$V = 377,1$ (4) $Å^3$

$Z = 2$

0,375 × 0,075 × 0,062 mm

Farblos

Datensammlung

Enraf–Nonius CAD-4
  Diffraktometer
ω-Abtastung
Absorptionskorrektur:
  empirisch nach ψ-scans
  $T_{min} = 0,90$, $T_{max} = 1,0$
774 gemessene Reflexe
652 unabhängige Reflexe
491 beobachtete Reflexe
  $[F > 3\sigma(F)]$

$R_{int} = 0,020$
$\theta_{max} = 25°$
$h = -4 \rightarrow 4$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 9$
3 Kontrollreflexe
  Häufigkeit: 90 min
  Intensitätsschwankung:
  keine

Verfeinerung

Verfeinerung auf F
$R = 0,040$
$wR = 0,023$
$S = 1,5$
652 Reflexe
47 Parameter
H-Atome: ein gemeinsamer
  isotroper Temperaturfaktor

$w = 1/[\sigma^2(F_o)]$
$(\Delta/\sigma)_{max} = 0,13$
$\Delta\rho_{max} = 0,23$ e $Å^{-3}$
$\Delta\rho_{min} = -0,40$ e $Å^{-3}$
Extinktionskorrektur: keine
Atomformfaktoren aus
  Cromer & Mann (1968)

Datensammlung: CAD-4 Meßsoftware. Gitterverfeinerung: CAD-4 Meßsoftware. Datenreduktion: *XCAD4* (Harms, 1987). Lösung der Struktur mit Programmen: *SHELXTL* (Sheldrick, 1989). Verfeinerung der Struktur mit Programmen: *SHELXTL.*

Tabelle 1. *Atomkoordinaten und Parameter für den äquivalenten isotropen (Hamilton, 1959) bzw. isotropen (H-Atome) Temperaturfaktor* ($Å^2$)

$$U_{äq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{äq}$
S(1)	0,2689 (3)	0,13726 (8)	0,1318 (1)	0,0481 (3)
S(2)	0,0669 (3)	−0,09514 (8)	0,2252 (1)	0,0543 (4)
C(1)	0,4340 (9)	0,1268 (3)	0,3487 (4)	0,054 (1)
C(2)	0,0800 (8)	0,0065 (3)	0,0904 (3)	0,036 (1)
H(1)	0,541 (8)	0,198 (3)	0,379 (4)	0,075 (7)
H(2)	0,594 (9)	0,065 (3)	0,369 (4)	0,075 (7)
H(3)	0,252 (9)	0,114 (3)	0,413 (4)	0,075 (7)

Tabelle 2. *Bindungsabstände* (Å), *-winkel und -torsionwinkel* (°)

S(1)—C(1)	1,790 (4)	C(1)—H(1)	0,96 (3)
S(1)—C(2)	1,721 (4)	C(1)—H(2)	0,97 (4)
S(2)—C(2)	1,629 (3)	C(1)—H(3)	0,98 (3)
C(2)—C(2^i)	1,518 (4)		
C(1)—S(1)—C(2)	102,2 (2)	S(1)—C(2)—C(2^i)	112,5 (2)
S(1)—C(2)—S(2)	125,6 (2)	S(2)—C(2)—C(2^i)	121,9 (2)
S(2)—C(2)—S(1)—C(1)	0,5 (3)	S(2)—C(2)—C(2^i)—S(1^i)	0,0 (7)
S(1)—C(2)—C(2^i)—S(2^i)	0,0 (6)		

Symmetriebezeichnung: (i) $-x, -y, -z$.

Die kristalline Substanz haben wir von K. Hartke erhalten; sie war nach Hartke, Kissel, Quante & Matusch (1980) hergestellt worden.

