It was noted that the resolution of close-lying reflections was improved by the partial closure of the vertical diffractometer after-slits. A new data collection over four octants was carried out under these conditions but there appeared to be no obvious solution for any of the four possible space groups.

Packing considerations led ultimately to the structure being solved. The molecules cannot be both simultaneously linear, parallel to **y** and packed end-to-end, as this would require a **b** repeat of *ca* 100 Å. Thus, the alkane chains, if linear or nearly linear, must make an angle of about 40° with the *y* axis. Moreover, as seen in **y** projection, the chains cannot lie parallel to the *x* or *z* axes because those in adjacent cells would conflict. Thus, in this projection, the alkane chains must make substantial angles with both the *x* and *z* axes. With such chain orientation, the **b** spacing of 67 Å could be more readily explained. To overcome uncertainty in the space group, the data were indexed as belonging to the monoclinic space group $P2_1$. The *E* map corresponding to the highest figure of merit was promising. It showed, in addition to two prominent peaks for Br separated by **b**/2, both isolated atoms and short isolated lengths of zigzag chains, each of three or four atoms (37 peaks in all). Guided by the above packing considerations, it was found that when suitably translated parallel to **x** and/or **z** into neighbouring cells, 26 of these peaks became part (with many gaps) of just two zigzag chains; the remaining peaks proved spurious. Refinement by least squares and ΔF maps proceeded slowly to reveal the whole structure (36 C atoms in each of two molecules per cell) in space group $P2_1$. It immediately gave the missing symmetry elements, showing the true space group to be unambiguously $P2_12_12$ (No. 18). In this space group, the Br^- ion and N atom are in special positions $(0,\frac{1}{2},z_{\rm Br})$ and $(0,0,z_{\rm N})$. Only 18 of the 36 C atoms found in $P2_1$ are independent in the true space group as the molecule possesses a diad axis.

After making the necessary change in the origin of the coordinates, the requisite atomic positions obtained from the $P2_1$ structure were refined in $P2_12_12$. The Br^-, N and C atomic positions were obtained by anisotropic least-squares refinement. H-atom positions were allocated to calculated positions using C—H and N—H distances of 1.08 Å, with isotropic displacement parameters. Intensity data were also refined for secondary extinction. The high residuals and poor goodness-of-fit can be traced to the large values of $R_{\rm int}$ referred to above. These, in turn, certainly result from the poor quality of the crystal. Absorption corrections were applied to the intensity data, but these resulted in higher residuals, possibly due to uncertainty in the true thickness of the very thin crystal plate used.

A four-circle diffractometer system (Grant & Gabe, 1974) was used for data collection and cell refinement, and *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) was used for all calculations. Molecular graphics were obtained using *ORTEP* (Johnson, 1965).

The sample of the title compound was kindly prepared by Dr A. W. Parkins.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1031). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 194–197

4-(4-*n*-Heptylbenzoyloxy)benzoic Acid

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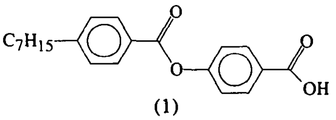
(*Received 18 May 1995; accepted 19 July 1995*)

Abstract

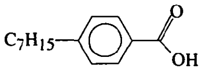
In the title compound, $C_{21}H_{24}O_4$, the molecules exist as hydrogen-bonded dimers. The hydrogen bonds occur pairwise, involve the carboxylic acid groups and are of the form $C{=}O\cdots HO{-}C$. The $O\cdots O$ distances are 2.53 (1) and 2.59 (1) Å.

Comment

The asymmetric unit of the title compound, (1), contains two independent molecules, which exhibit both similarities with and differences from molecules of 4-*n*-heptylbenzoic acid, (2), a simpler analogue of (1). The similarities (Fig. 1) include the extended all-*trans* con-



(1)



(2)

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formation of the *n*-heptyl chains and the coplanarity of the CO_2H groups with their adjacent aromatic rings. The relative orientations of the alkyl chain and the attached aromatic ring, however, are different. In compound (2), these moieties are approximately orthogonal (Blake, Bruce, Fallis, Parsons & Schröder, 1995), while in (1), atom C6*A* is rotated by −23 (2)° from planarity with C13*A* and atom C6*B* by 56 (2)° from the C7*B*, C8*B*, C13*B* plane.

