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Crystal and Molecular Structures of 3-Methyl-4-isopropylphenol and 4-Isopropylphenol

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The crystal structures of 3-methyl-4-isopropylphenol ($C_{10}H_{14}O$) and 4-isopropylphenol ($C_9H_{12}O$) have been determined from Cu $K\alpha$ data and refined to R values of 0·07 and 0·06 respectively. Both compounds belong to space group $P4_1$ with four molecules in the unit cell; the parameters are respectively $a = b = 10{\cdot}060$ (5), $c = 8{\cdot}890$ (5) Å and $a = b = 9{\cdot}937$ (5), $c = 8{\cdot}327$ (5) Å. In both structures, molecules are linked by hydrogen bonds and form infinite chains running along 4_1 axes. The molecular configuration shows the relative position of the isopropyl group to the benzene ring: the two methyl groups of the isopropyl group are not symmetrically situated below and above the mean plane of the molecule.

Introduction

This work forms part of the crystal structure investigations of some *para*-substituted phenols: we have already studied 4-methylphenol (unstable form) (Perrin & Thozet, 1974) and 4-chlorophenol (two forms) (Perrin & Michel, 1973) and we introduce now a larger substituent: the isopropyl group. The study of the binary system between 3-methyl-4-isopropylphenol and 4-isopropylphenol reveals a continuous solid solution and the existence of two forms of 4-isopropylphenol at temperatures greater than 0 °C (Perrin *et al.*, 1976).

In this paper we are interested in the stable forms, at ordinary temperatures, of both compounds. The determination of the crystal structures was undertaken mainly to ascertain the geometry of the molecule, particularly the relative position of the isopropyl group and the benzene ring plane, but also to study the arrangement of the molecules in such chiral hydrogen-bonded structures.

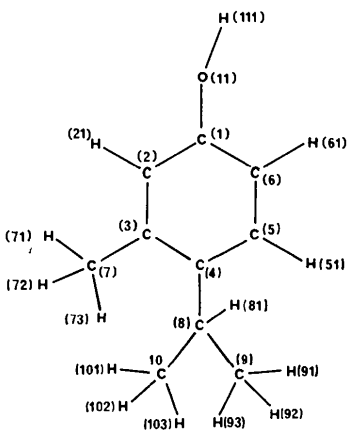

Fig. 1. Numbering scheme of the molecule.

Fig. 1 gives the numbering scheme of the different atoms of the molecules, the methyl group in position 3 being replaced by H(31) in 4-isopropylphenol.

Morphological characteristics and crystal data

Crystals of the two compounds were obtained by recrystallization from saturated solutions in chloroform or ethyl alcohol. They consist of a tetragonal prism {100} with pyramids {101} and {10$\bar{1}$}. Sometimes some faces of the prisms {110} and {120} appear.

Precession and Weissenberg photographs were used to determine preliminary unit-cell dimensions and space-group extinctions. Intensity data were collected with Cu $K\alpha$ radiation on a diffractometer with a crystal sealed in a glass capillary. The results are given in Table 1.

Table 1. *Crystal data*

3-Methyl-4-isopropylphenol	4-Isopropylphenol
$a = b = 10{\cdot}060$ (5) Å	$a = b = 9{\cdot}937$ (5) Å
$c = 8{\cdot}890$ (5)	$c = 8{\cdot}327$ (5)
Space group $P4_1$	Space group $P4_1$
$F(000) = 328$	$F(000) = 296$
$Z = 4$, $D_x = 1{\cdot}107$ g cm^{-3}	$Z = 4$, $D_x = 1{\cdot}098$ g cm^{-3}
953 observed reflexions	1013 observed reflexions

Structure determination and refinement

The observed reflexions for 3-methyl-4-isopropylphenol were converted to normalized $|E|$ values and *MULTAN* techniques for non-centrosymmetric space groups were applied (Germain, Main & Woolfson, 1971). An initial E map based on 92 reflexions ($E >$

