of measured reflections	1810	1813	5340	3808
No. of unique reflections	1295	1238	4500	1135
Unobserved $< n\sigma(F)$; $n =$	2	2	3	3
No. of unobserved reflections	95	88	1597	248
No. of reflections in least-squares fit	1200	1150	2903	887
No. of parameters refined	96	100	302	94
R	0·063	0·050	0·103	0·097
wR	0·086	0·073	0·117	0·074
Goodness of fit, S	3·05	2·46	3·21	2·36
Maximum/minimum peaks in final difference map (e Å^{-3})	0·30	0·26	0·78[b]	0·46
	−0·22	−0·28	−0·57	−0·47

Notes: (*a*) MC, methylene chloride; T, toluene; THF, tetrahydrofuran. (*b*) The peaks for (III) were in the region of the counterion, indicating deficiencies in the model for the disorder. We used a scattering curve for Na^+, with neutral scattering factors for all other atoms, so one electron was unaccounted for in the model for (III).

Difference maps were used to locate initially all H atoms of each structure, except for some of those on the solvent molecules of (III) and (IV), which were partially disordered.

The structures of (I), (II) and (III) were solved with *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); (IV) was solved with *SHELX76* (Sheldrick, 1976). Some initial refinement was carried out with local programs, but all final refinements were with *SHELX76*. In the final refinements, all H atoms were restrained to be about 1·08 Å from the attached C, and methyl groups were refined as rigid groups (H—C—H angles fixed at 109·5°; no restraints on C—C—H angles). The isotropic $\langle u^2\rangle$ values for the H atoms of (I), (II) and (in part) (IV) were allowed to refine; those for (III) and (in part) (IV) were fixed at the values shown in Tables 2(*c*) and 2(*d*). The identification and location of the counterion in (III), $CH_3OSO_3^-$, and the toluene solvent in the same structure, were difficult. Since the Na^+ ion lies at a center of symmetry, there are only two Na^+ and thus only two counterions in the unit cell. Similarly, both density information and consideration of space available indicate that only two toluene molecules are present in the cell. Neither the counterion nor the solvent can have a center of symmetry; the counterion cannot have a twofold axis. Consequently, the solvent and counterion must either be disordered or not follow the full symmetry of the space group.

The space-group absences (Table 1) were quite unequivocal for the presence of the *c* glide. We therefore considered the possibility that the space group might be *Pc* instead of *P*2/*c*, which has the same Laue group, although intensity statistics supported *P*2/*c*. (Indeed, the counterion and solvent positions were developed from initial coordinates found in difference maps in *Pc*.) It seemed plausible that the toluene and the methyl sulfate ion might obey only the symmetry operations of *Pc*, with the centrosymmetric spherand and Na^+ dominating the intensity statistics. When a model with that assumption was tried, peaks of 0·5–0·8 e Å^{-3} remained, and no great advantage in the refinement was observed. We finally settled on a model in *P*2/*c* in which the counterion is disordered about a twofold axis of the structure, and the toluene disordered about a center of symmetry, each having occupancy 0·5. The toluene was refined as a rigid group, and the methyl sulfate positions were restrained to have nearly the same distances and angles as similar species in the literature [for example: 3-methylcytidine methyl sulfate monohydrate; Shefter, Singh, Brennan & Sackman (1974)]. There were, however, some undesirably close contacts between counterion and solvent moieties. We used packing-energy calculations with Gavezzotti's (1983) program *OPEC* to study these interactions. If only a single counterion position is chosen, the two possible solvent positions differ by about 40 kJ mol^{-1} in intermolecular energy. A rotation of the methyl group in the counterion by about 25° around the attached O—S bond eliminates most short intermolecular contacts (shortest C···H distances remaining are C33···H22*A*,

Table 2. *Positional and displacement parameters*

Displacement parameters are commonly called vibration or thermal parameters. Units of $\langle u^2\rangle$ are Å^2. Units of each e.s.d., in parentheses, are those of the least significant digit of the corresponding parameter.

(*a*) Prototype spherand, $C_{48}H_{48}O_6$ (I)

	x	*y*	*z*	$\langle u^2\rangle$
C1	0·2782 (3)	0·4976 (3)	0·6611 (3)	0·044
C2	0·1474 (3)	0·3968 (3)	0·6481 (3)	0·045
C3	0·1385 (3)	0·2881 (3)	0·6746 (3)	0·045
C4	0·0049 (3)	0·1901 (3)	0·6740 (3)	0·056
C5	0·2575 (3)	0·2733 (3)	0·7018 (3)	0·046
C6	0·3885 (3)	0·3698 (3)	0·7122 (3)	0·045
C7	0·4042 (3)	0·4903 (3)	0·7036 (3)	0·047
O8	0·5445 (2)	0·6052 (2)	0·7361 (3)	0·061
C9	0·7115 (4)	0·7250 (4)	0·9088 (4)	0·079
H2[iv]	0·050	0·403	0·617	0·04 (1)[i]
H4*A*	−0·086	0·202	0·629	0·14 (2)[i]
H4*B*	0·084	0·264	0·811	0·19 (2)[i]
H4*C*	−0·066	0·054	0·601	0·18 (2)[i]
H5	0·248	0·184	0·715	0·06 (1)[i]
H9*A*	0·811	0·832	0·938	0·14 (2)[i]
H9*B*	0·739	0·646	0·904	0·18 (2)[i]
H9*C*	0·711	0·776	1·010	0·27 (3)[i]

