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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1026). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Two Mesogenic Nitrobenzoxazoles

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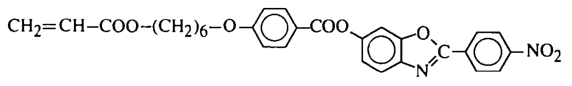
## Abstract

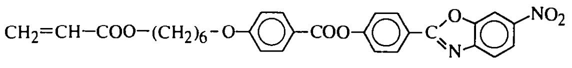
The crystal and molecular structures of two isomeric benzoxazoles, 2-(4-nitrophenyl)benzoxazol-6-yl 4-(acryloyloxyhexyloxy)benzoate, $C_{29}H_{26}N_2O_8$, (1), and 4-(6-nitro-2-benzoxazolyl)phenyl 4-(acryloyloxyhexyloxy)benzoate, $C_{29}H_{26}N_2O_8$, (2), are reported. Both compounds are mesogenic and are of potential interest for non-linear optics. Some differences in the molecular conformations of the two compounds are observed, mainly in the torsion angle around the bond from the aromatic C to ester O atoms and in the dihedral angle between the planes of the benzoxazole system and the phenyl group attached to it. The torsion angle is −23.6 (3)° for compound (1) and 32.2 (7) and −67.0 (6)° for the two independent molecules of (2). These differences, which are probably due to packing effects, do not affect the pattern of bond lengths and angles within the molecules to any significant extent.

## Comment

The title compounds, (1) and (2), are monomer precursors of comb-like polymers, the investigation of which is underway in our laboratory. Owing to the expected planarity and $\pi$-electron cojugation in the 2-phenylbenzoxazole moiety and to the strong electron-withdrawing effect of the nitro group, these polymers are likely to show non-linear optical properties of the second order (Williams, 1984). Compounds (1) and (2) were prepared by interfacial esterification of 4-(6-acryloyloxyhexyloxy)benzoyl chloride with 2-(4-nitrophenyl)-6-hydroxybenzoxazole and 2-(4-hydroxyphenyl)-6-nitrobenzoxazole, respectively. Detailed descriptions of both the syntheses of the nitrohydroxybenzoxazoles by intramolecular cyclization of parent Schiff bases and the esterification procedure are planned (Centore, Panunzi, Roviello & Sirigu, 1996).



(1)



(2)

Both compounds are mesogenic, but notwithstanding their closely related chemical natures, their mesophasic behaviours are quite different. Compound (1) is nematogenic and the interval of stability of the mesophase is rather small (melting point 407 K, isotropization temperature 415.1 K). Compound (2), on the other hand, melts at 375 K to a smectic A phase that trasforms, at 441 K, into a nematic phase; isotropization of this latter phase is at 463 K. Furthermore, both compounds are polymorphic in the solid state. The crystal structures reported in this paper refer to a low-temperature polymorph of (1) and to a high-temperature polymorph of (2). For compound (1), in particular, the low-temperature polymorph transforms, at 397 K, into another crystal phase that melts at 407 K.

Bond lengths and angles in the molecules of compounds (1) and (2) have close to expected values, with the exception of some bond lengths in the acryl-

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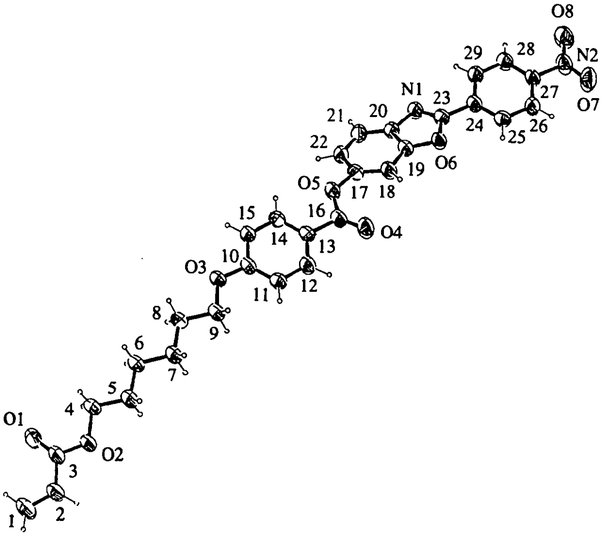

Fig. 1. *ORTEP*II view (Johnson, 1976) of the molecule of compound (1). Displacement ellipsoids are shown at the 50% probability level. C atoms are labelled by number only.