The two aromatic rings in each molecule of (1) are twisted with respect to each other, largely due to torsions about the O15*A*—C16*A* and O15*B*—C16*B* bonds [C14*A*—O15*A*—C16*A*—C17*A* −60.6 (12) and C14*B*—O15*B*—C16*B*—C17*B* −74.8 (11)°]. A possible reason for this is avoidance of the unfavourable steric interactions of 2.21 and 2.13 Å which would arise between atom pairs O14*A*/H21*A* and O14*B*/H21*B*, respectively, were they coplanar.

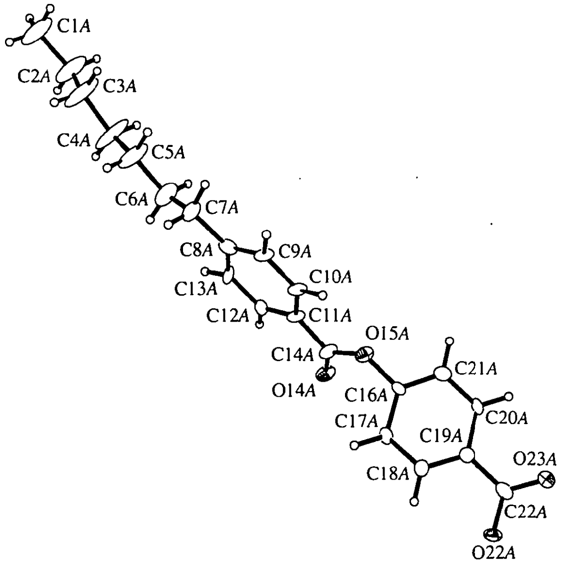

Fig. 1. A view of one of the two independent molecules of (1) in the asymmetric unit showing the atom-numbering scheme used. Atoms of the second molecule carry the suffix *B*. Displacement ellipsoids represent 30% electron probability and the H atoms shown have arbitrary radii. The H atoms of the carboxylic acid groups could not be located.

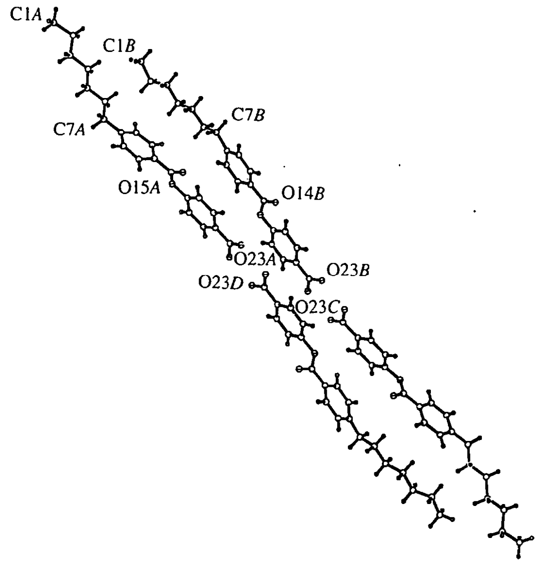

Fig. 2. Head-to-head hydrogen-bonded dimers of (1). Hydrogen bonding occurs between molecules of types *A* and *D* (defined by their suffix letters), and types *B* and *C*. Type *A* is related to type *C* and type *B* to type *D* by the symmetry operation ($1-x$, $1-y$, $2-z$); O22*A*···O23*D* 2.53 (1) and O22*B*···O23*C* 2.59 (1) Å.

