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STRUCTURE OF, AND INTERNAL ROTATION IN, HEXAKIS [4-(2-PHENYLPROPAN-2-YL)PHENOXY] BENZENE, AND STRUCTURAL COMPARISON WITH ITS PRECURSOR PHENOL 4-(2-PHENYLPROPAN-2-YL)PHENOL

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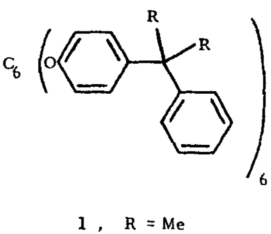
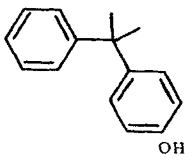
The title compounds (1 and 3, respectively) were studied by X-ray crystal structure analysis. Both are trigonal, space group $R\bar{3}$, with lattice parameters $a = 27{\cdot}718(6)$, $c = 8{\cdot}161(2)$ Å, $Z = 3$ and $a = 31{\cdot}267(7)$, $c = 6{\cdot}560(2)$, $Z = 18$, respectively. The dodecamethyl compound 1 is isomorphous with its parent hexakis(4-benzylphenoxy)benzene (2), a known host. However, 'collapse' along the *c*-axial direction has occurred such that the appreciable clathrate cavity of 2 has been replaced by only a very small residual void for 1. Phenol 3 does not pack in discrete $[OH]_6$ hydrogen-bonded hexamers; instead, molecules are assembled in infinite chains, linked by OH···O hydrogen bonds of length 2·735(3) Å, which are propagated along threefold screw axes. A variable-temperature CPMAS NMR study of side-chain aryl group rotation in 1 gives a value $\Delta G^{\neq}$ of $14{\cdot}0 \pm 0{\cdot}7$ kcal mol^{-1} (at 42 °C) for the (crystallographically unique) *para*-disubstituted ring, a similar 14 kcal mol^{-1} free energy barrier being found hindering rotation of this ring, and of the outer phenyl ring of 1, at 9 °C.

INTRODUCTION

We have recently employed hexakis(4-benzylphenoxy)benzene (2) and structurally related hexakis(4-phenoxyphenoxy)benzene as a potentially useful method for storage of volatile and reactive reagents as clathrates.[1] To ascertain the host packing in these crystalline inclusion compounds, detailed X-ray analyses were carried out.[1] We now report the synthesis and structure of hexakis[4-(2-phenylpropan-2-yl)phenoxy]benzene (1), which corresponds to the formal addition of twelve bulky methyl groups to 2, in order to see how this would affect inter-column packing. Interestingly, this leads to the retention of the rhombohedral space group $R\bar{3}$, but with marked changes in molecular packing and in unit cell dimensions, as discussed below. Compound 1 was prepared from hexafluorobenzene and the sodium salt of 3, as described under Experimental. In this paper, for the purpose of comparison, we also describe a detailed crystal structure of the isomorphous precursor phenol 4-(2-phenylpropan-2-yl)phenol (3). An NMR study of intramolecular group rotation in 1 in the molecular crystal is also described.



1, R = Me
2, R = H



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EXPERIMENTAL

Compound 1 was prepared in high yield by reaction of hexafluorobenzene with 12 molar equivalents of the sodium salt of phenol 3 for 6 weeks at 90° C in 1,3-dimethylimidazolin-2-one (DMEU) as a polar aprotic solvent, in a sealed tube.[2] The hexaether 1 has m.p. 211–212 °C (from acetonitrile; *m/z* 1338 (M^+), ^{1}H NMR, δ(CDCl$_3$) 1·54 (36H, s), 6·71 (24H, AA'BB' pattern, $\delta_{AB} = 0{\cdot}40$ ppm), 7·14 (30H, m); ^{13}C NMR, δ_C(CDCl$_3$) 30·8, 42·3, 115·2, 125·5, 126·7, 127·4, 127·9, 139·7, 144·6, 150·7, 155·1; elemental analysis: found, C 86·06, H 6·69; $C_{96}H_{90}O_6$ requires C 86·05, H, 6·78%. In addition, solid-state NMR spectra, discussed later, were in complete accord with the assigned structure and X-ray analysis of 1.