(*b*) LiCl complex of the prototype spherand, $C_{48}H_{48}O_6.LiCl$ (II)

	x	*y*	*z*	$\langle u^2\rangle$
Cl	0·0000	0·0000	0·0000	0·056
Li	0·5000	0·5000	0·5000	0·034
C1	0·7153 (2)	0·4151 (2)	0·3227 (2)	0·032
C2	0·7169 (3)	0·2995 (2)	0·2220 (2)	0·037
C3	0·7118 (3)	0·1799 (3)	0·2392 (3)	0·038
C4	0·7104 (4)	0·0543 (3)	0·1258 (3)	0·055
C5	0·7010 (3)	0·1764 (2)	0·3589 (3)	0·038
C6	0·6990 (2)	0·2903 (2)	0·4619 (2)	0·031
C7	0·7110 (2)	0·4112 (2)	0·4448 (2)	0·029
O8	0·7154 (2)	0·5289 (2)	0·5499 (3)	0·032
C9	0·8684 (3)	0·6544 (3)	0·6681 (3)	0·062
H2[iv]	0·724	0·303	0·129	0·05 (1)[i]
H4*A*	0·688	−0·040	0·141	0·15 (2)[i]
H4*B*	0·821	0·103	0·140	0·15 (2)[i]
H4*C*	0·624	0·014	0·012	0·18 (2)[i]
H5	0·695	0·084	0·372	0·06 (1)[i]
H9*A*	0·863	0·741	0·746	0·08 (1)[i]
H9*B*	0·928	0·702	0·622	0·21 (2)[i]
H9*C*	0·928	0·616	0·728	0·21 (3)[i]

(*c*) $C_{48}H_{48}O_6.NaCH_3SO_4.CH_3C_6H_5$ (III)

S28–C33, H33*A*–H33*C* and H40*A*–H40*C* are in positions adjusted to give reasonable packing energy; see text.

	x	*y*	*z*	$\langle u^2\rangle$
Na	0·0000	0·0000	0·5000	0·048
C1	0·2623 (5)	0·1594 (6)	0·4631 (3)	0·055
C2	0·3159 (5)	0·1680 (6)	0·4149 (3)	0·059
C3	0·2506 (6)	0·2164 (7)	0·3559 (3)	0·064
C4	0·3092 (6)	0·2290 (9)	0·3037 (3)	0·093
C5	0·1280 (6)	0·2486 (7)	0·3426 (3)	0·064
C6	0·0715 (5)	0·2391 (6)	0·3890 (3)	0·055
C7	0·1409 (6)	0·1986 (6)	0·4491 (3)	0·052
O8	0·0887 (4)	0·1930 (4)	0·4979 (2)	0·056
C9	0·0898 (9)	0·3113 (8)	0·5299 (4)	0·100
C10	−0·0639 (6)	0·2617 (7)	0·3742 (3)	0·054
C11	−0·1205 (6)	0·3777 (6)	0·3552 (3)	0·059
C12	−0·2438 (6)	0·3949 (6)	0·3455 (3)	0·057
C13	−0·3053 (7)	0·5212 (7)	0·3206 (4)	0·080
C14	−0·3103 (6)	0·2923 (7)	0·3580 (3)	0·054
C15	−0·2580 (5)	0·1744 (7)	0·3772 (3)	0·052
C16	−0·1358 (5)	0·1589 (6)	0·3812 (3)	0·046
O17	−0·0841 (3)	0·0376 (4)	0·3945 (2)	0·053
C18	−0·0957 (7)	−0·0361 (8)	0·3380 (3)	0·089
C19	−0·3236 (5)	0·0645 (6)	0·3945 (3)	0·045
C20	−0·4230 (6)	0·0060 (7)	0·3509 (3)	0·062
C21	−0·4778 (6)	−0·1005 (7)	0·3674 (3)	0·067
C22	−0·5891 (7)	−0·1625 (9)	0·3187 (3)	0·105
C23	−0·4275 (6)	−0·1534 (7)	0·4278 (3)	0·066
C24	−0·3264 (5)	−0·0986 (6)	0·4726 (3)	0·050
C25	−0·2805 (5)	0·0137 (6)	0·4557 (3)	0·051
O26	−0·1839 (3)	0·0743 (4)	0·5015 (2)	0·053
C27	−0·2211 (8)	0·1556 (8)	0·5428 (4)	0·101
S28[ii]	0·0289 (9)	0·6662 (7)	0·2719 (4)	0·197
O30[ii]	−0·0146 (14)	0·6625 (11)	0·3259 (6)	0·183
O31[ii]	0·1030 (15)	0·7775 (13)	0·2714 (7)	0·282
O29[ii]	−0·089 (1)	0·686 (2)	0·212 (1)	0·26 (2)[i]
O32[ii]	0·081 (2)	0·548 (1)	0·260 (1)	0·28 (1)[i]
C33[ii]	−0·194 (1)	0·609 (2)	0·208 (1)	0·18 (1)[i]
C34[iii]	0·424 (1)	0·508 (2)	0·478 (1)	0·17 (1)[i]
C35	0·519	0·493	0·453	0·11 (1)[i]
C36	0·639	0·480	0·493	0·10 (1)[i]
C37	0·664	0·481	0·560	0·22 (2)[i]
C38	0·569	0·496	0·585	0·14 (1)[i]
C39	0·449	0·510	0·544	0·23 (2)[i]
C40	0·297	0·525	0·435	0·36 (3)[i]
H2[iv]	0·409	0·137	0·424	0·07[v]
H4*A*	0·406	0·207	0·321	0·10
H4*B*	0·296	0·328	0·290	0·10
H4*C*	0·265	0·170	0·263	0·10
H5	0·076	0·282	0·295	0·07
H9*A*	0·054	0·298	0·569	0·10
H9*B*	0·044	0·391	0·501	0·10
H9*C*	0·187	0·330	0·549	0·10
H11	−0·067	0·457	0·348	0·07
H13*A*	−0·401	0·516	0·316	0·10
H13*B*	−0·295	0·538	0·274	0·10
H13*C*	−0·264	0·598	0·353	0·10
H14	−0·405	0·306	0·353	0·07
H18*A*	−0·051	−0·128	0·349	0·10
H18*B*	−0·056	0·018	0·308	0·10
H18*C*	−0·192	−0·050	0·313	0·10
H20	−0·459	0·044	0·303	0·07
H22*A*	−0·622	−0·248	0·335	0·10
H22*B*	−0·577	−0·181	0·273	0·10
H22*C*	−0·655	−0·087	0·314	0·10
H23	−0·468	−0·238	0·440	0·07
H27*A*	−0·150	0·207	0·578	0·10
H27*B*	−0·274	0·101	0·566	0·10
H27*C*	−0·280	0·222	0·510	0·10
H33*A*	−0·267	0·631	0·165	0·20
H33*B*	−0·222	0·628	0·249	0·20
H33*C*	−0·170	0·509	0·208	0·20
H35	0·500	0·492	0·401	0·20
H36	0·712	0·468	0·474	0·20
H37	0·757	0·471	0·591	0·20
H38	0·589	0·497	0·636	0·20
H39	0·376	0·521	0·564	0·20
H40*A*	0·286	0·620	0·415	0·31
H40*B*	0·278	0·456	0·397	0·31
H40*C*	0·235	0·512	0·462	0·31