Table 2. *Atomic coordinates* ($\times 10^4$) *for the non-hydrogen atoms, with standard deviations in parentheses*

	x	*y*	*z*
3-Methyl-4-isopropylphenol			
C(1)	2542 (6)	9402 (6)	7500
C(2)	3042 (6)	8506 (6)	6467 (8)
C(3)	4351 (6)	8036 (6)	6578 (9)
C(4)	5157 (6)	8467 (6)	7759 (9)
C(5)	4621 (7)	9359 (7)	8798 (9)
C(6)	3326 (7)	9837 (7)	8691 (9)
C(7)	4825 (7)	7064 (7)	5411 (9)
C(8)	6583 (7)	7992 (8)	7944 (9)
C(9)	7576 (8)	9118 (9)	8208 (12)
C(10)	6660 (9)	6990 (11)	9197 (16)
O(11)	1258 (4)	9892 (5)	7412 (6)
4-Isopropylphenol			
C(1)	2613 (4)	9328 (4)	7500
C(2)	3096 (4)	8346 (4)	6474 (6)
C(3)	4386 (4)	7829 (4)	6704 (6)
C(4)	5193 (4)	8279 (4)	7965 (6)
C(5)	4693 (4)	9265 (5)	8937 (7)
C(6)	3411 (5)	9805 (5)	8699 (6)
C(8)	6578 (5)	7693 (6)	8259 (7)
C(9)	7649 (5)	8779 (6)	8370 (9)
C(10)	6595 (7)	6806 (7)	9714 (11)
O(11)	1337 (3)	9877 (3)	7273 (5)

Table 3. *Atomic coordinates* ($\times 10^3$) *and isotropic temperature factors for the hydrogen atoms, with standard deviations in parentheses*

	x	*y*	*z*	*β*
3-Methyl-4-isopropylphenol				
H(21)	240 (6)	828 (7)	563 (8)	3·01
H(51)	516 (7)	965 (6)	971 (8)	3·02
H(61)	304 (7)	044 (7)	963 (8)	3·03
H(71)	532 (7)	611 (7)	598 (9)	3·06
H(72)	547 (7)	737 (7)	464 (9)	3·07
H(73)	426 (7)	660 (7)	466 (9)	3·08
H(81)	679 (7)	777 (7)	712 (9)	3·05
H(91)	766 (7)	993 (7)	714 (9)	3·10
H(92)	848 (7)	869 (7)	862 (9)	3·11
H(93)	754 (7)	978 (7)	937 (10)	2·86
H(101)	697 (7)	757 (7)	1027 (10)	3·00
H(102)	586 (7)	623 (7)	946 (9)	3·01
H(103)	780 (7)	638 (7)	914 (10)	2·90
H(111)	94 (7)	964 (8)	638 (8)	2·72
4-Isopropylphenol				
H(21)	250 (4)	797 (4)	545 (5)	3·15
H(31)	470 (4)	708 (4)	573 (5)	3·72
H(51)	539 (4)	979 (4)	974 (6)	3·84
H(61)	307 (4)	1039 (4)	948 (5)	3·51
H(81)	674 (4)	757 (4)	713 (5)	3·50
H(91)	769 (5)	938 (5)	711 (6)	5·73
H(92)	858 (4)	828 (5)	867 (6)	5·73
H(93)	743 (5)	940 (5)	937 (6)	5·73
H(101)	609 (5)	725 (5)	1079 (7)	6·82
H(102)	591 (5)	596 (5)	961 (7)	6·82
H(103)	758 (5)	645 (5)	992 (7)	6·82
H(111)	82 (4)	943 (4)	793 (5)	3·46

1·50) revealed some atoms of the molecule: the benzene ring, C(7) of the methyl group, C(8) of the isopropyl group and the O atom.

A Fourier synthesis with these positions, calculated with all the reflexions, showed the structure; the first calculation of the *R* index gave 0·17. The structure was refined by least-squares methods (Ahmed, Hall, Pippy & Huber, 1966). The weighting scheme used was: $\sqrt{w} = 1$ if $|F_o| < P_1$; $\sqrt{w} = P_1/|F_o|$ if $|F_o| > P_1$, where $P_1^2/F_{max}^2 = 0{\cdot}1$.