Literatur

Bacher, A. D., Sens, I. & Müller, U. (1992). *Z. Naturforsch. Teil B,* **47,** pp. 702–705.
Cromer, D. & Mann, J. B. (1968). *Acta Cryst.* A24, 321–324.
Dougill, M. W. & Jeffrey, G. A. (1953). *Acta Cryst.* 6, 831.
Hamilton, W. C. (1959). *Acta Cryst.* 12, 609–610.
Harms, K. (1987). *XCAD4. Programm zur Datenreduktion von CAD4-Meßdaten.* Univ. Marburg, Deutschland.
Hartke, K., Kissel, T., Quante, J. & Matusch, R. (1980). *Chem. Ber.* 113, 1898–1906.
Kiel, G., Dräger, M. & Reuter, U. (1974). *Chem. Ber.* 107, 1483–1487.
Lund, H., Hoyer, E. & Hazell, R. (1982). *Acta Chem. Scand.* B36, 207–211.
Niemer, U., Mennemann, K. & Mattes, R. (1978). *Chem. Ber.* 111, 2113–2117.
Niemer, U. & Mattes, R. (1978). *Chem. Ber.* 111, 2118–2122. Dort weitere Literatur.
Sheldrick, G. M. (1989). *SHELXTL-Plus, Release* 4,0. *Programme zur Kristallstrukturbestimmung.* Siemens Analytical X-ray Instruments, Inc., Madison WI, VStA.

18-Crown-6–Methyl 2-Naphthalenesulfonate (1/2) Complex

ROBERT CHÊNEVERT AND RENÉ GAGNON

Département de Chimie, Université Laval, Québec (Qué.), Canada G1K 7P4

MICHEL SIMARD*

Département de Chimie, Université de Montréal, CP 6128, Succ. A, Montréal (Qué.), Canada H3C 3J7

Abstract

The guest molecules are coordinated above and below the crown (1,4,7,10,13,16-hexaoxacyclooctadecane) in such a way that the dipoles are compensated. The methyl group of each sulfonate yields two C—H···O weak contacts of 2.63 (3) and 2.70 (3) Å; the third methyl H atom is directed away from the crown ether. The 18-crown-6 molecule has approximately D_{3d} symmetry and the sulfonate molecule is disordered over two orientations (rotation of C—S bonds) of unequal proportion (80/20).

Comment

The complex was prepared in 85% yield by mixing methyl 2-naphthalenesulfonate (1) and 18-crown-6 (2) in tetrahydrofuran followed by addition of diethyl ether and cooling. The complex was recrystallized from diethyl ether. The melting point of the complex (356–357 K) is above those of the crown (314–318 K) and the sulfonate (liquid at room temperature).

(1)   (2)
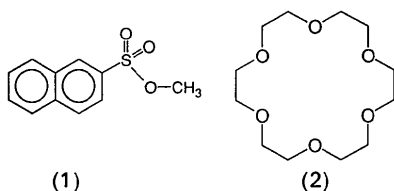
The study of well defined complexes formed between crown ethers and neutral organic molecules promotes the understanding of the molecular recognition of neutral molecules, which is a key process in biological systems.

The title compound belongs to a small group of complexes where hydrogen-bond-like interactions

(Desiraju, 1991) play a significant role in stabilizing the complexes through multiple C—H···O interactions (Vögtle, Müller & Watson, 1985).
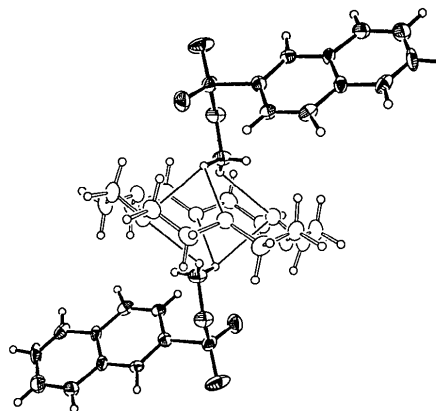

Fig. 2. *ORTEP* (Johnson, 1965) view of the association of the 2:1 complex. Hydrogen-bond-like interactions are represented by thin bonds.

