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Diethyl 4,4'-(3,4-Diphenyl-2,5-thiophenediyl)dibenzenecarbamate

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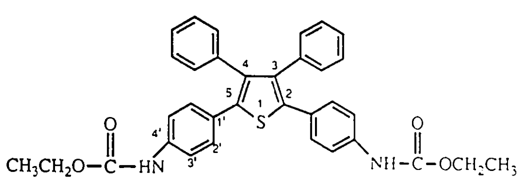
Abstract. $C_{34}H_{30}N_2O_4S$, $M_r = 562{\cdot}69$, monoclinic, $C2/c$, $a = 33{\cdot}447$ (5), $b = 9{\cdot}505$ (3), $c = 9{\cdot}571$ (3) Å, $\beta = 92{\cdot}44$ (2)°, $V = 3040$ (1) Å^3, $Z = 4$, $D_x = 1{\cdot}229$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 1·38 cm^{-1}, $F(000) = 1184$, $T = 295$ K. Final $R = 0{\cdot}042$ for 1258 observed reflections. Bond distances in the thiophene ring are: S—C, 1·717 (3), C=C, 1·368 (4) and C—C, 1·435 (6) Å; the C—S—C angle is 92·1 (2)°. Each molecule is involved in four hydrogen bonds of the type N—H···O with its neighbors; the N···O distance is 3·015 (4) Å.

Introduction. Recently, a number of novel urethane polymers were synthesized in our laboratory by solution copolymerization of 2,5-bis(4-isocyanatophenyl)-3,4-diphenylthiophene (I) with a variety of aliphatic diols such as ethylene glycol, diethylene glycol, 1,4-butanediol, *etc.*, as low molecular weight species with intrinsic viscosities of about 0·15 dL/g (Maldar & Hosmane, 1986). Compound (I) is an air-sensitive amorphous solid and its structure is not known. The spectroscopic characterizations of polyurethanes derived from (I) suggested that the repeated urethane linkages are at the 2 and 5 positions of the thiophene ring. In order to provide definitive characterizations of these novel polyurethanes and the precursor (I), we have prepared several model urethane monomers from (I) and have conducted an X-ray investigation of one of the model compounds (II) and report herein the results.



(II)

Experimental. Crystals of the title compound are colorless square plates decomposing rapidly in air; a fragment (0·55 × 0·23 × 0·16 mm) was coated in an epoxy resin; unit-cell parameters by least-squares fit of 15 reflections in the range $15 < 2\theta < 23°$, space group Cc or $C2/c$ from systematic absences (*hkl*, $h+k$ odd; *h0l*, *l* odd), the latter being confirmed by the subsequent satisfactory refinement of the structure; automatic Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\theta/2\theta$ scan mode, 2002 independent reflections in the range $3 < 2\theta < 45°$, *hkl* range h −35→36, k 0→10, l 0→10, 1258 observed reflections with $I > 3\sigma(I)$, $\sigma(I)$ from counting statistics; three standard reflections remeasured after every 100 reflections did not show any significant change in intensity during data collection; Lorentz–polarization correction, no absorption or extinction corrections. Direct methods, *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refinement by full-matrix least-squares using *SHELX*76 (Sheldrick, 1976), anisotropic; H atoms located in difference Fourier maps, except for methyl H positions which were calculated; H atoms included as a 'fixed atom contribution' with isotropic temperature factors set at 1·2 times U_{eq} of their parent atoms; $w = 1/[\sigma^2(F) + 0{\cdot}001454F^2]$, $\sum w(|F_o| - |F_c|)^2$ minimized, $R = 0{\cdot}042$, $wR = 0{\cdot}048$; $(\Delta/\sigma)_{\max} = 0{\cdot}05$, $\Delta\rho_{\max(\min)} = 0{\cdot}25$ $(-0{\cdot}17)$ e Å^{-3} in final difference Fourier map. Atomic scattering factors for C, H, O, N and S and the effects of the anomalous-dispersion correction for S used were those stored in *SHELX*76.