(*d*) $C_{42}H_{30}F_6.2CH_2Cl_2$ (IV)

	x	*y*	*z*	$\langle u^2\rangle$
C1	0·2989 (3)	0·1163 (3)	0·4295 (3)	0·037
C2	0·2189 (3)	0·1498 (3)	0·4486 (3)	0·040
C3	0·2056 (3)	0·2028 (3)	0·5195 (3)	0·040
C4	0·1187 (3)	0·2424 (3)	0·5357 (3)	0·056
C5	0·2735 (3)	0·2169 (3)	0·5751 (3)	0·039
C6	0·3557 (3)	0·1850 (2)	0·5585 (3)	0·036
C7	0·3662 (3)	0·1394 (3)	0·4841 (3)	0·039
F8	0·4468 (1)	0·1163 (2)	0·4605 (1)	0·047
Cl1[ii]	0·4348 (2)	0·4348 (2)	0·4348 (2)	0·191
Cl2[ii]	0·3580 (6)	0·3100 (16)	0·3244 (21)	0·166
C9[ii]	0·337 (1)	0·388 (1)	0·404 (1)	0·11 (1)[i]
H2[iv]	0·165	0·135	0·408	0·05
H41	0·113	0·290	0·585	0·10
H42	*0·084*	*0·185*	0·554	*0·10*
H43	0·092	0·267	0·477	0·10
H5	0·263	0·253	0·633	0·04
H91	0·306	0·359	0·459	0·10
H92	0·295	0·436	0·377	0·10

Notes: (i) Atom refined isotropically. Other isotropic values are $[1/(8\pi^2)]$ times the 'equivalent *B* value' for an anisotropic atom, as defined by Hamilton (1959). (ii) Distances and angles restrained. (iii) Pivot atom in rigid group; other atoms in group (toluene) follow. (iv) H atoms were refined as parts of rigid groups or riding on the attached aromatic C atom. (v) For H, $\langle u^2\rangle$ was not refined.

in the host, 2·5 Å, and C33···H37, in toluene, 2·6 Å). Thus we believe that the model is reasonable but that the distribution of solvent and counterion in the crystal is not random. The nominal e.s.d.'s of the atomic positions in the counterion and the solvent (Table 2*c*) should not be taken as a measure of the uncertainty in these positions; on the other hand, we are confident that those of the host in (III) are meaningful.

Similarly, although the host in (IV) refined well, the solvent in the structure was difficult to model. The crystal was grown from a mixture of CH_2Cl_2 and THF (C_4H_8O). Two peaks of distinctly different magnitude appeared along the threefold axis in early difference maps. The observed density agreed with the presence of a disordered CH_2Cl_2 molecule rather than with THF, and our final model has such a disordered CH_2Cl_2, with one Cl (Cl1 in Table 2*d*) along an extension of the threefold axis of the host molecule. The C atom (C9 in Table 2*d*), the other Cl (Cl2 in Table 2*d*), and the two H atoms of the CH_2Cl_2 molecule have occupancy $\frac{1}{3}$, corresponding to the overall stoichiometry of one host for every two CH_2Cl_2 molecules. The packing-energy program *OPEC* was used with this structure as well, to confirm that the position for the solvent was reasonable and to choose between the present model and one in which both Cl atoms lie on the threefold axis.