Crystal data for $C_{96}H_{90}O_6$ (1): $M = 1339{\cdot}74$, rhombohedral, space group $R\bar{3}$, $a = 27{\cdot}718(6)$, $c = 8{\cdot}161(2)$

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Å, $V = 5430(2)$ Å^3, $Z = 3$, $D_c = 1{\cdot}23$ g cm^{-3}, λ(Mo K_α) = 0·7107 Å, $\mu = 0{\cdot}70$ cm^{-1}, $T = 293$ K. Number of independent reflections = 2637 from colourless prism, 0·6 × 0·3 × 0·2 mm. $R = 0{\cdot}043$, $R' = 0{\cdot}036$ for 1459 observed $[F_o^2 > 2\sigma(F_o^2)]$ reflections.

Crystal data for $C_{15}H_{16}O$ (**3**): $M = 212{\cdot}29$, rhombohedral, space group $R\bar{3}$, $a = 31{\cdot}267(7)$, $c = 6{\cdot}560(2)$ Å, $V = 5554(2)$ Å^3, $Z = 18$, $D_c = 1{\cdot}14$ g cm^{-3}, λ(Mo K_α) = 0·7107 Å, $\mu = 0{\cdot}65$ cm^{-1}, $T = 293$ K. Number of independent reflections = 2683 from colourless, hexagonal needle, 1·0 × 0·3 × 0·3 mm. $R = 0{\cdot}065$, $R' = 0{\cdot}070$ for 1412 observed $[F_o^2 > 2\sigma(F_o^2)]$ reflections.*

X-ray intensity measurements for all possible reflections with $\sin\theta/\lambda > 0{\cdot}64$ Å^{-1} were made by $2\theta - \omega$ scan on an Enraf-Nonius CAD4F diffractometer. Unit cell parameters were determined by least-squares refinement of diffractometer setting angles for 25 reflections with $12° < \theta < 14°$. Least-squares refinement minimized $\Sigma w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F)$. The final difference map revealed maximum electron density 0·6, minimum −0·3 e Å^{-3} for **1** and 0·4 and −0·4 e Å^{-3}, respectively, for **3**. The principal computer programs used in structure solution and refinement are listed in Ref. 3.

Table 1. Fractional coordinates and isotropic displacement parameters (Å^2) for hexakis[4-(2-phenylpropan-2-yl) phenoxyl]benzene (**1**)

Atom	x	y	z	U^a
C(1)	0·04833(6)	0·99711(7)	0·99839(23)	0·036
C(2)	0·11457(7)	0·98296(7)	0·85268(24)	0·037
C(3)	0·16782(7)	0·99077(8)	0·85375(27)	0·045
C(4)	0·18778(7)	0·97830(7)	0·71527(27)	0·046
C(5)	0·15604(7)	0·95699(7)	0·57524(25)	0·040
C(6)	0·10338(7)	0·95078(8)	0·57641(27)	0·048
C(7)	0·08251(7)	0·96383(8)	0·71373(27)	0·047
C(8)	0·18021(7)	0·94156(7)	0·42687(26)	0·046
C(9)	0·13773(10)	0·91477(11)	0·28858(34)	0·064
C(10)	0·19640(12)	0·89838(10)	0·48100(36)	0·069
C(11)	0·23077(7)	0·99492(7)	0·36559(25)	0·042
C(12)	0·28517(8)	1·00792(9)	0·39541(32)	0·059
C(13)	0·32974(9)	1·05702(10)	0·33939(35)	0·068
C(14)	0·32123(11)	1·09395(9)	0·25203(35)	0·071
C(15)	0·26764(11)	1·08205(9)	0·22151(36)	0·074
C(16)	0·22336(9)	1·03357(8)	0·27866(29)	0·056
O(1)	0·09736(4)	0·99546(5)	0·99980(17)	0·044
H(3)	0·1909(7)	1·0055(7)	0·9550(28)	0·054(1)
H(4)	0·2253(7)	0·9858(7)	0·7160(25)	0·050(1)
H(6)	0·0790(7)	0·9350(7)	0·4756(27)	0·047(1)
H(7)	0·0429(8)	0·9587(7)	0·7080(25)	0·066(1)
H(9a)	0·1228(8)	0·9397(8)	0·2495(29)	0·063(1)
H(9b)	0·1057(9)	0·8793(8)	0·3287(30)	0·075(1)
H(9c)	0·1553(9)	0·9050(9)	0·1948(32)	0·081(1)
H(10a)	0·2247(8)	0·9118(8)	0·5761(32)	0·084(1)
H(10b)	0·2148(8)	0·8903(8)	0·3882(32)	0·083(1)
H(10c)	0·1637(8)	0·8637(8)	0·5171(31)	0·078(1)
H(12)	0·2919(8)	0·9813(8)	0·4509(28)	0·062(1)
H(13)	0·3680(8)	1·0649(7)	0·3610(30)	0·074(1)
H(14)	0·3539(9)	1·1302(9)	0·2117(32)	0·081(1)
H(15)	0·2606(9)	1·1079(9)	0·1605(35)	0·092(1)
H(16)	0·1869(7)	1·0269(7)	0·2608(29)	0·059(1)