Experimental

Crystal data

$2C_{11}H_{10}O_3S.C_{12}H_{24}O_6$	Cu $K\alpha$ radiation
$M_r = 708.84$	$\lambda = 1.54178$ Å
Monoclinic	Cell parameters from 24
$P2_1/c$	reflections
$a = 15.220$ (5) Å	$\theta = 40.0$–$44.0°$
$b = 8.229$ (5) Å	$\mu = 1.85$ mm^{-1}
$c = 15.717$ (5) Å	$T = 190$ K
$\beta = 116.84$ (3)°	Trapezoidal
$V = 1756.4$ (13) Å^3	0.46 (01$\bar{1}$, 0$\bar{1}$0) × 0.25
$Z = 2$	(001, 00$\bar{1}$) × 0.22 (100,
$D_x = 1.340$ Mg m^{-3}	100) mm
	White

Data collection

Enraf–Nonius diffractometer	$\theta_{max} = 140°$
$\omega/2\theta$ scans	$h = -12 \rightarrow 12$
Absorption correction:	$k = 0 \rightarrow 6$
none	$l = 0 \rightarrow 13$
7493 measured reflections	6 standard reflections
1976 independent reflections	frequency: 60 min
1846 observed reflections	intensity variation: +24 to
$[I \geq 3\sigma(I)]$	-16%
$R_{int} = 0.040$	

Refinement

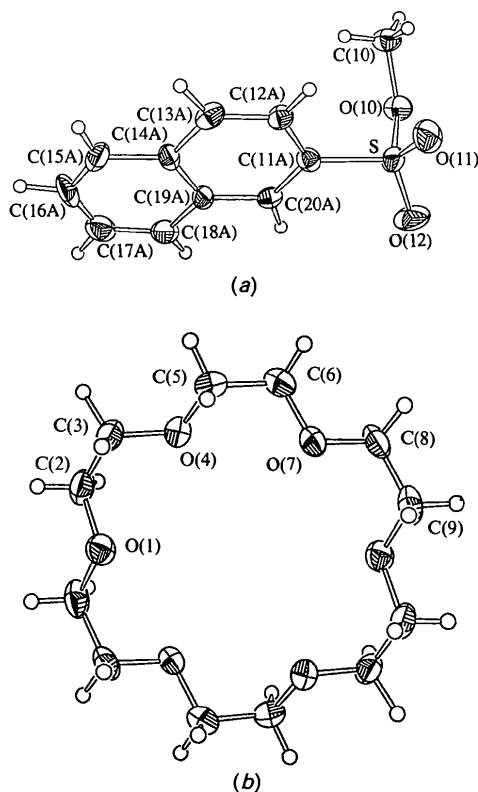|	
Refinement on F	$(\Delta/\sigma)_{max} = 0.38$
$R = 0.040$	$\Delta\rho_{max} = 0.18$ e Å^{-3}
$wR = 0.055$	$\Delta\rho_{min} = -0.36$ e Å^{-3}
$S = 2.88$	Atomic scattering factors
1846 reflections	from Cromer & Liberman
352 parameters	(1970)
$w = 1/[\sigma^2(F) + 0.0001F^2]$	