All calculations were carried out on an IBM 3090, DEC VAX 11/750, 11/780 or 3100 computers, with the *UCLA Crystallographic Package* (1984), which includes locally edited versions of *CARESS*, *PROFILE* and *ORTEP* (Johnson, 1965), and with *PLUTO*78 (Motherwell & Clegg, 1978), a local molecular-geometry program, and *THMA*11 (Trueblood, 1978; Dunitz, Schomaker & Trueblood, 1988). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) and Cromer & Mann (1968).

The final positional parameters and isotropic temperature factors (equivalent values for atoms refined anisotropically) are given in Tables 2(*a*–*d*).*

Results and discussion

Most of the interatomic distances, bond angles and torsion angles in these molecules (included in the supplementary material) fall within the normal ranges.† Some features of the geometries of the different molecules are compared in Table 3. The numbering scheme is shown in Fig. 1. The considerable strain in the spherand hosts is manifested especially in the distortions from coplanarity of the individual aromatic rings and their immediately attached atoms, and the folding of these rings about the $CH_3—C_{Ar}\cdots C_{Ar}—O$ (or —F) axis. That this strain is chiefly a consequence of the crowding of the OCH_3 groups or F atoms in the central cavity becomes apparent on comparison with hexametaphenylene (HMP) (Irngartinger, Leiserowitz & Schmidt, 1970), where the distortion is minimal. What little there is results principally from the fact that the rings are tipped alternately up and down about 19°, to minimize H···H contacts in the central cavity. This is a smaller cant than in any of the present molecules. Some data for HMP are included in Table 3 for convenience, and a comparison of van der Waals models of HMP and the most non-planar of the spherand hosts [that in (III)] is shown in Fig. 2.

If molecular distortion is measured by the folding of the aromatic rings, the r.m.s. deviations of the ring atoms from their best plane, or the deviation of the O (or F) atoms from that plane, the most distorted of the present molecules are the two uncomplexed hosts, (I) and (IV). It is not surprising that the highly electronegative O and F atoms should repel one another strongly when forced together as they are in these molecules; in (II) and (III), the strong attractive fields of the Li^+ and Na^+ ions offset much of this repulsion, reducing the strain. It is interesting that (IV) shows absolutely no complexing ability for Li^+ and Na^+, despite the fact that the electron pairs of the highly electronegative F atoms should be ideally disposed for such complexing (Cram *et al.*, 1984). The F···F distance across the cavity in the center of (IV) is 4·18 Å; with a van der

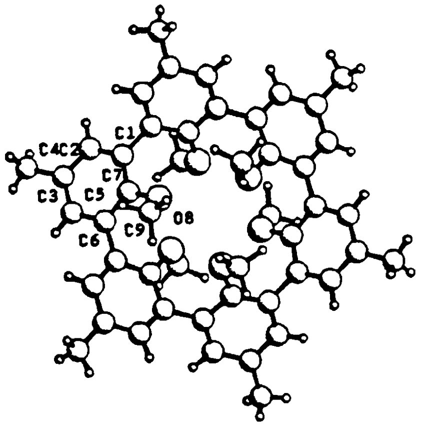

Fig. 1. Numbering scheme for the present hosts, illustrated for the asymmetric unit of the host of (I) and (II). It is similar for (IV), in which O8 and C9 have been replaced by F8. In (III), the asymmetric unit is half a molecule; the numbering for chemically equivalent atoms continues in adjacent rings, by adding 9 or 18 to the numbers shown here.

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* Lists of structure factors and anisotropic displacement parameters, as well as bond distances, bond angles and torsion angles for each structure, and matrices of differences of mean-square displacement amplitudes for pairs of atoms in the different crystals have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53705 (54 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† For distances see Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987). For some information about the geometry of and deformations in *para*-substituted anisoles see Di Rienzo, Domenicano, Portalone & Vaciago (1976).

Table 3. *Comparison of some features of the molecular geometry of* (I)–(IV) *and of a related molecule*

HMP is hexametaphenylene, $C_{36}H_{24}$ (Irngartinger *et al.*, 1970), the hydrocarbon consisting of six C_6H_4 rings linked in the *meta* positions. It is thus the unsubstituted skeleton of the four spherand hosts studied here. Average values are given for (III) and HMP, for which the asymmetric unit consists of a half molecule. For (I), (II) and (IV), the asymmetric unit is one sixth of the molecule. R.m.s. deviations of individual values are given in square brackets when averages were taken, in units of the least significant digit.

	(I)	(II)	(III)	(IV)	HMP
Interplanar angle (°) between adjacent rings^a	52	56	60 [1]	44	33 [4]
Angle (°) between aromatic ring planes and median molecular plane^b	30	33	35 [2]	26	19 [5]
Fold angle (°) of aromatic rings about C3—C7 axis	6·2	2·9	4·6 [8]	5·6	0·7 [9]
R.m.s. deviation (Å) of aromatic ring atoms from their best plane^c	0·032	0·014	0·024	0·028	0·006
Deviation (Å) of O (or F) from aromatic ring plane	0·21	0·06	0·11 [4]	0·21	-
Deviation (Å) of attached aromatic C's from ring plane^d	0·17 [6]	0·13 [0]	0·16 [2]	0·07 [3]	0·05 [4]
Bond angle (°), C_{Ar}—O—CH_3	115	112	114 [1]	–	–
Torsion angle (°), C_{Ar}—C_{Ar}—O—CH_3	62	86	88 [4]	-	–
Shortest intramolecular O···O distance (Å)	2·92	2·79	2·99	-	-
Longest intramolecular O···O distance (Å)	4·43	4·28	4·53	-	–
Cation···O distance (Å)	–	2·14	2·27 [1]	-	-
Intramolecular interplanar^e distances (Å)					
Planes of O atoms (*d* in Fig. 5)	2·20	2·06	2·24 [14]	1·85^e	0·91 [4]^e
Planes of CH_3 (*D* in Fig. 5)	4·83	4·84	4·98	-	–