[a] For hydrogen atoms U is the isotropic displacement parameter and for other atoms $U = 1/3\ \Sigma_{i=1}^{3}\ \Sigma_{j=1}^{3}\ U_{ij}a_i^*a_j^*(\vec{a}_i \cdot \vec{a}_j)$.

Table 2. Fractional coordinates and isotropic displacement parameters (Å^2) for 4-(2-phenylpropan-2-yl)phenol) (**3**)

Atom	x	y	z	U^a
C(1)	0·55801(10)	0·07844(10)	0·24535(43)	0·057
C(2)	0·56834(13)	0·05541(13)	0·40304(48)	0·078
C(3)	0·59794(12)	0·03472(13)	0·37664(50)	0·075
C(4)	0·61814(10)	0·03648(10)	0·18969(45)	0·056
C(5)	0·61005(12)	0·05995(11)	0·03083(48)	0·066
C(6)	0·57996(12)	0·08033(11)	0·05855(46)	0·066
C(7)	0·52170(11)	0·09764(11)	0·26439(46)	0·066
C(8)	0·54328(10)	0·14826(11)	0·16607(44)	0·063
C(9)	0·59010(12)	0·18577(12)	0·22266(49)	0·067
C(10)	0·60965(15)	0·23313(13)	0·14849(56)	0·078
C(11)	0·58381(16)	0·24465(15)	0·01251(57)	0·087
C(12)	0·53796(17)	0·20849(17)	−0·05015(58)	0·099
C(13)	0·51758(13)	0·16027(15)	0·02538(55)	0·082
C(14)	0·47348(15)	0·05889(18)	0·16550(86)	0·095
C(15)	0·51081(19)	0·10341(19)	0·49010(61)	0·090
O(4)	0·64698(9)	0·01524(9)	0·15557(37)	0·078
H(2)	0·5539(12)	0·0521(12)	0·5365(54)	0·079(3)
H(3)	0·6062(12)	0·0215(11)	0·4862(52)	0·071(3)
H(O4)	0·6500(12)	0·0020(12)	0·2504(52)	0·063(3)
H(5)	0·6267(10)	0·0629(10)	−0·1037(52)	0·061(3)
H(6)	0·5769(13)	0·1003(13)	−0·0542(58)	0·089(3)
H(9)	0·6093(12)	0·1771(11)	0·3025(50)	0·070(3)
H(10)	0·6419(13)	0·2571(13)	0·1830(51)	0·077(3)
H(11)	0·5976(14)	0·2799(15)	−0·0508(56)	0·102(3)
H(12)	0·5164(15)	0·2196(15)	−0·1388(70)	0·130(3)
H(13)	0·4817(13)	0·1346(12)	−0·0086(50)	0·076(3)
H(14a)	0·4578(16)	0·0708(16)	0·1682(70)	0·103(3)
H(14b)	0·4624(13)	0·0228(15)	0·2285(60)	0·096(3)
H(14c)	0·4816(13)	0·0550(14)	0·0071(67)	0·100(3)
H(15a)	0·5412(14)	0·1268(13)	0·5577(55)	0·077(3)
H(15b)	0·4894(11)	0·1192(11)	0·4965(48)	0·069(3)
H(15c)	0·4941(12)	0·0727(13)	0·5586(54)	0·077(3)

[a] For hydrogen atoms U is the isotropic displacement parameter and for other atoms $U = 1/3\ \Sigma_{i=1}^{3}\ \Sigma_{j=1}^{3}\ U_{ij}a_i^*a_j^*(\vec{a}_i \cdot \vec{a}_j)$.