Isotropic, followed by anisotropic, block-diagonal least-squares refinement yielded an *R* of 0·081. H atoms were located on a difference map, but some of the positions of those of the methyl groups are not in good agreement with theoretical distances and angles. The final *R* after isotropic refinement of the H atoms was 0·07.

The same positions for the O and C atoms were introduced in the refinement for the second compound. When *R* took the value 0·10, a difference synthesis located the H atoms. The final *R* was 0·06.

For both molecules, the atomic positional parameters are listed in Tables 2 and 3.* We can see the similarity in H positions for both structures.

Results and discussion

Molecular dimensions

Bond distances and angles with their standard deviations are given in Tables 4 and 5. In the benzene ring the mean value for C–C is 1·393 Å for the first compound and 1·384 Å for the second; the mean values for C–C–C angles are 119·98 and 119·97° respectively.

We note the difference between the two angles C(2)–C(1)–O(11) and C(6)–C(1)–O(11), the value being greater than 120° on the side of atom H(111). This difference is most important in 3-methyl-4-isopropylphenol. This inequality has been observed in other phenols and has been interpreted as a result of the repulsion between the H atom and the C carrying the hydroxyl group (Hirshfeld, 1964).

The equations of the benzene-ring planes and deviations of atoms from them are given in Table 6 for both molecules. C(7), C(8) and O(11) are in the plane but C(9) is above and C(10) below the plane. They are not symmetrically situated relative to the mean plane, and this destroys the symmetry of the second molecule.

The direction C(9)–C(10) is not perpendicular to the benzene-ring plane: it is at an angle of about 78°

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32749 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

for 3-methyl-4-isopropylphenol and 80° for 4-isopropylphenol.

Figs. 2 and 3 show stereoscopic views of the two molecules.

Table 4. *Bond lengths* (Å), *with their standard deviations in parentheses*

	3-Methyl-4-isopropylphenol	4-Isopropylphenol
C(1)–C(2)	1·382 (8)	1·384 (6)
C(2)–C(3)	1·403 (9)	1·395 (6)
C(3)–C(4)	1·395 (10)	1·397 (7)
C(4)–C(5)	1·397 (10)	1·366 (7)
C(5)–C(6)	1·391 (10)	1·399 (6)
C(6)–C(1)	1·390 (9)	1·362 (6)
C(1)–O(11)	1·384 (8)	1·395 (5)
C(4)–C(8)	1·520 (9)	1·516 (7)
C(8)–C(9)	1·529 (11)	1·520 (8)
C(8)–C(10)	1·504 (15)	1·500 (10)
C(3)–C(7)	1·504 (10)	
C(2)–H(21)	1·01 (7)	1·10 (4)
C(3)–H(31)		1·14 (4)
C(5)–H(51)	1·02 (7)	1·09 (4)
C(6)–H(61)	1·08 (7)	0·94 (4)
C(7)–H(71)	1·19 (7)	
C(7)–H(72)	0·99 (7)	
C(7)–H(73)	0·99 (8)	
C(8)–H(81)	0·79 (8)	0·96 (4)
C(9)–H(91)	1·25 (8)	1·21 (5)
C(9)–H(92)	1·08 (7)	1·08 (5)
C(9)–H(93)	1·23 (8)	1·06 (5)
C(10)–H(101)	1·16 (9)	1·12 (5)
C(10)–H(102)	1·13 (8)	1·09 (5)
C(10)–H(103)	1·30 (7)	1·06 (5)
O(11)–H(111)	1·00 (7)	0·88 (4)

