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Molecular Complexes of *N,N,N',N'*-Tetraisopropyloxamide. Crystal Structures of Its 1:1 Adduct with *m*-Cresol, and Its 1:1 and 1:2 Adducts with *p*-Cresol

Fumio Toda,* Yasunori Tagami, and Thomas C. W. Mak*,†

Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790

†Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

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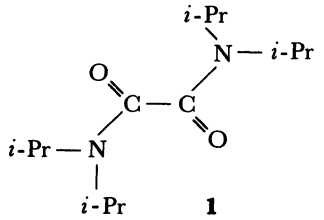
The crystal structures of a 1:1 complex (I) of *N,N,N',N'*-tetraisopropyloxamide with *m*-cresol, a 1:1 complex (**II**) with *p*-cresol, and a 1:2 complex (**III**) with *p*-cresol have been determined by X-ray crystallography. The crystal data are: **I**, $C_{21}H_{36}N_2O_3$, $P2_1/c$, a=12.104(4), b=6.860(3) c=27.186(8) Å, β=93.46(2)°, Z=4, and R_F=0.093 for 1661 observed Mo$K\alpha$ data; **II**, $C_{21}H_{36}N_2O_3$, $P2_1/n$, a=7.825(2), b=11.379(4), c=25.39(1) Å, β=91.01(2)°, Z=4, and R_F=0.105 for 1326 data; **III**, $C_{28}H_{44}N_2O_4$, $C2/c$, a=11.744(3), b=10.658(2), c=23.576(4) Å, β=102.07(2)°, Z=4, R_F=0.045 for 1382 data. The stoichiometric formulas faithfully represent the structures of all three complexes, with each phenolic OH group forming a donor hydrogen bond to an O atom of the oxamide host molecule.

Recently we reported that *N,N,N',N'*-tetraisopropyloxamide (**1**) forms crystalline inclusion compounds of 1:1 stoichiometry with a variety of aromatic guest molecules such as benzene, *m*- and *p*-xylenes, phenol, *m*- and *p*-cresols, naphthalene, 1- and 2-methylnaphthalenes, and 1- and 2-naphthols.[1] X-Ray analysis of its 1:1 complex (**IV**) with 1-methylnaphthalene showed that the aromatic molecules are accommodated in channels, with no significant interaction between host and guest components other than dispersion forces.[1] For a better understanding of the inclusion properties of **1**, we have carried out crystal structure determinations of its 1:1 complexes (**I** and **II** respectively) with *m*- and *p*-cresols, with anticipation of hydrogen bonding but uncertainty as to whether host-guest or guest-guest association would be the dominating factor. In the course of our studies we further isolated a 1:2 crystalline adduct (**III**) of **1** with *p*-cresol, whose structure is also reported in the present paper.



1

Experimental

Diamide **1** (mp 102—103 °C) was synthesized from oxalyl dichloride and diisopropylamine according to a literature method.[2] Complexes **I—III** were obtained as colorless prisms from slow evaporation of a solution of **1** and the appropriate cresol in hexane. Complexes **II** and **III** were prepared separately by using different stoichiometric amounts of *p*-cresol, and crystals of **II** ($\nu_{C=O}$ 1615, 1648 cm^{-1}) are generally bigger and better formed than those of **III** ($\nu_{C=O}$ 1625 cm^{-1}).

X-Ray Data Collection. All three complexes quickly turned milky upon exposure to air, and each selected crystal was therefore enclosed inside an 0.5 mm Lindemann glass capillary. Intensity measurement[3] was performed on a Nicolet R3m four-circle diffractometer[4] using graphite-monochromatized Mo$K\alpha$ radiation (λ=0.71069 Å). Accurate unit-cell parameters were derived from a least-squares fit of the angular settings for 25 reflections in the range $14° < 2\theta < 18°$. Reflection intensities were recorded at an ambient laboratory temperature of 22 °C, and three standards monitored every 50 data measurements showed only random fluctuations within ±2% of their mean values. The raw intensities were processed with the learnt-profile procedure.[5] No absorption correction was applied. The crystal data and processing parameters for **I—III** are summarized in Table 1.