Experimental

4-*n*-Heptylbenzoyl chloride (Lancaster synthesis) was dissolved in dry CH_2Cl_2. Benzyl 4-hydroxybenzoate (1.1 eq., Aldrich) and pyridine (1.1 eq.) were added and the solution was stirred under an N_2 atmosphere for 1 h, before being washed with 0.5 *M* HCl, saturated $NaHCO_3$ and brine. The organic layer was separated, dried and the solvent removed. The residue was dissolved in tetrahydrofuran. Palladium (5%) on carbon was added and H_2 gas passed through the solution at atmospheric pressure for 3 h. Filtration and removal of solvent afforded compound (1) as a white solid. Recrystallization from hot acetone yielded analytically pure material. Crystals for diffraction studies were grown by slow evaporation from a CH_2Cl_2 solution diluted with *n*-heptane.

Crystal data

$C_{21}H_{24}O_4$
$M_r = 340.40$
Monoclinic
$P2_1/c$
$a = 31.26\,(3)$ Å
$b = 7.500\,(11)$ Å
$c = 15.790\,(14)$ Å
$\beta = 99.78\,(7)°$
$V = 3648\,(7)$ Å^3
$Z = 8$
$D_x = 1.240$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 13 reflections
$\theta = 9.5–18.5°$
$\mu = 0.085$ mm^{-1}
$T = 150.0\,(2)$ K
Plate
0.58 × 0.35 × 0.08 mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer
ω scans with scan width ($1.0 + 0.35\tan\theta$)°
Absorption correction: none
2900 measured reflections
2900 independent reflections

1055 observed reflections [$I > 2\sigma(I)$]
$\theta_{max} = 19.99°$
$h = 0 \rightarrow 30$
$k = -7 \rightarrow 0$
$l = -15 \rightarrow 7$
3 standard reflections
frequency: 60 min
intensity decay: 2.5%

Refinement

Refinement on F^2
$R(F) = 0.1078$
$wR(F^2) = 0.3500$
$S = 1.051$

$(\Delta/\sigma)_{max} = 0.102$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}
Extinction correction: none