Fig. 1. *ORTEP* (Johnson, 1965) view of the two molecules (sulfonate, major model only) with the numbering scheme adopted. Ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S	0.28850 (5)	0.73099 (8)	0.04800 (5)	0.039
O(1)	0.15424 (12)	0.2713 (2)	0.1124 (2)	0.040
O(4)	0.09520 (11)	0.5303 (2)	0.19955 (11)	0.040
O(7)	−0.01686 (12)	0.7939 (2)	0.08107 (11)	0.039
O(10)	0.17508 (13)	0.7317 (2)	−0.01818 (13)	0.045
O(11)	0.30781 (14)	0.6862 (3)	0.14108 (13)	0.060
O(12)	0.32062 (15)	0.8832 (3)	0.03038 (18)	0.075
C(2)	0.1647 (2)	0.2711 (4)	0.2067 (2)	0.045
C(3)	0.1836 (2)	0.4379 (4)	0.2452 (4)	0.043
C(5)	0.1093 (2)	0.6948 (4)	0.2276 (2)	0.047
C(6)	0.0116 (2)	0.7796 (4)	0.1794 (2)	0.050
C(8)	−0.1095 (2)	0.8715 (4)	0.0324 (2)	0.045
C(9)	−0.1338 (2)	0.8863 (3)	−0.0707 (2)	0.048
C(10)	0.1148 (2)	0.5974 (4)	−0.0142 (2)	0.045
C(11A) †	0.3309 (3)	0.5690 (7)	0.0032 (3)	0.033
C(12A)	0.3406 (2)	0.4127 (4)	0.0430 (2)	0.033
C(13A)	0.3713 (2)	0.2860 (4)	0.0064 (2)	0.038
C(14A)	0.3932 (2)	0.3084 (6)	−0.0715 (3)	0.035
C(15A)	0.4227 (3)	0.1821 (5)	−0.1131 (3)	0.044
C(16A)	0.4379 (5)	0.2067 (10)	−0.1852 (5)	0.059
C(17A)	0.4282 (3)	0.3599 (7)	−0.2283 (3)	0.059
C(18A)	0.4020 (2)	0.4882 (6)	−0.1908 (3)	0.046
C(19A)	0.3836 (3)	0.4675 (6)	−0.1097 (3)	0.033
C(20A)	0.3521 (2)	0.5963 (5)	−0.0721 (2)	0.032
C(11B)	0.3350 (13)	0.611 (2)	−0.0148 (14)	0.019
C(12B)	0.3385 (10)	0.708 (2)	−0.0863 (10)	0.033
C(13B)	0.3721 (8)	0.6246 (15)	−0.1470 (9)	0.038
C(14B)	0.3931 (12)	0.453 (2)	−0.1317 (14)	0.025
C(15B)	0.4206 (16)	0.375 (3)	−0.1974 (15)	0.065
C(16B)	0.445 (2)	0.198 (3)	−0.1973 (19)	0.039
C(17B)	0.4320 (12)	0.120 (2)	−0.1065 (11)	0.027
C(18B)	0.4076 (10)	0.199 (2)	−0.0436 (12)	0.051
C(19B)	0.3882 (9)	0.3632 (18)	−0.0544 (10)	0.016
C(20B)	0.3564 (10)	0.466 (2)	0.0057 (10)	0.035

† Labels A and B stand for the major (occupancy 0.80) and minor (occupancy 0.20) disorder models, respectively.

Table 2. Selected bond lengths (Å), bond angles (°) and torsion angles (°)

S—O(10)	1.562 (2)	S—C(11A)	1.761 (5)
S—O(11)	1.405 (2)	S—C(11B)	1.75 (2)
S—O(12)	1.416 (2)	O(10)—C(10)	1.455 (4)
O(1)—C(2)	1.418 (3)	C(5)—C(6)	1.502 (5)
O(1)—C(9^i)	1.422 (3)	C(6)—O(7)	1.409 (3)
C(2)—C(3)	1.475 (4)	O(7)—C(8)	1.417 (4)
C(3)—O(4)	1.425 (4)	C(8)—C(9)	1.495 (4)
O(4)—C(5)	1.410 (4)		
O(10)—S—O(11)	110.06 (12)	O(10)—S—O(12)	104.00 (13)
O(10)—S—C(11A)	103.35 (18)	O(10)—S—C(11B)	103.5 (6)
O(11)—S—O(12)	120.48 (14)	S—O(10)—C(10)	119.81 (18)
O(11)—S—C(11A)	106.00 (19)	O(11)—S—C(11B)	119.4 (6)
O(12)—S—C(11A)	111.70 (19)	O(12)—S—C(11B)	97.1 (6)
S—C(11A)—C(12A)	119.8 (4)	S—C(11B)—C(12B)	107.9 (13)
S—C(11A)—C(20A)	119.4 (4)	S—C(11B)—C(20B)	121.3 (15)
C(2)—O(1)—C(9^i)	112.2 (2)	C(5)—C(6)—O(7)	109.6 (2)
O(1)—C(2)—C(3)	109.7 (2)	C(6)—O(7)—C(8)	111.6 (2)
C(2)—C(3)—O(4)	109.0 (2)	O(7)—C(8)—C(9)	108.7 (2)
C(3)—O(4)—C(5)	112.3 (2)	O(1^i)—C(9)—C(8)	108.7 (2)
O(4)—C(5)—C(6)	108.2 (2)		

O(1)—C(2)—C(3)—O(4)	72.3 (3)
C(2)—C(3)—O(4)—C(5)	−175.6 (2)
C(3)—O(4)—C(5)—C(6)	−177.4 (2)
O(4)—C(5)—C(6)—O(7)	−70.7 (3)
C(5)—C(6)—O(7)—C(8)	179.2 (2)
C(6)—O(7)—C(8)—C(9)	178.6 (2)
O(7)—C(8)—C(9)—O(1^i)	69.9 (3)
C(8)—C(9)—O(1^i)—C(2^i)	−171.9 (2)
C(9)—O(1^i)—C(2^i)—C(3^i)	178.8 (2)

Symmetry code: (i) $-x$, $1-y$, $-z$.