Discussion. The final atomic parameters of the non-H atoms are given in Table 1.† The identification of the atoms and the configuration of the molecule are shown in the *ORTEP* (Johnson, 1965) drawing of Fig. 1. The molecule lies on a diad axis which passes through the S atom and the center of the C(2)—C(2') bond. The bond lengths, bond angles and selected torsion angles with their standard deviations are given in Table 2. The geometry of the thiophene ring is in good agreement with the data we have recently obtained for 2,5-bis(4-nitrophenyl)-3,4-diphenylthiophene (de Meester, Maldar, Hosmane & Chu, 1986), where the bond

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† Lists of structure factors, anisotropic temperature factors, H parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43116 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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distances are S—C, 1·724 (3), C=C, 1·381 (4), C—C, 1·429 (3) Å and the angle C—S—C is 93·0 (1)°. In the title compound, the corresponding values are 1·717 (3), 1·368 (4), 1·435 (6) Å and 92·1 (2)°. The angle between the phenyl and the thiophene rings is 46·3 (1)° while that between the phenylcarbamate and the thiophene rings is 50·4 (1)°.

Each molecule is involved in four hydrogen bonds of the type N—H···O with its neighbors as shown in the stereoscopic view of Fig. 2. The distances N(15)···O(17), H(15)···O(17) and the angle N(15)—H(15)—O(17) have the values 3·015 (4), 2·22 Å and 161°, respectively.

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Table 1. *Fractional atomic coordinates with equivalent isotropic thermal parameters for the non-*H *atoms (e.s.d.'s in parentheses)*

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	U_{eq}(Å^2)
S	$\frac{1}{2}$	0·1061 (1)	$\frac{1}{4}$	0·0624 (3)*
C(1)	0·5361 (1)	0·2315 (3)	0·2837 (3)	0·0560 (8)
C(2)	0·5209 (1)	0·3647 (3)	0·2704 (3)	0·0513 (7)
C(3)	0·5450 (1)	0·4931 (4)	0·2995 (3)	0·0591 (8)
C(4)	0·5827 (1)	0·5097 (4)	0·2491 (4)	0·0720 (9)
C(5)	0·6054 (1)	0·6269 (6)	0·2853 (5)	0·0936 (13)
C(6)	0·5901 (2)	0·7291 (5)	0·3692 (6)	0·1062 (16)
C(7)	0·5522 (2)	0·7167 (4)	0·4167 (5)	0·0928 (14)
C(8)	0·5300 (1)	0·5991 (4)	0·3830 (4)	0·0687 (9)
C(9)	0·5777 (1)	0·1835 (3)	0·3176 (3)	0·0533 (7)
C(10)	0·5999 (1)	0·2346 (3)	0·4323 (3)	0·0622 (8)
C(11)	0·6387 (1)	0·1893 (4)	0·4591 (3)	0·0628 (8)
C(12)	0·6562 (1)	0·0920 (3)	0·3743 (3)	0·0541 (8)
C(13)	0·6343 (1)	0·0414 (3)	0·2598 (3)	0·0597 (8)
C(14)	0·5957 (1)	0·0867 (3)	0·2333 (3)	0·0588 (8)
N(15)	0·6956 (1)	0·0488 (3)	0·4108 (3)	0·0689 (7)
C(16)	0·7194 (1)	−0·0338 (4)	0·3356 (4)	0·0754 (11)
O(17)	0·7119 (1)	−0·0820 (3)	0·2213 (3)	0·0972 (9)
O(18)	0·7538 (1)	−0·0558 (3)	0·4080 (3)	0·1017 (9)
C(19)	0·7836 (1)	−0·1421 (7)	0·3413 (5)	0·1390 (20)
C(20)	0·8186 (2)	−0·1457 (8)	0·4304 (7)	0·1703 (25)

* The standard deviations of U_{eq} were calculated according to Schomaker & Marsh (1983).

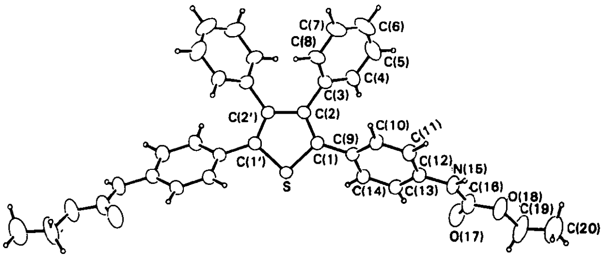

Fig. 1. *ORTEP* drawing of the molecule. Thermal ellipsoids scaled to enclose 35% probability. H atoms are represented as spheres of arbitrary radii.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