2882 reflections
453 parameters
$w = 1/[\sigma^2(F_o^2) + (0.14P)^2 + 1.06P]$
where $P = (F_o^2 + 2F_c^2)/3$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1*A*	0.0125 (4)	0.678 (3)	−0.3459 (7)	0.160 (8)
C2*A*	0.0332 (4)	0.6156 (19)	−0.2564 (7)	0.157 (6)
C3*A*	0.0620 (4)	0.749 (2)	−0.2104 (6)	0.140 (5)
C4*A*	0.0798 (4)	0.701 (2)	−0.1176 (6)	0.138 (5)
C5*A*	0.1160 (3)	0.8117 (19)	−0.0729 (6)	0.106 (5)
C6*A*	0.1377 (3)	0.7649 (16)	0.0163 (6)	0.081 (4)
C7*A*	0.1766 (3)	0.8683 (15)	0.0512 (5)	0.068 (4)
C8*A*	0.2027 (2)	0.8224 (13)	0.1358 (5)	0.039 (3)
C9*A*	0.2460 (2)	0.8750 (12)	0.1602 (5)	0.033 (3)
C10*A*	0.2698 (3)	0.8378 (11)	0.2398 (5)	0.032 (3)
C11*A*	0.2516 (2)	0.7379 (12)	0.3007 (4)	0.030 (3)
C12*A*	0.2091 (2)	0.6857 (12)	0.2769 (5)	0.033 (3)
C13*A*	0.1849 (3)	0.7275 (13)	0.1980 (5)	0.043 (3)
C14*A*	0.2750 (2)	0.6986 (13)	0.3872 (5)	0.039 (3)
O14*A*	0.2594 (2)	0.6214 (9)	0.4409 (4)	0.046 (2)
O15*A*	0.3174 (2)	0.7475 (9)	0.3981 (4)	0.040 (2)
C16*A*	0.3436 (2)	0.7143 (13)	0.4795 (5)	0.036 (3)
C17*A*	0.3325 (3)	0.7942 (12)	0.5519 (5)	0.032 (3)
C18*A*	0.3614 (2)	0.7744 (13)	0.6274 (5)	0.039 (3)
C19*A*	0.4000 (2)	0.6857 (13)	0.6314 (4)	0.036 (3)
C20*A*	0.4089 (3)	0.6037 (12)	0.5561 (5)	0.035 (3)
C21*A*	0.3806 (2)	0.6227 (12)	0.4798 (5)	0.035 (3)
C22*A*	0.4307 (3)	0.6688 (13)	0.7140 (5)	0.037 (3)
O22*A*	0.4222 (2)	0.7594 (9)	0.7778 (4)	0.045 (2)
O23*A*	0.4665 (2)	0.5896 (9)	0.7186 (4)	0.046 (2)
C1*B*	0.0611 (5)	0.290 (2)	0.0328 (6)	0.148 (7)
C2*B*	0.0761 (4)	0.337 (2)	0.1271 (7)	0.126 (5)
C3*B*	0.1132 (4)	0.237 (2)	0.1658 (6)	0.127 (5)
C4*B*	0.1286 (3)	0.2703 (19)	0.2611 (6)	0.097 (5)
C5*B*	0.1712 (3)	0.1938 (17)	0.2962 (6)	0.075 (4)
C6*B*	0.1905 (3)	0.2165 (18)	0.3897 (6)	0.074 (4)
C7*B*	0.2355 (3)	0.1530 (18)	0.4124 (5)	0.072 (4)
C8*B*	0.2592 (2)	0.1847 (14)	0.5013 (5)	0.038 (3)
C9*B*	0.3003 (2)	0.2619 (12)	0.5167 (5)	0.037 (3)
C10*B*	0.3241 (3)	0.2759 (13)	0.5981 (5)	0.036 (3)
C11*B*	0.3079 (2)	0.2083 (12)	0.6696 (4)	0.027 (2)
C12*B*	0.2667 (2)	0.1356 (12)	0.6552 (5)	0.031 (3)
C13*B*	0.2423 (3)	0.1259 (14)	0.5734 (5)	0.041 (3)
C14*B*	0.3330 (2)	0.2084 (12)	0.7575 (5)	0.031 (3)
O14*B*	0.3220 (2)	0.1327 (9)	0.8172 (4)	0.050 (2)
O15*B*	0.3700 (2)	0.3058 (9)	0.7632 (4)	0.039 (2)
C16*B*	0.3987 (2)	0.3025 (12)	0.8429 (5)	0.030 (3)
C17*B*	0.3869 (3)	0.3999 (13)	0.9102 (5)	0.037 (3)
C18*B*	0.4160 (2)	0.4039 (12)	0.9861 (5)	0.030 (3)
C19*B*	0.4555 (2)	0.3208 (12)	0.9955 (4)	0.030 (3)
C20*B*	0.4657 (3)	0.2252 (12)	0.9240 (5)	0.037 (3)
C21*B*	0.4366 (2)	0.2174 (13)	0.8479 (5)	0.036 (3)
C22*B*	0.4869 (2)	0.3240 (12)	1.0774 (5)	0.031 (3)
O22*B*	0.4770 (2)	0.4147 (9)	1.1406 (4)	0.045 (2)
O23*B*	0.5217 (2)	0.2383 (9)	1.0861 (4)	0.048 (2)

Table 2. *Selected geometric parameters (Å, °)*

C14*A*—O14*A*	1.197 (9)	C14*B*—O14*B*	1.201 (9)
C14*A*—O15*A*	1.358 (8)	C14*B*—O15*B*	1.356 (9)
O15*A*—C16*A*	1.424 (8)	O15*B*—C16*B*	1.417 (8)
C22*A*—O23*A*	1.258 (9)	C22*B*—O23*B*	1.250 (9)
C22*A*—O22*A*	1.280 (9)	C22*B*—O22*B*	1.289 (9)
O14*A*—C14*A*—O15*A*	123.2 (7)	C9*B*—C10*B*—C11*B*	120.6 (7)
O14*A*—C14*A*—C11*A*	124.0 (7)	O14*B*—C14*B*—O15*B*	123.9 (7)
O15*A*—C14*A*—C11*A*	112.6 (7)	O14*B*—C14*B*—C11*B*	124.2 (7)
C14*A*—O15*A*—C16*A*	117.9 (6)	O15*B*—C14*B*—C11*B*	112.0 (7)
C21*A*—C16*A*—O15*A*	117.2 (7)	C14*B*—O15*B*—C16*B*	116.9 (6)
C17*A*—C16*A*—O15*A*	118.8 (7)	C21*B*—C16*B*—O15*B*	118.8 (7)
O23*A*—C22*A*—O22*A*	120.5 (7)	C17*B*—C16*B*—O15*B*	117.4 (7)
O23*A*—C22*A*—C19*A*	121.7 (7)	O23*B*—C22*B*—O22*B*	120.4 (7)
O22*A*—C22*A*—C19*A*	117.0 (7)	O23*B*—C22*B*—C19*B*	121.4 (8)
C10*B*—C9*B*—C8*B*	122.2 (7)	O22*B*—C22*B*—C19*B*	118.2 (7)