Notes: (*a*) The angle between the normals to the least-squares planes of adjacent aromatic rings. (*b*) This is the angle between the normal to the least-squares plane of the aromatic ring and the molecular axis, defined as the normal to the plane of the six O (or six F) atoms. (*c*) The e.s.d.'s of the atomic distances from the planes vary from 0·002–0·003 Å in HMP, (I) and (II) to 0·005–0·006 Å in (III), so these deviations are (highly) significant in all but HMP. (*d*) The attached C atoms of adjacent rings *always* lie on the opposite side of the plane from the OCH_3 group or F atom, reflecting the fact that the folding of the rings is due primarily to crowding in what would be the central cavity of an unsubstituted molecule. (*e*) See Fig. 5. CH_3 here refers to the methoxymethyl groups. Distance between planes of F in (IV) and of H in HMP.

Waals radius* of about 1·35 Å for F, this leaves (4·18 − 2·70) = 1·48 Å, so there would seem to be just enough room for an Li^+ ion, with an ionic radius† of about 0·76 Å.

Because of the crowding at the center of the hosts in (I), (II) and (III), the methoxy groups are twisted far out of the plane of the attached rings. Normally, even in *o*-dimethoxybenzenes, the carbon of the methoxymethyl is coplanar with the ring, or close to this conformation (Di Rienzo *et al.*, 1976; Anderson, Kollman, Domelsmith & Houk, 1979; Caillet, 1982), and in an acyclic compound related to these spherands, where there is no overcrowding, we found (Trueblood & Maverick, 1986) essentially coplanar conformations. The crowding also results in a small but significant decrease in the C—O—C bond angle from that usual in anisole derivatives (about 118°).

The differences between the arrangements of the O atoms and their attached methyls in the spherand host in (I), (II) and (III) are small but noteworthy. The O atoms are arrayed with $\bar{3}$ symmetry in (I) and (II), and close to $\bar{3}$ symmetry in (III), around the center of the molecule, which is empty in (I) and occupied by a cation in (II) and in (III). As indicated in Table 3, the closest O···O distance shortens by 0·13 Å when the small Li^+, with its strong field, enters the cavity; the Li^+—O distance is 2·138 (2) Å, quite in accord with usual Li^+—O distances. The distance between the centrosymmetrically related O atoms on opposite sides of the cavity also becomes shorter, by 0·15 Å. Li^+ is small enough to fit in the original cavity, and its field contracts that cavity. On the other hand, Na^+, with a radius for sixfold

Fig. 2. Comparison of van der Waals models of hexametaphenylene (HMP) (left), and of the prototype spherand complexed with Na^+ in (III) (right), where the tilt of the rings is almost twice as great as in HMP (Table 3). The lower view of each is along the molecular axis, the upper one at 90° to that. The much greater thickness of the spherand is due both to the tilt of the rings and to the presence of the methyl groups in the *para* positions and in the methoxy groups. The sodium ion in (III) can be seen in the center of the cavity of the host. Because of the inflexibility of this spherand host, this view of (III) looks essentially identical to the similar views of (II) and of (I) (except for the presence of the ion) that have been shown earlier (*e.g.*, Trueblood, 1984).

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* Nyburg & Faerman (1985) discuss the 'polar flattening' of the shapes of bonded halogen and other atoms. They give two contact radii for F, 1·55 and 1·34 Å, for contacts in the equatorial and polar directions respectively, but the precision of these values is low. Pauling's original van der Waals radius for F was 1·35 Å, but this was criticized by Bondi (1964) as being too low if the atom was assumed spherical. The present cross-cavity contacts are chiefly in the 'polar' direction, so we use 1·35 Å.

† This value, very slightly revised by Shannon (1976) from the 0·74 Å given by Shannon & Prewitt (1969), is for coordination number 6 and is based on assuming an ionic radius of 1·40 Å for O, which is also the van der Waals radius we use here. Note that twice (0·74 + 1·40) is 4·28, which is just the distance between opposite O atoms in (I) (Table 3).

Table 4. *Some results of analysis of the anisotropic displacement parameters*

All calculations were made with our program *THMA*11 (Trueblood, 1978; Dunitz *et al.*, 1988). Numbers in parentheses represent e.s.d.'s, given in units of the least significant digit of the corresponding quantity.