Structure Determination and Refinement

For each complex the statistical distributions of the normalized structure factors strongly favoured a centrosymmetric space group, and structure solution was achieved by direct phase determination based on negative quartets.[6]

The structures of **I** and **II** were refined in the same manner. The N, O, and methyl C atoms were varied anisotropically, and the remaining C atoms isotropically. In view of the unfavorable data-to-parameter ratio,[7] the phenyl ring was treated as a rigid group (regular hexagon of side 1.395 Å). All H atoms were generated geometrically (C–H=0.96 Å) and included in structure factor calculations with fixed isotropic temperature factors.

In complex **III**, the oxamide molecule **1** is located on a crystallographic diad. All non-hydrogen atoms in the asymmetric unit (half of an oxamide molecule and one *p*-cresol) were refined anisotropically. A difference Fourier map revealed the proton belonging to the phenolic group at a reasonable location, and all H atoms were included with assigned isotropic thermal parameters in subsequent refinement.

Computations were performed on a Data General Corporation Nova 3/12 minicomputer using the SHELXTL program package.[8] Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.[9] Blocked-cascade least-squares refinement[10] converged to the R indices and parameters listed in Table 1.

Table 1. Data Collection and Processing Parameters

Complex	I	II	III
Molecular formula	$C_{14}H_{28}N_2O_2 \cdot C_7H_8O$	$C_{14}H_{28}N_2O_2 \cdot C_7H_8O$	$C_{14}H_{28}N_2O_2 \cdot 2C_7H_8O$
Molecular weight	364.52	364.52	472.66
Cell constants	a=12.104(4)Å β=93.46(2)°	a=7.825(2)Å β=91.01(2)°	a=11.744(3)Å β=102.07(2)°
	b=6.860(3) V=2253(1)Å^3	b=11.379(4) V=2260(1)Å^3	b=10.658(2) V=2886(1)Å^3
	c=27.186(8) Z=4	c=25.39(1) Z=4	c=23.576(4) Z=4
Density (calcd)	1.075 g cm^{-3}	1.071 g cm^{-3}	1.088 g cm^{-3}
Space Group	$P2_1/c$	$P2_1/n$	$C2/c$
Absorption coefficent	0.66 cm^{-1}	0.66 cm^{-1}	0.67 cm^{-1}
Crystal size	0.40×0.36×0.36 mm	0.42×0.40×0.28 mm	0.44×0.40×0.40 mm
Scan type and speed		ω–2θ; 2.02—8.37 deg min^{-1}	
Scan range		1° below $K\alpha_1$ to 1° above $K\alpha_2$	
Background counting	stationary counts for one-half of scan time at each end of scan		
Collection range	h, k, $\pm l$; $2\theta_{max}$=42°	h, k, $\pm l$; $2\theta_{max}$=40°	h, k, $\pm l$; $2\theta_{max}$=45°
Unique data measured	2034	1635	1616
Observed data with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$, n	1661	1326	1382
Number of variables, p	190	190	169
$R_F=\sum\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$	0.093	0.105	0.045
Constant g in weighting scheme $w=[\sigma^2(F_o)+g\lvert F_o\rvert^2]^{-1}$	0.0020	0.0020	0.0015
$R_G=[\sum w(\lvert F_o\rvert-\lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.140	0.140	0.063
$S=[\sum w(\lvert F_o\rvert-\lvert F_c\rvert)^2/(n-p)]^{1/2}$	2.454	2.410	1.250
Residual extrema in final difference map	+0.48 to −0.30 e Å^{-3}	+0.36 to −0.41 e Å^{-3}	+0.13 to −0.13 e Å^{-3}

Table 2. Atomic Coordinates (×10^4) and Thermal Parameters[a] (Å^2×10^3) for Complexes I and II