S—C(1)	1·717 (3)	C(9)—C(14)	1·379 (4)
C(1)—C(2)	1·368 (4)	C(10)—C(11)	1·381 (5)
C(2)—C(2^i)	1·435 (6)	C(11)—C(12)	1·377 (5)
C(1)—C(9)	1·487 (4)	C(12)—C(13)	1·379 (4)
C(2)—C(3)	1·482 (5)	C(12)—N(15)	1·410 (4)
C(3)—C(4)	1·378 (5)	C(13)—C(14)	1·374 (4)
C(3)—C(8)	1·393 (5)	N(15)—C(16)	1·348 (5)
C(4)—C(5)	1·384 (6)	C(16)—O(17)	1·203 (5)
C(5)—C(6)	1·373 (7)	C(16)—O(18)	1·334 (5)
C(6)—C(7)	1·370 (8)	O(18)—C(19)	1·459 (6)
C(7)—C(8)	1·373 (6)	C(19)—C(20)	1·419 (9)
C(9)—C(10)	1·387 (4)		
C(1)—S—C(1^i)	92·1 (2)	C(1)—C(9)—C(14)	120·3 (3)
S—C(1)—C(2)	111·7 (2)	C(10)—C(9)—C(14)	117·7 (3)
S—C(1)—C(9)	118·2 (2)	C(9)—C(10)—C(11)	120·3 (3)
C(2)—C(1)—C(9)	130·1 (3)	C(10)—C(11)—C(12)	121·3 (3)
C(1)—C(2)—C(2^i)	112·3 (3)	C(11)—C(12)—C(13)	118·6 (3)
C(1)—C(2)—C(3)	123·2 (3)	C(11)—C(12)—N(15)	117·8 (3)
C(2^i)—C(2)—C(3)	124·5 (3)	C(13)—C(12)—N(15)	123·7 (3)
C(2)—C(3)—C(4)	121·8 (3)	C(12)—C(13)—C(14)	120·0 (3)
C(2)—C(3)—C(8)	119·8 (3)	C(9)—C(14)—C(13)	122·1 (3)
C(4)—C(3)—C(8)	118·4 (3)	C(12)—N(15)—C(16)	127·2 (3)
C(3)—C(4)—C(5)	120·3 (4)	N(15)—C(16)—O(17)	127·1 (4)
C(4)—C(5)—C(6)	120·1 (4)	N(15)—C(16)—O(18)	109·3 (3)
C(5)—C(6)—C(7)	120·4 (5)	O(17)—C(16)—O(18)	123·7 (4)
C(6)—C(7)—C(8)	119·4 (5)	C(16)—O(18)—C(19)	116·8 (3)
C(3)—C(8)—C(7)	121·3 (4)	O(18)—C(19)—C(20)	108·2 (5)
C(1)—C(9)—C(10)	122·0 (3)		
C(1)—C(2)—C(3)—C(4)	46·3 (5)	C(11)—C(12)—N(15)—C(16)	−173·0 (3)
C(1)—C(2)—C(3)—C(8)	−132·0 (4)	C(13)—C(12)—N(15)—C(16)	7·7 (5)
C(2^i)—C(2)—C(3)—C(8)	46·1 (5)	C(12)—N(15)—C(16)—O(17)	2·7 (6)
C(2^i)—C(2)—C(3)—C(4)	−135·7 (4)	C(12)—N(15)—C(16)—O(18)	−177·3 (3)
C(2)—C(1)—C(9)—C(10)	51·0 (5)	N(15)—C(16)—O(18)—C(19)	−179·2 (3)
C(2)—C(1)—C(9)—C(14)	−128·1 (4)	O(17)—C(16)—O(18)—C(19)	0·8 (6)
S—C(1)—C(9)—C(14)	49·9 (4)	C(16)—O(18)—C(19)—C(20)	176·4 (4)
S—C(1)—C(9)—C(10)	−131·0 (3)		

Symmetry code: (i) $1-x, y, \frac{1}{2}-z$.

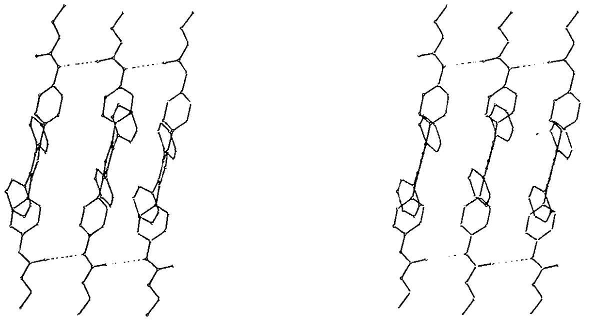

Fig. 2. Stereoscopic pair of drawings approximately down the *b* axis showing the hydrogen-bonding scheme.