Atomic coordinates are given in Tables 1 and 2 for **1** and **3**, respectively. The labelling of the atoms is shown in Figures 1 and 4.

DISCUSSION

^{13}C solid-state CPMAS NMR study

Figure 1 shows ^{13}C NMR spectra of crystalline

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* Supplementary data are obtainable from the authors: observed and calculated structure factors, anisotropic displacement parameters, bond lengths, bond angles and torsion angles for **1** and **3**.

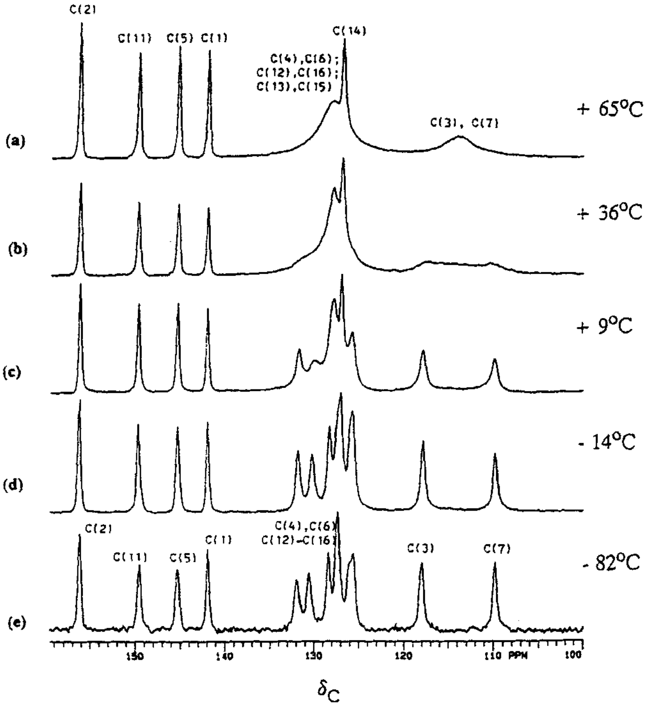

Figure 1. ^{13}C solid-state NMR spectra of crystalline hexakis[4-(2-phenylpropan-2-yl)phenoxy]benzene (**1**) measured under CPMAS conditions on a Varian VXR spectrometer, at carbon frequency 75·4 MHz, and at temperatures (a) 65, (b) 36, (c) 9, (d) −14 and (e) −82°C. NQS was employed to identify non-protonated carbons (see text). The chemical shift scale is relative to an external sample of tetramethylsilane

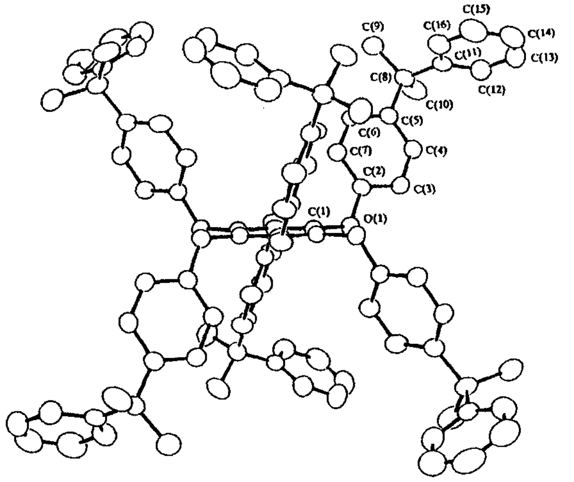

Figure 2. View showing the molecular structure of hexakis[4-(2-phenylpropan-2-yl)phenoxy]benzene (**1**) in its crystal. The indicated atomic numbering scheme is common to the x-ray and CPMAS NMR studies