Atom	I				II			
	x	y	z	U/U_{eq}	x	y	z	U/U_{eq}
Host Molecule								
O(1)	3769(3)	5467(6)	3430(1)	69(2)*	4620(8)	5052(5)	1760(3)	66(3)*
O(2)	1510(3)	5695(6)	3899(2)	67(2)*	8384(8)	4293(6)	1580(3)	69(3)*
N(1)	2553(3)	3299(7)	3082(2)	48(2)*	5395(8)	3553(6)	2286(3)	45(3)*
N(2)	2653(3)	3503(7)	4312(2)	50(2)*	6578(9)	3257(6)	1040(3)	49(3)*
C(1)	2942(4)	4391(8)	3450(2)	50(1)	5563(10)	4182(8)	1854(4)	42(2)
C(2)	1579(4)	2003(9)	3134(2)	58(2)	6565(12)	2498(7)	2381(4)	54(3)
C(3)	1874(6)	−111(10)	3026(3)	90(3)*	5505(15)	1383(9)	2459(5)	83(5)*
C(4)	586(5)	2721(12)	2821(3)	84(3)*	7767(15)	2707(10)	2827(5)	93(6)*
C(5)	3049(4)	3352(9)	2601(2)	60(2)	4225(11)	3842(8)	2701(4)	54(3)
C(6)	4209(5)	2554(13)	2633(3)	89(3)*	2348(13)	3689(10)	2506(5)	93(5)*
C(7)	2939(6)	5366(11)	2368(3)	84(3)*	4487(16)	5021(9)	2941(5)	85(5)*
C(8)	2290(4)	4541(9)	3908(2)	51(2)	6942(10)	3893(7)	1472(3)	45(2)
C(9)	3566(4)	2059(9)	4285(2)	63(2)	4813(12)	2863(8)	928(4)	61(3)
C(10)	3181(6)	48(10)	4415(3)	88(3)*	4747(16)	1534(8)	846(5)	89(5)*
C(11)	4587(5)	2737(14)	4600(3)	95(3)*	4045(14)	3508(10)	465(5)	89(5)*
C(12)	2102(5)	3691(10)	4778(2)	66(2)	7902(12)	3015(8)	643(4)	57(3)
C(13)	934(5)	2964(13)	4733(3)	93(3)*	9285(14)	2221(10)	884(5)	85(5)*
C(14)	2196(6)	5743(10)	4989(3)	82(3)*	8630(14)	4116(9)	410(4)	77(5)*
Guest Molecule								
O(3)	5310(4)	7804(10)	3878(2)	135(3)*	4702(8)	6813(6)	1065(3)	82(3)*
C(15)	6389(3)	7216(8)	3813(2)	89(2)	3113(5)	7249(5)	966(2)	55(3)
C(16)	6634(3)	5389(8)	3622(2)	101(3)	2952(5)	8354(5)	732(2)	58(3)
C(17)	7731(3)	4874(8)	3557(2)	109(3)	1334(5)	8816(5)	622(2)	62(3)
C(18)	8582(3)	6186(8)	3683(2)	106(3)	−124(5)	8172(5)	744(2)	54(3)
C(19)	8337(3)	8014(8)	3873(2)	96(2)	38(5)	7066(5)	977(2)	54(3)
C(20)	7240(3)	8529(8)	3938(2)	94(2)	1656(5)	6605(5)	1088(2)	56(3)
C(21)	9265(10)	9321(19)	3987(4)	186(7)*	−1876(14)	8693(10)	625(5)	87(5)*

a) Asterisk indicates equivalent isotropic temperature factor U_{eq} defined as 1/3 of the trace of the orthogonalised U matrix. The exponent of the isotropic temperature factor takes the form $-8\pi^2 U\sin^2\theta/\lambda^2$.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Thermal Parameters[a] ($Å^2 \times 10^3$) for Complex **III**