C6*A*—C7*A*—C8*A*—C9*A*	159.4 (10)
C6*A*—C7*A*—C8*A*—C13*A*	−22.7 (16)
C12*A*—C11*A*—C14*A*—O14*A*	0.2 (15)
C10*A*—C11*A*—C14*A*—O14*A*	176.4 (10)
C12*A*—C11*A*—C14*A*—O15*A*	175.5 (8)
C10*A*—C11*A*—C14*A*—O15*A*	−8.3 (13)
O14*A*—C14*A*—O15*A*—C16*A*	−4.0 (14)
C11*A*—C14*A*—O15*A*—C16*A*	−179.4 (8)
C14*A*—O15*A*—C16*A*—C21*A*	126.6 (9)
C14*A*—O15*A*—C16*A*—C17*A*	−60.6 (12)
O15*A*—C16*A*—C17*A*—C18*A*	−173.0 (8)
O15*A*—C16*A*—C21*A*—C20*A*	173.5 (8)
C18*A*—C19*A*—C22*A*—O23*A*	−179.2 (9)
C20*A*—C19*A*—C22*A*—O23*A*	4.0 (15)
C18*A*—C19*A*—C22*A*—O22*A*	−8.9 (14)
C20*A*—C19*A*—C22*A*—O22*A*	174.3 (9)
C6*B*—C7*B*—C8*B*—C9*B*	−129.2 (12)
C6*B*—C7*B*—C8*B*—C13*B*	55.5 (15)
C12*B*—C11*B*—C14*B*—O14*B*	7.9 (14)
C10*B*—C11*B*—C14*B*—O14*B*	−170.6 (9)
C12*B*—C11*B*—C14*B*—O15*B*	−171.4 (8)
C10*B*—C11*B*—C14*B*—O15*B*	10.0 (13)
O14*B*—C14*B*—O15*B*—C16*B*	6.1 (13)
C11*B*—C14*B*—O15*B*—C16*B*	−174.5 (7)
C14*B*—O15*B*—C16*B*—C21*B*	109.8 (10)
C14*B*—O15*B*—C16*B*—C17*B*	−74.8 (11)
O15*B*—C16*B*—C17*B*—C18*B*	−176.7 (8)
O15*B*—C16*B*—C21*B*—C20*B*	175.5 (8)
C18*B*—C19*B*—C22*B*—O23*B*	175.7 (9)
C20*B*—C19*B*—C22*B*—O23*B*	−2.9 (14)
C18*B*—C19*B*—C22*B*—O22*B*	−2.7 (14)
C20*B*—C19*B*—C22*B*—O22*B*	178.7 (9)

The temperature of the crystal was controlled using an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986). The precision of this structure was limited by the quality of the crystals available to us and possibly by the incipient disorder in the *n*-heptyl chain evident in the appearance of the displacement ellipsoids in Fig. 1. The H atoms of the CO_2H groups could not be located, although their existence can be inferred from the greater length of one of the C—O distances in each CO_2H group and from the presence of hydrogen-bonded dimers. Other H atoms were included in the refinement at calculated positions and were allowed to ride on their respective C atoms.

Data collection: *DIF*4 (Stoe & Cie, 1990*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1990*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL*93.