	(I)	(II)	(III)	(IV)
(1) R.m.s. libration amplitude (°) of CH_3 about the C_{Ar}—O bond	10·5 (10)	10·9 (4)	13·5 (14) 12·2 (14) 13·0 (15)	-
(2) Mean MSDA ($Å^2$) difference between bonded atoms along bond direction*	0·0009	0·0008	0·0048	0·0022
(3) Mean e.s.d. of U^{ij} ($Å^2$)	0·0013	0·0012	0·0037	0·0023

* See discussion in text. Detailed tables of MSDA differences for each structure are included with the supplementary material.

coordination of 1·02 Å (Shannon, 1976), is too large for the original cavity and expands it somewhat, although not as much as it would a cavity lined with O atoms that were conformationally more mobile. The 'effective radius' of Na^+ in this cavity is only about* 0·87 Å, and the Na^+—O distances, about 2·27 Å (Table 3), are thus distinctly smaller than the usual range near 2·40 Å.

The *overall* librational motion of the host molecules, estimated from the anisotropic atomic displacement parameters (ADPs, 'thermal' parameters) with our program *THMA*11, is very small in each of these room-temperature structures: the *maximum* r.m.s. librational amplitudes are less than 1° in the uncomplexed hosts (I) and (IV), and only 2·1° in (II) and 2·8° in (III). On the other hand, there is evidence of significant torsional oscillation (libration) of the methyl groups about the C_{arom}—O bonds in the three hosts containing OCH_3 groups (Table 4), the r.m.s. librational amplitudes being uniformly in the range 10–13°. Because the overall librational motion is so small, the corrections to most bond distances for such motion are negligible, only a fraction of the e.s.d. of the distance. On the other hand, corrections to the O—CH_3 distances are appreciable, being an order of magnitude larger (0·020 to 0·033 Å). These distances have been corrected in the tables in the supplementary material.

For bonds of the kinds present in these molecules, the difference in mean-square displacement amplitudes (MSDAs) of the bonded atoms along the bond direction should be of the order of 0·0010 $Å^2$ or less (Hirshfeld, 1976) if the data are of good quality. The quality of the ADPs, as estimated from the mean e.s.d. of the U^{ij}, is good for (I) and (II), mediocre for (IV), and poor for (III) (Table 4). The data for (I) and (II) meet the Hirshfeld criterion well (Table 4), and although those for (III) and (IV) do not appear to, they fit about as well as might be expected, given the mean e.s.d. of U^{ij}.

In addition to not undergoing any appreciable overall librational motion in the crystals, these hosts, except for the internal torsion about the O—CH_3 bond in (I), (II) and (III), and a little wagging of the *para*-methyl groups in all four structures, are exceptionally rigid. Indeed, they are the most rigid molecules of their size we have ever encountered. Normally, there is significant relative motion of linked aromatic or aliphatic rings, easily detectable by a generalization of the Hirshfeld bond test (Rosenfield, Trueblood & Dunitz, 1978). These molecules were designed to be conformationally inflexible, as mentioned in the *Introduction*. All the chemical and structural evidence indicates that this objective was achieved, and it is gratifying that the evidence from ADP analysis provides independent confirmation.

Conformational flexibility is normally important in facilitating molecular packing in crystals, particularly for molecules of size comparable to those studied here. The unusual rigidity of these hosts doubtless plays a major role in the fact that they are often hard to crystallize, and that the crystals that do form frequently contain disordered solvent and/or disordered counterions. The form of (I) reported here has no significant intermolecular cavities. The rhombohedral unit cell contains a single molecule, with its axis along [111]; the host is essentially that depicted for (III) in Fig. 2 (without the cation).

Fig. 3 is a packing drawing of the structure of (I), viewed almost along the molecular axis, and Fig. 4 is a similar view of the structure of (II). In crystals of both (I) and (II), the hosts pack in stacks along [111], which is the *c* axis of the related hexagonal cell. The length of this axis is the distance between the centers of host molecules or complexes in these crystals; it is 8·56 Å in (I) and almost 2 Å larger in (II), 10·52 Å. The difference is due primarily to the presence of the Cl^- on this axis in (II), halfway between the Li^+ at the center of each complex. Each Cl^- is surrounded by two sets of six equivalent close-packed methyl groups, three methoxymethyl groups above and three below it, and six *para* methyls projecting in

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* This value was arrived at by taking half of 4·53 Å, the distance between opposite O atoms in (III) (Table 3), and subtracting an O radius of 1·40 Å. This arbitrary procedure assigns all of the contraction to Na^+, which is surely an oversimplification, but then so is the concept of radii itself. The point is that the host is strained in the complex; the O atoms are forced out of coplanarity with the attached ring, and the rings themselves are deformed.

from adjacent stacks. The fact that the Cl^- appears to take up only about 2 Å, when its radius is only slightly smaller than this, implies that it 'nestles' among the six equivalent methoxymethyl groups (the distance between the methyl C atoms within one plane is 4·0 Å; see Fig. 5). Each Cl^- is only 2·6 Å from the corners of a trigonal antiprism formed by six equivalent H9*A* atoms (H9*A* is one of the three H atoms on C9). This distance is certainly imprecise, but we do believe that there are six short Cl···H9*A* contacts. The final position of H9*A*, given in Table 2(*b*), is close to that found in a difference map, and since the C—H distance was constrained to be 1·08 Å, the final position should be close to the true position.

The planes of the methoxymethyl C atoms (Fig. 5) are almost the same distance apart within the hosts in (I) and (II), despite the fact that there is a contraction of the intra-cavity O···O distances in (II), which might be expected to move these planes closer together. The reason they are not closer in (II) is that the torsion angles about the C—O bonds are close to 90° in (II) [as well as in (III)], but only about 62° in (I). This difference compensates for the effect of contraction of the cavity in (II), the methyls moving further from the plane of their attached O atoms as the torsion angle increases. Distances between the planes of these O and C atoms within the different hosts are compared in Table 3.