Table 5. *Bond angles* (°) *with their standard deviations in parentheses*

	3-Methyl-4-isopropylphenol	4-Isopropylphenol
C(2)–C(1)–C(6)	120·2 (6)	119·8 (4)
C(2)–C(1)–O(11)	122·3 (5)	120·6 (3)
C(6)–C(1)–O(11)	117·5 (5)	119·6 (3)
C(1)–C(2)–C(3)	121·0 (6)	119·6 (4)
C(2)–C(3)–C(4)	119·6 (6)	120·9 (4)
C(2)–C(3)–C(7)	117·9 (6)	
C(4)–C(3)–C(7)	122·5 (6)	
C(3)–C(4)–C(5)	118·2 (6)	117·8 (4)
C(3)–C(4)–C(8)	122·1 (6)	121·4 (4)
C(5)–C(4)–C(8)	119·6 (6)	120·7 (4)
C(4)–C(5)–C(6)	122·5 (7)	121·6 (4)
C(5)–C(6)–C(1)	118·4 (6)	120·1 (4)
C(9)–C(8)–C(10)		
C(4)–C(8)–C(10)	109·9 (7)	111·5 (5)
C(4)–C(8)–C(9)	113·6 (6)	113·9 (5)
C(1)–C(2)–H(21)	114 (4)	122 (2)
C(3)–C(2)–H(21)	125 (4)	118 (2)
C(4)–C(5)–H(51)	120 (4)	118 (2)
C(6)–C(5)–H(51)	117 (4)	119 (2)
C(5)–C(6)–H(61)	113 (4)	118 (2)
C(1)–C(6)–H(61)	128 (4)	121 (2)
C(2)–C(3)–H(31)		113 (2)
C(4)–C(3)–H(31)		126 (2)
C(3)–C(7)–H(71)	111 (4)	
C(3)–C(7)–H(72)	119 (4)	
C(3)–C(7)–H(73)	126 (4)	
C(4)–C(8)–H(81)	104 (5)	102 (2)
C(9)–C(8)–H(81)	100 (5)	110 (2)
C(10)–C(8)–H(81)	119 (5)	110 (2)
C(8)–C(9)–H(91)	114 (4)	109 (2)
C(8)–C(9)–H(92)	108 (4)	107 (2)
C(8)–C(9)–H(93)	121 (4)	109 (3)
C(8)–C(10)–H(101)	106 (4)	114 (3)
C(8)–C(10)–H(102)	125 (4)	113 (3)
C(8)–C(10)–H(103)	109 (4)	110 (3)
C(1) O(11)–H(111)	105 (4)	105 (3)

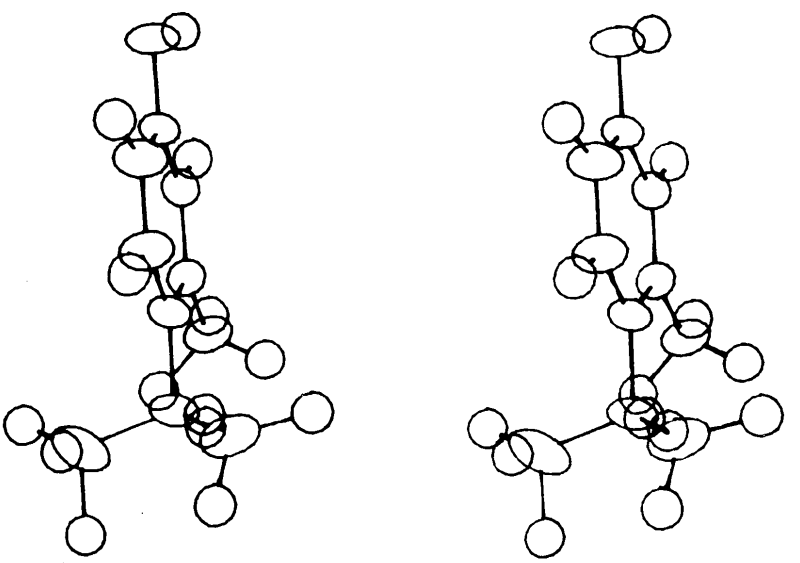

Fig. 2. Stereoscopic view of the molecule of 3-methyl-4-isopropylphenol.