The authors thank EPSRC for support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: MU1202). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 197–199

N-Hexyl-*N*-phenyl-5-ethylthioindole-2-carboxamide

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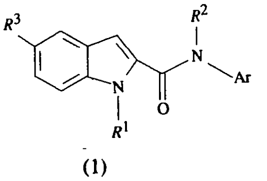
(*Received 4 January 1995; accepted 6 June 1995*)

Abstract

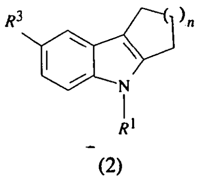
Knowledge of the position of the ethylthio group in the title compound, $C_{23}H_{28}N_2OS$, allows generalization of the behaviour of two families of indoles undergoing alkylthiolation reactions. The ^{1}H NMR spectrum of this compound is in agreement with that recently observed for other 1-carboxamide indole derivatives. The structure and conformation of the molecule is discussed and compared with that of the analogous compound *N*-methyl-*N*-phenyl-2-(5-methoxyindole)carboxamide.

Comment

A research program aimed at the synthesis of 5-hydroxyindole-2-carboxamides (1) (R^3 = OH) led us to study the demethylation of the corresponding methyl ethers (1) (R^3 = OMe) with $AlCl_3$/EtSH.



(1)



(2)

During previous investigations carried out with polycyclic indoles (2) (R^3 = OMe), a new reaction was discovered leading to the replacement of the methoxy group with an ethylthio substituent to give compound (2) (R^3 = EtS) (Caubère, Caubère, Renard, Bizot-Espiart & Jamart-Gregoire, 1994). Demethylation performed with (1) (R^3 = OMe) showed that the presence of the carboxamide group dramatically increased the reactivity of the substrates towards $AlCl_3$/EtSH.

The position of the ethylthio group could not be determined from the usual spectroscopic data. Moreover, taking into account the difference in reactivity observed between (1) and (2), it was not possible to conclude that the alkylthiolation observed with the two families of indoles was identical. Fortunately, compound (1) [R^3 = OMe, R^1 = H, R^2 = *n*-hexyl, Ar = Ph] gave single crystals suitable for X-ray diffraction, allowing us to conclude that the replacement of the OMe substituent of (1) took place analogously to the reaction observed with (2).

Fig. 1 shows an *ORTEP* (Johnson, 1965) drawing of the title molecule and Table 2 presents selected geometrical parameters which compare well with those recently found for the analogous *N*-methyl-*N*-phenyl-2-(5-methoxyindole)carboxamide (Ianelli, Nardelli, Belletti, Jamart-Grégoire, Caubère & Caubère, 1995). Bond distances and angles involving the disordered hexyl chain (see *Experimental*) have no chemical significance and have been omitted.

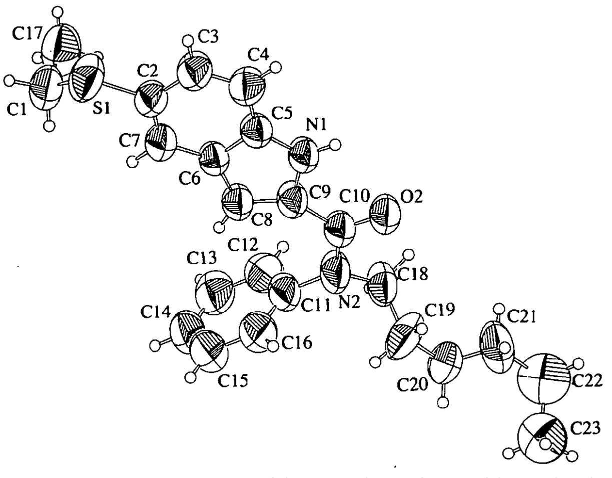


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title molecule. Ellipsoids are at the 50% probability level and only one of the two disorder components of the hexyl chain is shown.

An important aspect connected with the comparison of the two compounds is that the ^{1}H NMR spectrum of compound (1) shows a resonance at 5.1 p.p.m. indicating an aromatic H atom strongly shielded by the phenyl ring, as observed for the methoxy derivative. Other relevant observations are: (i) steric hindrance prevents