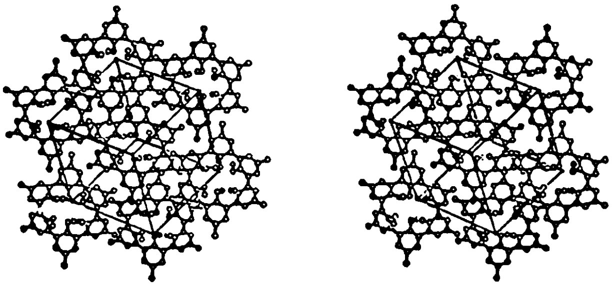

Fig. 3. Stereoview of the packing of (I). The view is nearly down [111], which coincides with the $\bar{3}$ axis of the molecule. Only one molecule in each 'stack' along [111] is shown. Note that each molecule shown lies, in this projection, nearly above or below a corner of the rhombohedral unit cell, which is outlined. The interleaving of molecules in adjacent stacks is apparent.

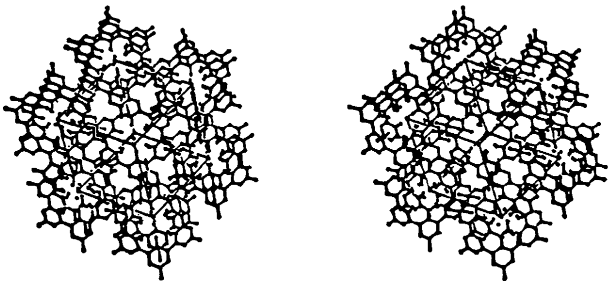

Fig. 4. Stereoview of the packing of (II), nearly along the [111] direction. The complexes are stacked along [111], just as the pure host molecules of (I) are. A Cl^- ion lies at each corner of the unit cell, which is outlined; an Li^+ ion is at the center of each cell, which is also the center of the cavity of the host molecule that occupies each cell.

The distance between the axes of adjacent stacks is 11·34 Å in the uncomplexed host, but only 10·59 Å in (II). Presumably this contraction in the crystal of the complex is a consequence of the lengthening of the [111] stacking axis, which results primarily from the insertion of the Cl^- ions. Since Cl^- is much smaller than the host, this lengthening permits more interleaving between the stacks. The contraction in the inter-stack distance is also favored by electrostatic attraction between the ions in the stacks. Each Cl^- has six Li^+ neighbors, and each Li^+ six Cl^- neighbors, in adjacent stacks at just 10·73 Å, arrayed with $\bar{3}$ symmetry. The shortest interionic contact along the axis of the stack is just half the length of [111], 5·26 Å. There are no other intermolecular contacts in crystals of (I) or (II) that seem worthy of comment.

It is of interest that the 4-methyl derivative of HMP forms crystals in $R\bar{3}$ or $R\bar{3}m$, with one molecule in a cell of dimensions $a = 11{\cdot}82$ Å and $\alpha = 115{\cdot}6°$ (Irngartinger *et al.*, 1970). These dimensions are very close to those of (I); the length of [111] in this cell is 7·55 Å, which is thus the distance between equivalent molecules in what are doubtless stacks along this direction in the crystal. The structure was not pursued by Irngartinger *et al.* (1970) because the crystals contained disordered solvent, either bromobenzene or xylene, depending on the medium used for crystallization. The densities they quote correspond to a cell content of about 0·75 to 0·9 molecules of solvent. We suspect that these disordered molecules of solvent pack in the stacks, parallel to and between the molecules of 4-methyl HMP, which is

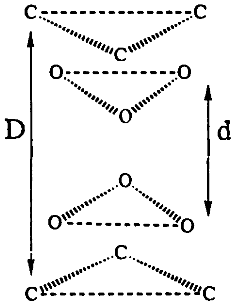

Fig. 5. The six methoxyl groups (H atoms not shown) in a single molecule of the host of (I), (II) and (III). Bonds joining the C and O atoms are not shown. The distances *d* and *D* between the planes of O and C atoms are given in Table 3 for the different structures; these planes are necessarily parallel in each structure, because the space groups are centrosymmetric.

probably nearly as flat in its center as HMP itself (Fig. 2). The combined thickness of the solvent and the 4-methyl HMP molecule should be around 7·5 to 8 Å, in accord with what is observed for the length of [111].

Fig. 6 is a drawing of the structure of (III) *without the counterion or the solvent*. The equivalent host molecules in this crystal pack at nearly 90° to one another, rather than parallel as in (I) and (II). The interstices left by this mode of packing are filled by the large counterion and the solvent. Efforts were made to grow crystals with monatomic counterions (and without solvent), but they were fruitless.

Fig. 7 shows the packing of (IV), which like (III) has large holes that are filled with solvent. Packing calculations indicate that the density and the intermolecular distances are reasonable when the solvent is modeled with CH_2Cl_2. When the solvent molecule is rotated around the threefold axis, the variation in energy with rotation is about 5 kJ mol^{-1}, with the maxima and minima repeating with the expected threefold symmetry. The minimum in energy is quite broad, varying by only about 2 kJ mol^{-1} over a 70° range. This suggests that the holes are not quite cylindrical, but that the preferred positions are favored only to a relatively small degree.