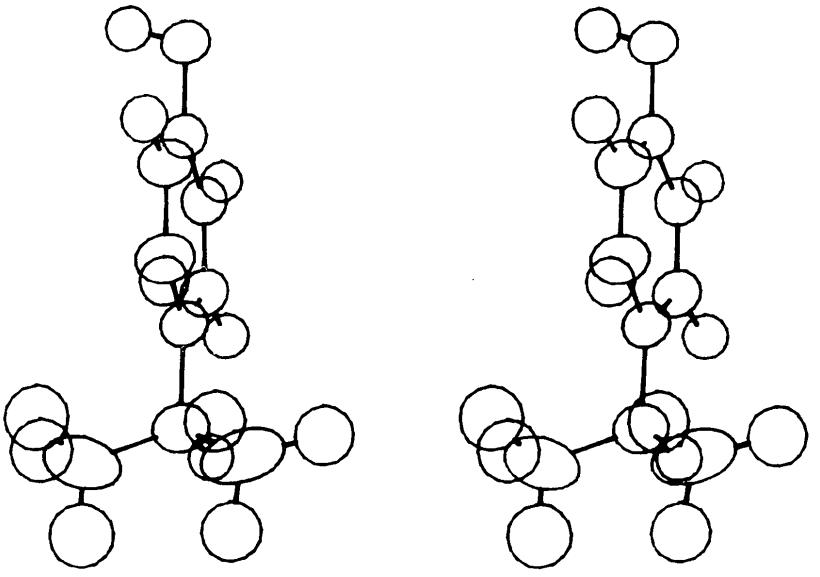

Fig. 3. Stereoscopic view of the molecule of 4-isopropylphenol.

Table 6. *Least-squares planes with displacements of atoms from the planes* (Å)

Asterisks indicate atoms not included in the calculation of the plane.

3-Methyl-4-isopropylphenol

$$0{\cdot}321X + 0{\cdot}763Y - 0{\cdot}561Z = 4{\cdot}30$$

C(1)	0·006	C(7)*	−0·011
C(2)	−0·006	C(8)*	0·006
C(3)	0·001	C(9)*	1·060
C(4)	0·003	C(10)*	−1·363
C(5)	−0·003	O(11)*	0·011
C(6)	−0·002		

4-Isopropylphenol

$$0{\cdot}378X + 0{\cdot}700Y - 0{\cdot}606Z = 3{\cdot}71$$

C(1)	−0·014	C(8)*	−0·047
C(2)	0·002	C(9)*	1·056
C(3)	0·010	C(10)*	−1·394
C(4)	−0·010	O(11)*	0·004
C(5)	−0·001		
C(6)	0·013		

The H positions found from the difference synthesis were refined and give the distances and angles listed in Tables 3 and 4. The mean value for distances involving H is about 1·08 Å, longer than the distance normally found (1·00 Å). Crystals of these compounds are soon to be studied by neutron diffraction, when the positions of the H atoms will be recalculated.

Table 7. *Intermolecular distances* (Å) *less than* 4·0 Å *with their estimated standard deviations in parentheses*

(i)	$1-y, 1+x, \frac{1}{4}+z$	(iv)	$1+x, y, z$
(ii)	$1-x, 2-y, \frac{1}{2}+z$	(v)	$y, 1-x, -\frac{1}{4}+z$
(iii)	$1-y, x, \frac{1}{4}+z$	(vi)	$2-y, 1+x, \frac{1}{4}+z$

	3-Methyl-4-isopropyl-phenol	4-Isopropylphenol
Within one chain		
O(11)···O(11^{i})	2·858 (8)	2·813 (8) (Hydrogen bond)
C(1)···O(11^{i})	3·751 (7)	3·705 (5)
O(11)···C(2^{i})	3·466 (8)	3·517 (5)
O(11)···C(1^{i})	3·584 (7)	3·608 (5)
C(6)···C(2^{i})	3·724 (10)	3·719 (6)
C(6)···O(11^{i})	3·702 (9)	3·718 (6)
Between chains		
C(5)···C(7^{ii})	3·913 (11)	
C(6)···C(7^{ii})	3·941 (11)	
C(5)···C(2^{ii})	3·971 (10)	3·868 (7)
C(3)···C(5^{ii})	3·747 (10)	3·810 (7)
C(2)···C(9^{ii})	3·807 (12)	3·929 (8)
C(1)···C(8^{iii})	3·987 (9)	3·868 (6)
C(1)···C(9^{iii})	3·781 (11)	3·550 (7)
C(2)···C(7^{iii})	3·921 (10)	
C(3)···C(7^{iii})	3·724 (10)	
C(6)···C(8^{iii})	3·859 (10)	3·803 (7)
C(6)···C(9^{iii})	3·798 (12)	3·553 (8)
C(7)···C(7^{iii})	3·691 (11)	
C(7)···C(10^{iii})	3·795 (16)	
C(9)···O(11^{iv})	3·850 (9)	3·937 (6)
C(9)···O(11^{v})	3·763 (11)	3·661 (8)
C(9)···O(11^{vi})	3·663 (10)	3·731 (8)