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Structures of Novel Dehydroxycycloleuconolam Alkaloid Derivatives

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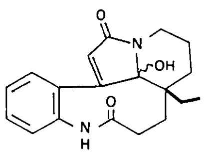
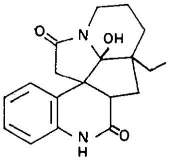
Abstract. $C_{19}H_{21}ClN_2O_2$, $M_r = 344{\cdot}84$, monoclinic, $P2_1$, $a = 9{\cdot}903$ (2), $b = 7{\cdot}513$ (1), $c = 11{\cdot}399$ (3) Å, $\beta = 106{\cdot}08$ (2)°, $V = 814{\cdot}9$ (2) Å^3, $Z = 2$, $D_m = 1{\cdot}41$ (by flotation in KI/H_2O), $D_x = 1{\cdot}405$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 4{\cdot}13$ cm^{-1}, $F(000) = 364$, $T = 297$ K, $R = 0{\cdot}047$ based on 1446 observed $[|F_o| > 2\sigma(|F_o|)]$ reflections. The easy recyclization of the ring-opened indole alkaloid, leuconolam, with hydrochloric acid provides alkaloidal derivatives possessing a new pentacyclic diazaspiro-indole skeleton.

Introduction. Among several natural products from *Leuconotis* species is the structurally interesting ring-opened indole alkaloid leuconolam (1*a*) (Goh, Wei & Mohd. Ali, 1984; Wei, Mohd. Ali, Goh, Sinn & Butcher, 1986), and our continuing studies have led to the isolation of the isomer epileuconolam (1*b*) from acidic extracts. Under basic conditions leuconolam (1*a*) is transformed into a pentacyclic melodinus-type alkaloid (2), but acid (HCl) treatment of (1*a*) yielded two novel products, (3*a*) and (3*b*), for which unambiguous structural assignments could not be made based on spectroscopic (NMR, IR and UV) data alone. Accordingly the minor product (3*b*) was subjected to X-ray analysis, which revealed the presence of a novel dehydroxycycloleuconolam skeleton.



1*a* β—OH
1*b* α—OH



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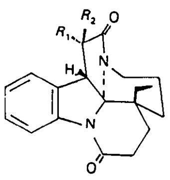

3*a* R_1=H, R_2=Cl
3*b* R_1=Cl, R_2=H

Experimental. Colorless polyhedral crystal (0·24 × 0·24 × 0·16 mm) of (3*b*) mounted on Nicolet *R*3*m* diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Unit-cell parameters from least-squares fit to refined angles of 21 independent reflections. ω–2θ scan mode at 2·02–8·37° min^{-1} for $2\theta_{max} = 50°$; scan range 1° below $K\alpha_1$ to 1° above $K\alpha_2$; ranges of h,k,l: 0 to 11, 0 to 8, −13 to 13; two standard reflections used to monitor every 125 reflections; absorption correction not applied; 1546 unique data collected, 1446 with $|F_o| > 2\sigma(|F_o|)$, phase determination by direct methods. All non-hydrogen atoms, other than the ring carbon atoms, were refined anisotropically, H atoms generated geometrically (C—H 0·96 Å), assigned fixed isotropic thermal parameters and allowed to ride on their respective parent C atoms; methyl group was handled as rigid group with d(C—H) = 0·98 Å and $U_{iso} = 0{\cdot}06$ Å^2; blocked cascade least-squares refinement (Schilling, 1970) on F for 134 parameters converged at $R = 0{\cdot}047$ and $wR = 0{\cdot}064$, $w = [\sigma^2(F_o) + 0{\cdot}0015|F_o|^2]^{-1}$, $S = 1{\cdot}273$; $(\Delta/\sigma)_{max} < 0{\cdot}003$ in final cycle; residual extrema in final difference map 0·29 to −0·27 e Å^{-3}; analytic expressions of neutral-atom scattering factors and anomalous-dispersion corrections taken from *International Tables for X-ray Crystallography* (1974); all computations performed on Data General Nova 3/12 minicomputer with *SHELXTL* program package (Sheldrick, 1982).†

Discussion. Table 1 lists the atomic coordinates and equivalent isotropic thermal parameters. Table 2

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† Tables of hydrogen coordinates, anisotropic thermal parameters, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43051 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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