Atom	*x*	*y*	*z*	U_{eq}	Atom	*x*	*y*	*z*	U_{eq}
Host Molecule					Guest Molecule				
O(1)	3870(2)	5136(2)	2712(1)	64(1)	O(2)	4083(2)	6103(2)	3792(1)	76(1)
N	3753(2)	3675(2)	2014(1)	46(1)	C(8)	4911(2)	6975(2)	4017(1)	58(1)
C(1)	4336(2)	4398(2)	2437(1)	47(1)	C(9)	4849(3)	7514(3)	4540(1)	78(1)
C(2)	4350(2)	2768(2)	1703(1)	58(1)	C(10)	5668(3)	8388(3)	4786(1)	83(1)
C(3)	4218(3)	3125(3)	1068(1)	90(1)	C(11)	6549(3)	8762(3)	4521(1)	72(1)
C(4)	3939(3)	1426(2)	1778(1)	78(1)	C(12)	6590(2)	8224(3)	3997(1)	72(1)
C(5)	2462(2)	3744(2)	1850(1)	52(1)	C(13)	5781(2)	7341(2)	3744(1)	65(1)
C(6)	2037(3)	5000(2)	1578(1)	70(1)	C(14)	7455(4)	9701(3)	4804(2)	102(2)
C(7)	1891(3)	3376(3)	2344(1)	70(1)					

a) U_{eq} defined as 1/3 of the trace of the orthogonalised U matrix.

Table 4. Bond Distances (*l*/Å) and Angles for Complexes **I** and **II**

	I	**II**		**I**	**II**
O(1)-C(1)	1.248(7)	1.256(11)	O(2)-C(8)	1.231(7)	1.243(10)
N(1)-C(1)	1.314(7)	1.318(11)	N(1)-C(2)	1.490(7)	1.527(11)
N(1)-C(5)	1.472(7)	1.446(11)	N(2)-C(8)	1.359(7)	1.340(11)
N(2)-C(9)	1.489(7)	1.475(12)	N(2)-C(12)	1.473(8)	1.484(12)
C(1)-C)8)	1.518(8)	1.500(12)	C(2)-C(3)	1.526(9)	1.530(14)
C(2)-C(4)	1.513(8)	1.479(16)	C(5)-C(6)	1.504(8)	1.552(14)
C(5)-C(7)	1.522(9)	1.487(14)	C(9)-C(10)	1.504(9)	1.528(13)
C(9)-C(11)	1.532(9)	1.502(15)	C(12)-C(13)	1.498(9)	1.529(15)
C(12)-C(14)	1.521(9)	1.503(14)	O(3)-C(15)	1.388(7)	1.357(8)
C(19)-C(21)	1.456(13)		C(18)-C(21)		1.519(12)
C(1)-N(1)-C(2)	121.5(5)	119.3(7)	C(1)-N(1)-C(5)	121.1(4)	123.8(7)
C(2)-N(1)-C(5)	117.8(4)	116.7(7)	C(8)-N(2)-C(9)	120.9(5)	120.5(7)
C(8)-N(2)-C(12)	120.5(5)	121.0(7)	C(9)-N(2)-C(12)	118.4(4)	118.3(7)
O(1)-C(1)-N(1)	123.7(5)	121.4(8)	O(1)-C(1)-C(8)	117.0(5)	118.4(8)
N(1)-C(1)-C(8)	118.9(5)	120.2(7)	N(1)-C(2)-C(3)	110.7(5)	110.3(8)
N(1)-C(2)-C(4)	111.0(5)	111.4(8)	C(3)-C(2)-C(4)	112.8(6)	111.9(9)
N(1)-C(5)-C(6)	111.6(5)	110.5(8)	N(1)-C(5)-C(7)	111.2(5)	114.8(8)
C(6)-C(5)-C(7)	114.3(6)	110.8(8)	O(2)-C(8)-N(2)	124.3(5)	123.8(8)
O(2)-C(8)-C(1)	117.5(5)	116.0(7)	N(2)-C(8)-C(1)	118.0(5)	120.2(7)
N(2)-C(9)-C(10)	110.9(5)	110.9(8)	N(2)-C(9)-C(11)	110.3(5)	111.3(8)
C(10)-C(9)-C(11)	113.5(6)	111.5(9)	N(2)-C(12)-C(13)	112.0(5)	109.6(8)
N(2)-C(12)-C(14)	112.2(5)	112.8(8)	C(13)-C(12)-C(14)	112.8(6)	112.3(8)
O(3)-C(15)-C(16)	122.1(4)	118.9(4)	O(3)-C(15)-C(20)	117.9(4)	121.1(4)
C(18)-C(19)-C(21)	117.0(5)		C(17)-C(18)-C(21)		119.3(5)
C(20)-C(19)-C(21)	123.0(5)		C(19)-C(18)-C(21)		120.7(5)

Results and Discussion

Perspective views, each with atom labelling, of the asymmetric units in complexes **I** and **III** are shown in Figs. 1 and 2, respectively. Figure 1 is also applicable to complex **II**, except that C(21) is bonded to C(18) instead of C(19). The final atomic parameters are listed in Table 2 and 3,[11,12] and molecular dimensions tabulated in Tables 4 and 5.