hexakis[4-(2-phenylpropan-2-yl)phenoxy]benzene (**1**) recorded with cross-polarization and magic angle spinning (CPMAS) at temperatures ranging from to −82 to +65°C. As will be seen, these spectra not only give definitive information about the asymmetric unit in the crystal but also provide dynamic information. Figure 1(e) shows the spectrum of the aromatic carbons at −82°C, along with assignments, which employ a common numbering scheme with the X-ray study described below (Figure 2). The signals close to 127·3 and 125·6 δ_C each correspond to two carbon atoms. The three remaining carbons C(8) and non-equivalent methyl carbons, not shown in Figure 1, give rise to sharp signals at 40·8, 29·4, and 26·0 δ_C measured at ambient temperature [interestingly, at −82°C the signals from methyl carbons C(9) and C(10) have broadened into the baseline; the origins of this type of effect have been discussed recently[4]]. The existence of just 16 carbon resonances indicates that the asymmetric unit comprises one sixth of the molecule of **1**. Further, since an all-*cisoid* arrangement is extremely unlikely for **1** (not coordinated to a metal atom), the exact symmetry of **1** can be assigned point group C_{3i} (S_6) or, less probably, D_3. A higher symmetry D_{3d} conformation is excluded since the geminal methyls, necessarily related by a dihedral plane, would give rise to a single signal, rather than two as observed. As seen from Figure 1, signals from C(3) and C(7), *ortho* to oxygen in the disubstituted ring, undergo coalescence on raising the sample temperature from −82 to +65°C, a single peak in the exchange narrowing region being observed from C(3) and C(7) at +65°C [Figure 1(a)]. At coalescence, 42(±5)°C, application of the equation $k = \pi \delta\nu/\sqrt{2}$ gives $\Delta G^{\neq} = 14{\cdot}0(\pm 0{\cdot}7)$ kcal mol^{-1} (1 kcal = 4·184 kJ) for 180° rotation of the *para*-disubstituted ring around an axis defined by C(2) and C(5). The large chemical shift difference between C(3) and C(7), *ca* 8 ppm, is consistent with substantial γ-*gauche* effects[5] arising from the small value of torsion angle C(1)—O(1)—C(2)—C(7), −11°, measured by X-ray diffraction analysis (see below). Interestingly, all of the signals for C(3), C(4), C(6), C(7), C(12), C(13), C(15) and C(16) exhibit onset of significant exchange broadening in a narrow temperature range, indicating that the free energy barrier hindering 180° rotation of the outer phenyl moiety is close to that of the inner side-chain ring. Estimates of line broadening of non-coalesced signals (approximate because of overlaps in range 125–133 δ_C) suggest[6] common value for $\Delta G^{\neq}$ of *ca* 14 kcal mol^{-1} for both rotations at 9°C. At +65°C [Figure 1(a)], not yet at limiting fast exchange, coalesced pairs C(4), C(6); C(12), C(16); C(13), C(15) give rise to a single broad feature centred near 128 δ_C. C(14), which has a unique environment unaffected by aryl moiety rotation, gives rise to a prominent feature at 126·6 δ_C at +65 °C. Likewise, aromatic carbons C(1), C(2), C(5) and C(11) do not undergo site exchange as a consequence of rotation; these give four sharp resonances, unchanged as the temperature is raised from −82 to +65 °C (Figure 1). As expected, the resonance for quaternary carbon C(8), not shown in Figure 1, also remains a sharp single line in this temperature range. In contrast to the above behaviour, a preliminary CPMAS study of crystalline hexakis(4-benzylphenoxy)benzene (**2**) (CCl_4 clathrate), analogous to **1** but lacking its methyl groups, is consistent with rapid rotation of both side-chain rings at +36 °C. The signal for the carbons *ortho* to oxygen in **2**, corresponding to C(3) and C(7) in **1**, appears as a narrow singlet at 115·7 δ_C at +36 °C; at −82 °C decoalescence has not yet occurred but the exchange narrowing region has been entered. From this (and the large chemical shift difference expected between these *ortho* carbons for **2**), it may be inferred that rotation of the *para*-disubstituted ring of **1** is much more hindered than it is for the corresponding ring in **2**. Further CPMAS studies on **2** and related molecules are in progress.