Table 3. Bond lengths (Å) and angles (°) related to the hydrogen-bond-like interactions

O(10)—C(10)· · ·O(1)	135.36 (18)	O(10)—C(10)· · ·H(103)	106 (2)
O(10)—C(10)· · ·O(4)	118.88 (17)	H(101)—C(10)· · ·H(102)	117 (3)
O(10)—C(10)· · ·O(4^i)	124.66 (17)	H(101)—C(10)· · ·H(103)	98 (3)
O(10)—C(10)· · ·H(101)	106 (2)	H(102)—C(10)· · ·H(103)	119 (3)
O(10)—C(10)· · ·H(102)	110 (2)		
C(2)—O(1)· · ·C(10)	123.13 (17)	C(2)—O(1)· · ·H(101)	109.4 (7)
C(9^i)—O(1)· · ·C(10)	122.18 (16)	C(9^i)—O(1)· · ·H(101)	136.5 (7)
C(3)—O(4)· · ·C(10)	95.50 (15)	C(3)—O(4)· · ·H(101)	87.9 (7)
C(5)—O(4)· · ·C(10)	94.63 (16)	C(5)—O(4)· · ·H(101)	94.8 (7)
C(3)—O(4)· · ·C(10^i)	125.38 (16)	C(3)—O(4)· · ·H(102^i)	112.9 (6)
C(5)—O(4)· · ·C(10^i)	121.33 (16)	C(5)—O(4)· · ·H(102^i)	132.6 (6)

D—H· · ·A	D· · ·H	H—A	D· · ·A	D—H· · ·A
C(10)—H(101)· · ·O(1)	0.94 (3)	2.63 (3)	3.231 (3)	122 (2)
C(10)—H(101)· · ·O(4)	0.94 (3)	2.72 (4)	3.528 (3)	148 (3)
C(10)—H(101)· · ·O(4^i)	0.95 (3)	2.70 (3)	3.376 (3)	128 (2)
C(10)—H(103)	0.94 (3)			

Symmetry code: (i) $-x$, $1-y$, $-z$.

The structure was solved by direct methods using *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Difference Fourier syntheses were carried out using *SHELX*76 (Sheldrick, 1976) and the stereodrawing was obtained using *ORTEP* (Johnson, 1965). The disorder model was introduced to account for high residual peaks in the naphthalene vicinity, with occupancies tied and initially refined (major = 0.80, minor = 0.20), and then fixed in final refinement cycles. Non-H atoms were refined anisotropically; minor disorder and H atoms isotropically. H atoms were found from a difference Fourier map and/or calculated. Minor-occupancy H atoms were introduced at ideal positions (C—H = 0.95 Å) with B_{iso} refined; major-occupancy H atoms were refined. The secondary-extinction coefficient was not refined. Scattering curves for the non-H atoms were taken from Cromer & Mann (1968) and those for the H atoms from Stewart, Davidson & Simpson (1965). Anomalous-dispersion contributions (f' and f'') were from Cromer & Liberman (1970).

References

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A24, 321–324.
Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* 53, 1891–1898.
Desiraju, G. R. (1991). *Acc. Chem. Res.* 24, 290–296.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* 22, 384–387.
Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Vögtle, F., Müller, W. M. & Watson, W. H. (1985). *Top. Curr. Chem.* **125**, 131–164.