The crystal structures of **I**—**III** are illustrated in Fig. 3—5, respectively. A common feature is the exclusive occurrence of host-guest, rather than guest-guest,* hydrogen bonding, giving rise to discrete molecular aggregates which are dimeric in **I** and **II** and trimeric [two-fold axis passing through the center of the C(1)-C(1)' bond] in **III**. In the two 1:1 com-

*Hydrogen bonding involving cresol molecules exclusively might be expected to yield a zigzag polymeric arrangement which fits the chennel structure of **IV**.

Table 5. Bond Distances (*l*/Å) and Angles for Complex **III**[a]

O(1)-C(1)	1.238(3)	N-C(1)	1.330(3)
N-C(2)	1.477(3)	N-C(5)	1.487(3)
C(1)-C(1)'	1.525(5)	C(2)-C(3)	1.519(4)
C(2)-C(4)	1.532(4)	C(5)-C(6)	1.522(3)
C(5)-C(7)	1.512(4)	O(2)-C(8)	1.369(3)
C(8)-C(9)	1.377(4)	C(8)-C(13)	1.373(4)
C(9)-C(10)	1.377(4)	C(10)-C(11)	1.375(5)
C(11)-C(12)	1.374(4)	C(11)-C(14)	1.510(4)
C(12)-C(13)	1.380(4)		
C(1)-N-C(2)	121.8(2)	C(1)-N-C(5)	120.2(2)
C(2)-N-C(5)	117.9(2)	O(1)-C(1)-N	123.9(2)
O(1)-C(1)-C(1)'	116.3(2)	N-C(1)-C(1)'	119.5(2)
N-C(2)-C(3)	111.3(2)	N-C(2)-C(4)	111.1(2)
C(3)-C(2)-C(4)	112.2(2)	N-C(5)-C(6)	112.3(2)
N-C(5)-C(7)	112.3(2)	C(6)-C(5)-C(7)	113.2(2)
O(2)-C(8)-C(9)	117.7(3)	O(2)-C(8)-C(13)	123.3(2)
C(9)-C(8)-C(13)	119.0(2)	C(8)-C(9)-C(10)	119.8(3)
C(9)-C(10)-C(11)	122.0(3)	C(10)-C(11)-C(12)	117.3(3)
C(10)-C(11)-C(14)	121.3(3)	C(12)-C(11)-C(14)	121.3(3)
C(11)-C(12)-C(13)	121.5(3)	C(8)-C(13)-C(12)	120.3(2)

a) Symmetry transformation for generating the primed atom: $1-x, y, 1/2-z$.

plexes, only one of the two amido groups of **1** is involved in acceptor hydrogen bonding [O(1)···O(3)= 2.694(8) and 2.67(1)Å, respectively], whereas both amide groups of the C_2 host molecule in **III** interact with the phenolic groups of a pair of *p*-cresol molecules [O(1)···O(2)=2.699(4)Å]. These modes of hydrogen bonding provide a rationale for the observed stoichiometries and infrared absorption spectra in the inclusion of *p*-cresol by **1**.

The oxamide host **1** adopts very similar configurations and molecular dimensions in this series of complexes, a planar bond configuration being found about each N atom (Tables 4 and 5). The O-C-C-O torsion angles take the values 91.8(6), 95.3(10) and −85.4(2)° for **I**—**III**, respectively, so that the two planar amide moieties of each host molecule behave as separate π systems with negligible conjugation across the central C-C single bond [1.518(8), 1.50(1), and 1.525(5) Å, respectively]. It is also noted that the involvement of either one or two amido groups in acceptor hydrogen bonding, as in complexes **II** and **III**, corresponds to a difference of about 10° (absolute value) in the O-C-C-O torsion angle.