X-ray analysis

Figure 2 shows the structure and conformation of hexakis[4-(2-phenylpropan-2-yl)phenoxy]benzene (**1**) in the molecular crystal. The molecule of **1**, located on a point of $\bar{3}$ symmetry, is constrained to have exact C_{3i} (S_6) symmetry. This, satisfyingly, is in complete accord with the above-described CPMAS study. Side-chain moieties are located alternately above and below the plane of the central benzene ring. The central ring is planar to ±0·01 Å and attacked oxygen atoms lie accurately in the mean plane. The *c*-axial dimension shortens markedly from 11·247(2) for **2** to 8·161(2) Å for **1**, corresponding to formal introduction of twelve methyl groups. This change mainly reflects reorientation of the aralkyl group, benzyl for **2** and cumyl for **1**, which dramatically changes torsion angle C(6)—C(5)—C(8)—C(11) to 117° in **1** from the corresponding value of −5° for **2**. Less pronounced changes occur in other torsion angles; for example, C(1′)—C(1)—O(1)—C(2) and C(1)—O(1)—C(2)—C(7), +78° and −11°, respectively, for **1**, may be compared with related values of +94° and −28° for **2**. This marked rotation of the aralkyl substituent corresponds to a splaying of the outer phenyl away from the *c*-axis in **1** resulting in closer packing along *c* in **1** than in **2**. In the 4-benzyl counterpart **2** the phenyl group projects roughly along the *c*-axial direction; it acts to prevent a closer approach between adjacent molecules along *c* in addition to forming an essential part of the clathrate cavity wall. The *a*-axial dimension undergoes an increase related to the decrease in *c*; *a* changes from 23·144(6) Å for **2** to 27·718(6) Å for **1**. The reorientation of the outer phenyl may reflect repositioning of the geminal dimethyl groups of **1** so that serious disruption of intercolumn packing is avoided. In **1**, like **2**, the molecules are assembled in infinite stacks along *c*, but for **1** only a

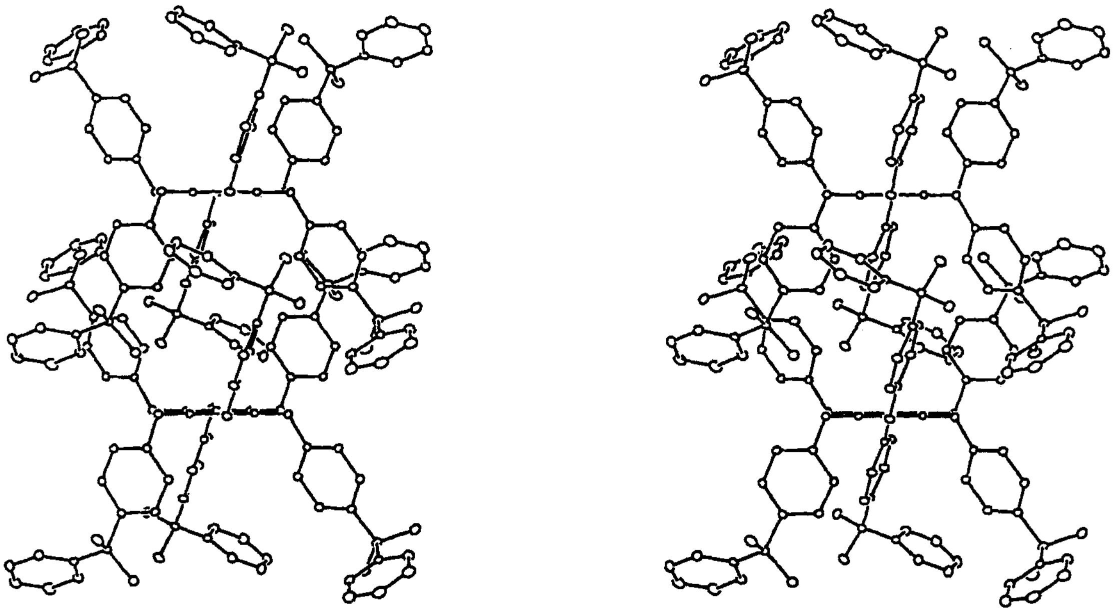

Figure 3. Stereoview illustrating the relationship of two adjacent molecules of **1** which represent a part of infinite stacks along *c*

residual void is left between adjacent molecules along *c*. A stereoview, normal to *c*, illustrates the packing of two adjacent molecules along *c* in the crystal of **1** (Figure 3).