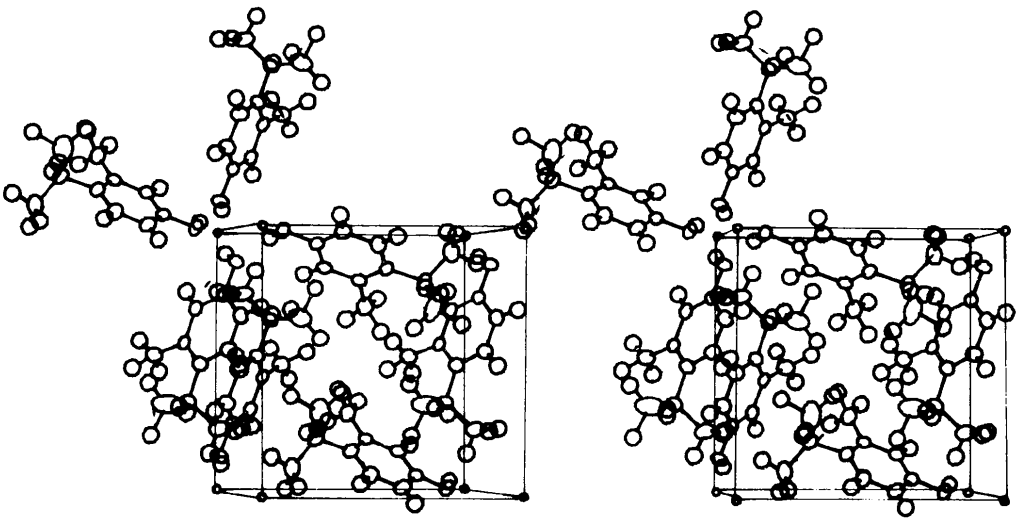

Fig. 4. Stereoscopic view of the structure of 3-methyl-4-isopropylphenol.

Hydrogen bonding

As in many phenols, molecules are interlinked by hydrogen bonds forming a helical H-bonded array along the 4_1 axis. The distance between two O atoms is about 2·85 Å. The direction O(11)–C(8) of each molecule is almost perpendicular to **c**.

Packing arrangements

The neighbouring molecules are held together by van der Waals interactions and are interrelated by translations equal to *a* or *b*. Table 7 gives the intermolecular shortest distances in one chain and between two chains.

Fig. 4 shows the stereoscopic view of the structure seen along **c**.

Conclusion

We can see that the molecular configuration, particularly the relative position of the isopropyl group to the benzene ring, is the same for both compounds. The structures show for the first time the geometry of the isopropyl group on an aromatic ring in simple molecules.

The presence of the CH_3 substituent does not modify the molecular configuration or the molecular arrangement. It will be interesting to see if the molecular geometry is the same for the high-temperature form of 4-isopropylphenol.

In the case of 3-methyl-4-isopropylphenol, the two CH_3 groups of the isopropyl group and the CH_3 group in the *meta* position on the benzene ring are as far apart as possible.

The arrangement of the molecules in this chiral crystal gives some interesting physical properties: non-linear optical properties have been studied and the results are interesting (Jerphagnon, Bergman & Perrin, 1977).

The results of these structures will be useful for the study in our group of reactions in the solid state.

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