Comparison of the present structures with that of the 1:1 complex (**IV**) of **1** with 1-methylnaphthalene (see Fig. 1 of Ref. 1) leads to the conclusion that the host system **1** adapts itself readily to the nature of the guest species present, forming crystalline lattices which are determined primarily by the bonding characteristics and steric requirement of the latter.

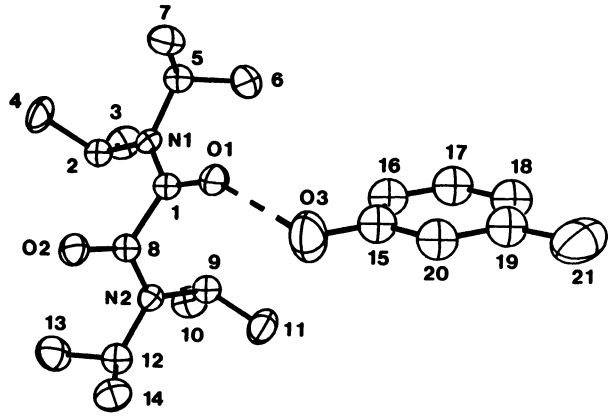


Fig. 1. Perspective view and atom labelling of the asymmetric unit in the 1:1 complex (**I**) of **1** with *m*-cresol. The atoms are represented as 30% thermal ellipsoids, and the hydrogen bond by a broken line. This figure also applies to the 1:1 complex (**II**) of **1** with *p*-cresol, with the modification that C(21) now bonds to C(18).

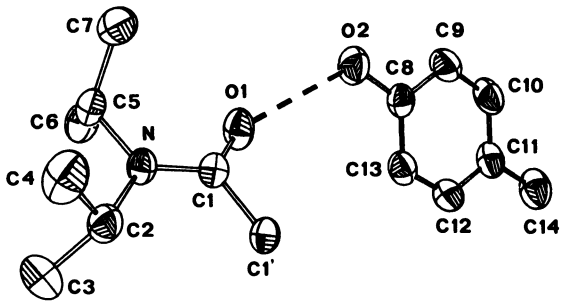


Fig. 2. Perspective view and atom labelling of the asymmetric unit in the 1:2 complex (**III**) of **1** with *p*-cresol. The atoms are represented as 35% thermal ellipsoids, and the hydrogen bond by a broken line. The primed atom is related to the unprimed one by the symmetry transformation $1-x, y, 1/2-z$.

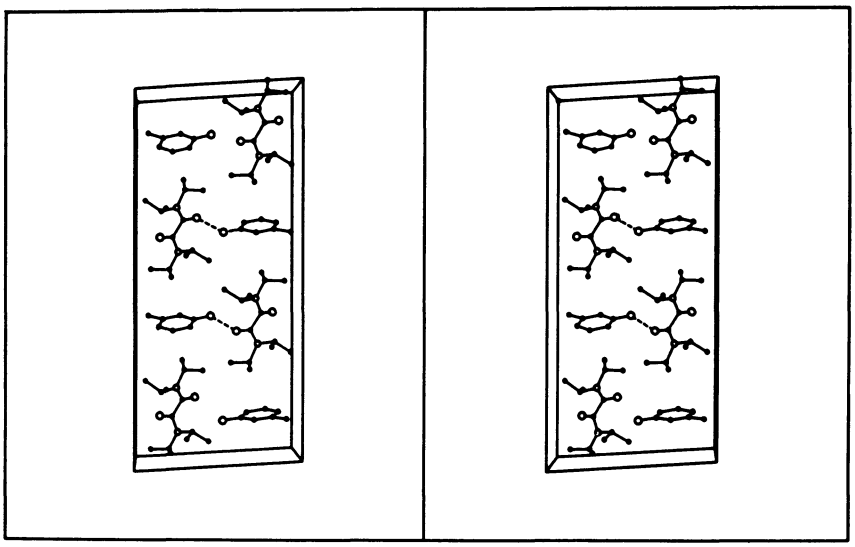


Fig. 3. Stereo view of the crystal structure of **1**·*m*-cresol, **I**. The origin of the unit cell lies at the upper left corner, with a pointing from left to right, b towards the reader, and c downwards. Hydrogen bonds are indicated by broken lines.