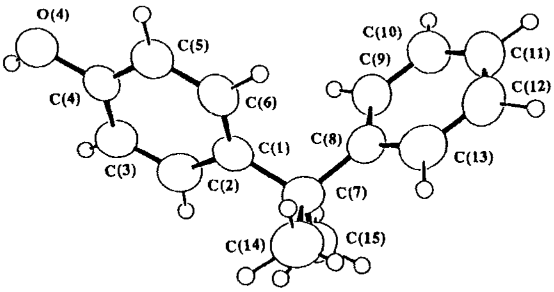

Figure 4. General view of the structure of 4-(2-phenylpropan-2-yl)phenol (**3**) in its rhombohedral molecular crystal

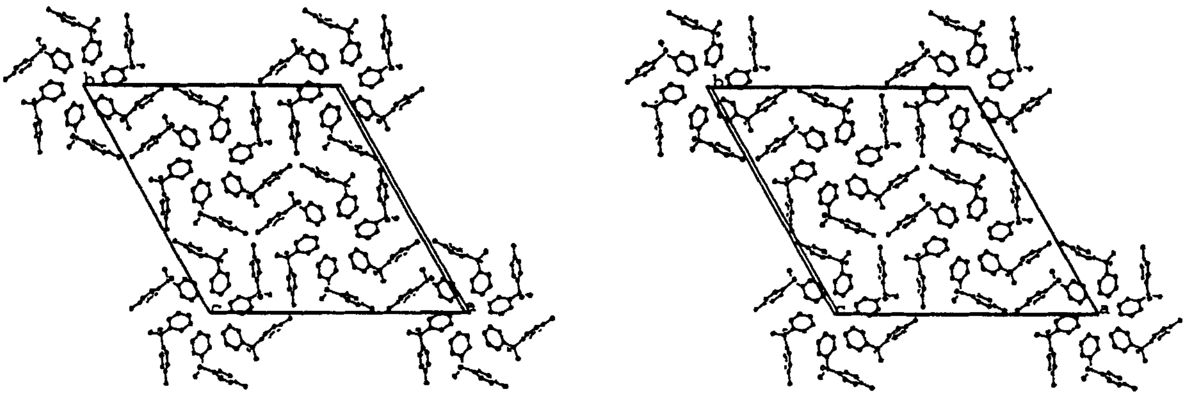

Figure 5. Stereo packing diagram for **3** illustrating the view looking along *c*. Infinite chains of molecules of **3** are propagated around threefold screw axes parallel to *c*

Knowledge of the space group of the precursor phenol of **2**, namely 4-(2-phenylpropan-2-yl)phenol (**3**), as $R\bar{3}$, prompted us to carry out a full X-ray analysis to establish whether **3** was comprised of hydrogen-bonded $[OH]_6$ hexamers and, if so, whether it possessed any sizeable voids. A view of the single molecule of **3** in the crystal is shown in Figure 4. More revealing, however, is the stereoview in Figure 5, illustrating the molecular packing of **3**. Although six molecules of **3** are grouped around a point of $\bar{3}$ symmetry, this occurs in such a way that their non-functionalized phenyl rings converge towards this site. As a consequence, there is no hydrogen bonding linking these molecules to form a discrete $[OH]_6$ unit as found in many clathrates formed by phenolic host molecules.[7] Instead of pointing inwards to form a closed cycle of hydrogen bonds, the OH groups point outwards and contribute to six separate infinite spirals of hydrogen bond-linked molecules of **3**, propagated along six threefold screw axes which surround the *c*-axis, and run parallel to it. The OH···O hydrogen bonds linking adjacent molecules in these spiral chains have length 2·735(3) Å, with H···O contact 1·96(3) Å and O—H···O 175(3)°. In the present study of potential host molecules, structural analysis by X-ray methods is nicely complemented by variable-temperature CPMAS NMR measurements which more directly provide dynamic information concerning such systems.

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