Structures of Ethyl 2-Cyano-3-(4-dimethylaminophenyl)propenoate (I) and Ethyl 2-Cyano-3-(4-hydroxy-3-methoxyphenyl)propenoate (II)

Shi Jianqiu, Su Genbo and He Youping

Fujian Institute of Research on the Structure of Matter, Academia Sinica, Fuzhou 350002, People's Republic of China

Abstract

The title compounds were prepared as part of a study of ethyl cyanoacetate derivatives which were obtained by condensation of an aldehyde and ethyl cyanoacetate in the presence of a small amount of
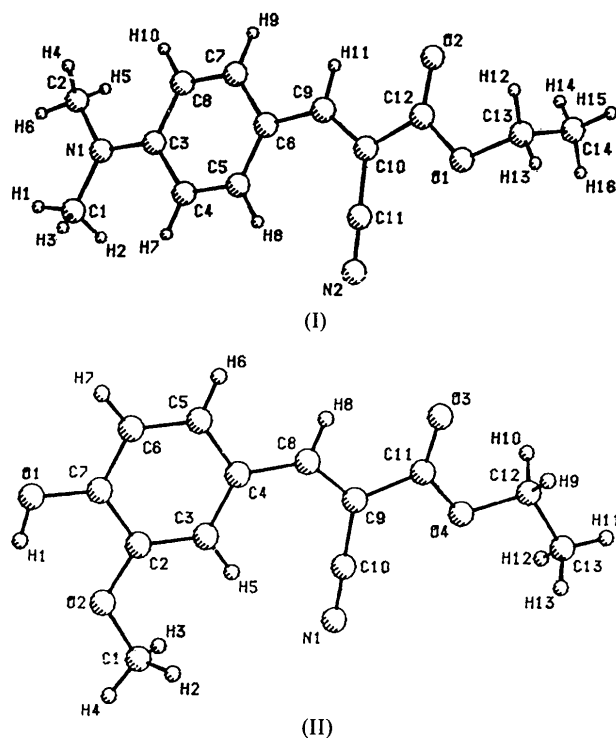
piperidine. The crystal structures of (I) and (II) have been determined; they belong to space groups $P\bar{1}$ and $P2_1/n$, respectively. The molecules of compound (II) are linked by O—$H\cdots O^i$ hydrogen bonds [symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$].

Comment

Methyl 2-cyano-3-(2-methoxyphenyl)propenoate (Nakatani, Hayashi & Hidaka, 1992) crystallizes in a non-centrosymmetric space group and has large second-harmonic generation (SHG) efficiencies. We have synthesized a series of substituted α-cyano-cinnamic acid esters, of which the title compounds are two.

This paper reports the results of the crystal structure analyses that allowed determination of the configuration at the substituted α-cyanocinnamic acid

(I)

(II)

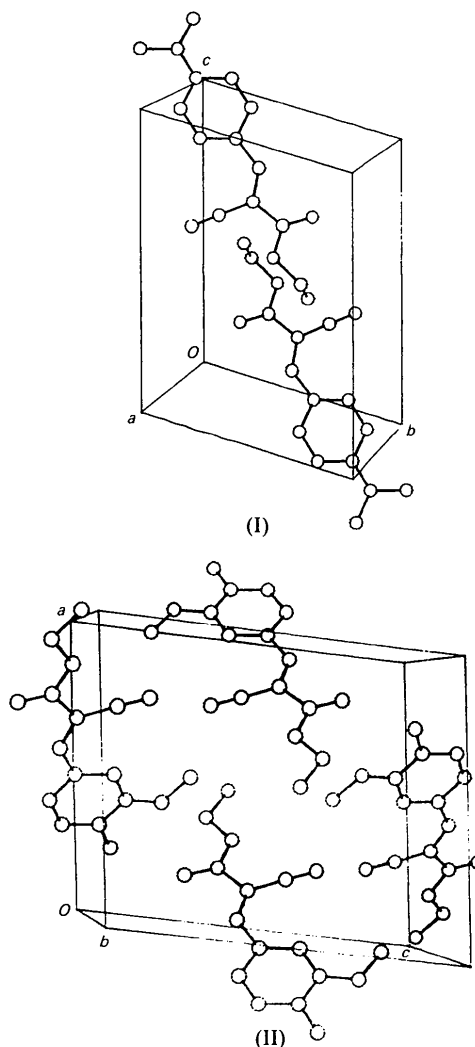Fig. 1. Structure of compounds (I) and (II).

Fig. 2. Packing of molecules in the unit cell for compound (I) and compound (II).