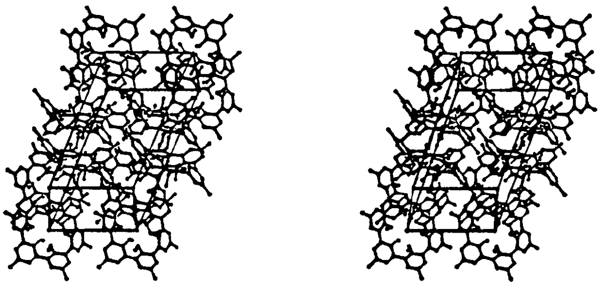

Fig. 6. Stereoview of the packing of the host, complexed with Na$^+$, in crystals of (III). The counterion and solvent have been omitted. The angle between the normals to the mean planes of host molecules related by the *c* glide is 86°; in contrast, these normals are parallel in crystals of (I) and (II). In this view, **a** is to the right, **c** approximately vertical.

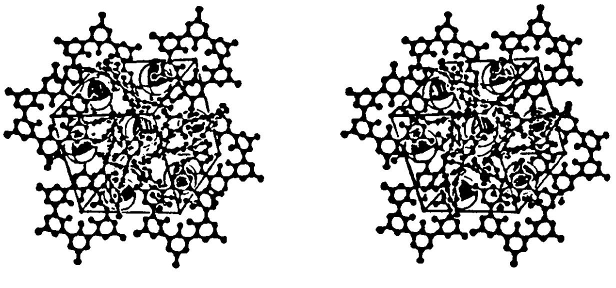

Fig. 7. Stereoview of the packing of (IV), with disordered CH_2Cl_2 represented by a sphere of radius 2·3 Å.

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Structure and Phase Transition of 1,3-Cyclohexanedione Crystals as a Function of Temperature

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Abstract

$C_6H_8O_2$, M_r = 112·13, monoclinic, $P2_1/c$, a = 6·1549 (6), b = 11·731 (1), c = 8·194 (1) Å, β = 99·386 (8)°, V = 583·7 (1) Å^3, Z = 4, D_x = 1·276 g cm^{-1}, λ(Cu $K\alpha$) = 1·54178 Å, μ(Cu $K\alpha$) = 7·05 cm^{-1}, F(000) = 240, T = 303 K, R = 0·084 for 558 reflections with $I \geq 1·96\sigma_I$. 1,3-Cyclohexanedione (enol form) is known to undergo a strong pressure-induced phase transition involving proton transfer in the hydrogen bond; it also forms inclusion compounds with benzene. In this paper we report the temperature dependence of the 1,3-cyclohexanedione structure. The unit-cell dimensions have been measured between 213 and 323 K and the structure has been determined at 213, 273 and 303 K. At T_c = 287 (1) K, the crystals undergo a strong structural transformation in which the crystal shape is markedly deformed; the transition is similar to that observed at high pressures. At the transition point the disordered methylene $C(5)H_2$ becomes ordered, molecules significantly change their positions in the crystal lattice and the enolic proton changes its donor and acceptor sites. This offers a unique opportunity for an analysis of the factors destabilizing the position of the proton forming a hydrogen bond. Despite a large change of the unit-cell dimensions [at 273 K a = 5·683 (1), b = 11·623 (2), c = 8·724 (2) Å, β = 95·40 (2)°] the crystal preserves its high-temperature space group $P2_1/c$, owing to the disappearance of the non-crystallographic mirror plane along $(10\bar{2})$ when the crystal is cooled below 287 K.

Introduction

The crystal structure of 1,3-cyclohexanedione (hereinafter referred to as CHD) was reported by Etter, Urbańczyk-Lipkowska, Jahn & Frye (1986); the same authors also reported the inclusion compound of CHD with benzene. Most recently the unit-cell dimensions and the structure of the CHD crystals were studied at high hydrostatic pressures by X-ray diffraction (Katrusiak, 1990*a*). When subjected to pressures of about 100 MPa the CHD crystals undergo a strong structural transformation which significantly changes the arrangement of the molecules and the shape of the crystals, but their space group ($P2_1/c$) remains unchanged. The pressure-induced transformation involves the ordering of the methylene group $C(5)H_2$ (which is disordered at room temperature and ambient pressure), and a transfer of the enolic proton between the donor and acceptor sites of the hydrogen bond.

In this contribution, we report the temperature dependence of the CHD structure. The crystals undergo a structural transformation at 287 (1) K, similar to that observed at high pressures. Two low-temperature structural determinations of CHD have been performed, at 213 and 273 K, and the low-temperature and the high-pressure structures have been compared. The main aim of this study was to determine the differences between the temperature- and pressure-induced changes in these crystals and to compare the changes in the low- and high-temperature phases. However, we were also interested in the geometry of the hydrogen bond in the low-temperature (high-pressure) phase which, due to the experimental limitations of the high-pressure X-ray experiments, could not be obtained under high-pressure conditions. The CHD structure has also been determined at 303 K, to show the temperature dependence of the high-temperature (ambient-pressure) phase. Since the high-pressure and low-temperature structures of CHD are similar, they will both be referred to as CHD2, and the high-temperature (ambient-pressure) phase will be referred to as CHD1.

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