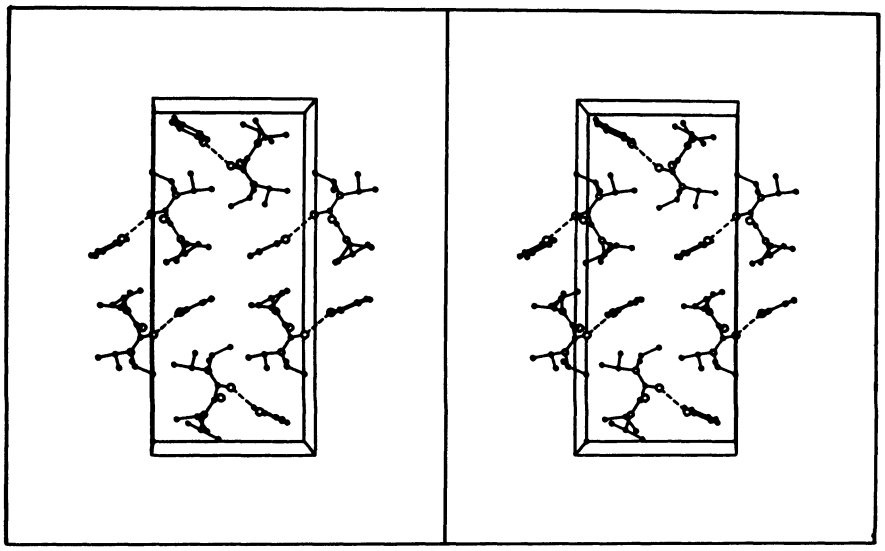


Fig. 4. Stereo view of the crystal structure of **1**·*p*-cresol, **II**. The origin of the unit cell lies at the lower left corner, with a pointing towards the reader, b from left to right, and c upwards. Hydrogen bonds are indicated by broken lines.

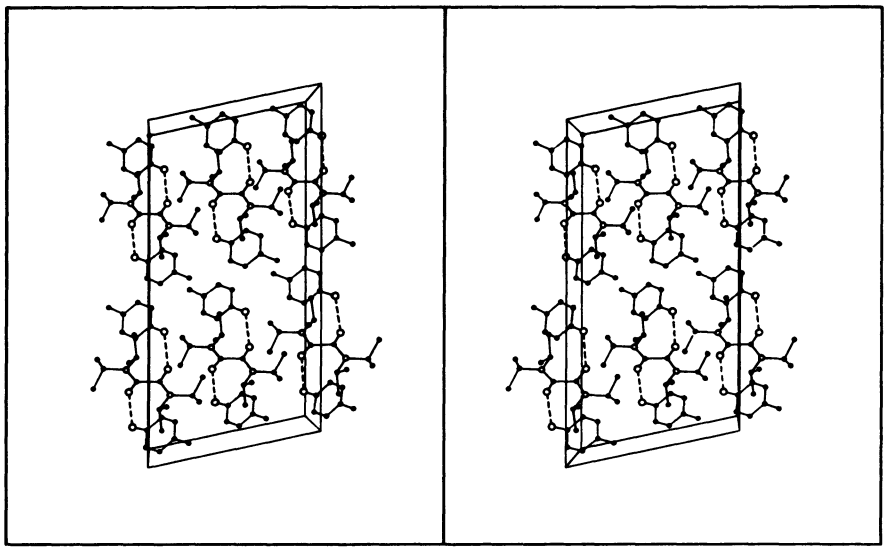


Fig. 5. Stereo view of the crystal structure of **1**·2*p*-cresol, **III**. The origin of the unit cell lies at the upper left corner, with a pointing from left to right, b towards the reader, and c downwards. Hydrogen bonds are indicated by broken lines.

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11) Tables of anisotropic thermal parameters, atomic parameters for hydrogen atoms, and structure factors have been deposited as Document No. 8626 at the Office of the Chemical Society of Japan.

12) The refined thermal parameters gave no evidence of non-stoichiometric ratio or disorder.