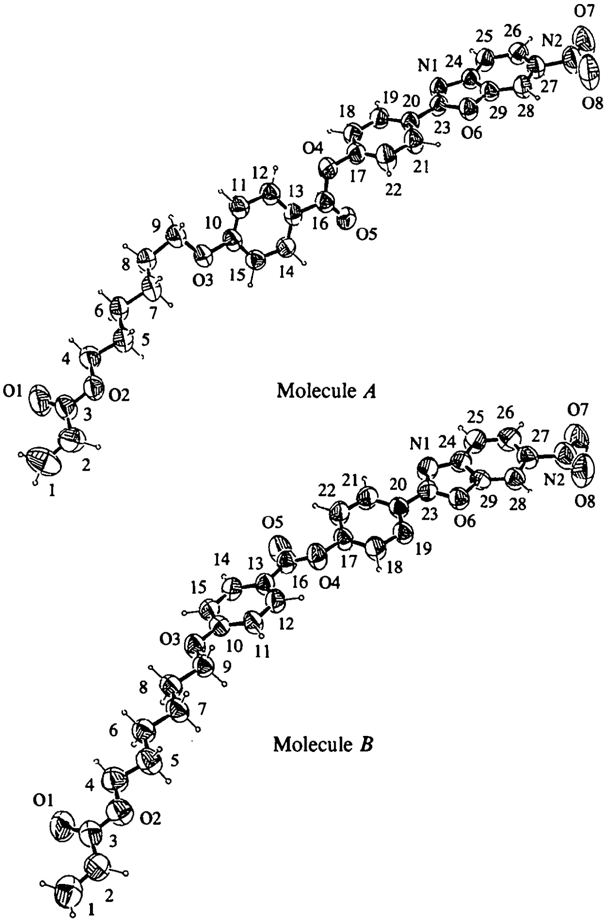

Fig. 2. *ORTEP*II view (Johnson, 1976) of the two independent molecules, *A* and *B*, of compound (2). Displacement ellipsoids are shown at the 50% probability level. C atoms are labelled by number only.

oyloxy group of molecules *A* and *B* of (2); these distances, however, are of low accuracy because of the high thermal motion of the atoms. Bond lengths and angles within the 2-phenylbenzoxazole group are in close agreement with those previously found in a related compound (Centore, 1994). In particular, some deviations from 120° are observed in the bond angles within the benzene ring of the benzoxazole group [C17—C18—C19 113.3 (1) and C20—C19—C18 125.0 (2)° for (1), and C27*A*—C28*A*—C29*A* 112.6 (4) and C24*A*—C29*A*—C28*A* 125.9 (4)° for molecule *A* of (2) and C27*B*—C28*B*—C29*B* 112.6 (5) and C24*B*—C29*B*—C28*B* 124.7 (4)° for molecule *B* of (2)]. Similar deviations are also observed around the C23 atom of the imino group [C24—C23—N1 126.2 (2)° for (1), and C20*A*—C23*A*—N1*A* 128.0 (4) and C20*B*—C23*B*—N1*B* 128.7 (5)° for (2)]; this effect might be a consequence of the repulsion between the lone pair of electrons on the N atom and the *ortho* H atom of the 2-phenyl group. The benzoxazole group and the adjacent 2-phenyl group are nearly coplanar in compound (2) [dihedral angles of 3.3 (6) and 7.5 (2)° for molecules of *A* and *B*, respectively], while in (1) a dihedral angle of 20.2 (1)° is observed between these groups. Such deviations from planarity are not surprising because of the low torsional barrier around the bond linking the benzoxazole and 2-phenyl groups (Welsh, Bhaumik & Mark, 1984). The orientation of the benzoyloxy group with respect to the phenylbenzoxazole group is defined by the torsion angle around the C—O aryloxy bond to the ester group. A small value, compared to theoretical predictions (Hummel & Flory, 1980), is observed in compound (1) [C16—O5—C17—C18 −23.6 (3)°] and in molecule *B* of compound (2) [C16*B*—O4*B*—C17*B*—C22*B* 32.2 (7)°], while a larger value is observed in molecule *A* of compound (2) [C16*A*—O4*A*—C17*A*—C22*A* −67.0 (6)°]. Furthermore, in the first two cases, an increase in the bond angle at the aryloxy O atom of the ester group is observed [C16—O5—C17 126.0 (1) and C16*B*—O4*B*—C17*B* 123.9 (4)° as opposed to C16*A*—O4*A*—C17*A* 117.2 (4)° in molecule *A* of (2)], probably as a result of the repulsion between the carbonyl O atom and the *ortho* H atom on the phenyl group [H on C18 for compound (1) and H on C22*B* for compound (2)].

The conformation of the aliphatic chain is all-*trans* planar in both compound (1) and molecule *B* of compound (2), but one *gauche*-type torsion angle is observed in molecule *A* of compound (2) [C7*A*—C8*A*—C9*A*—O3*A* 60.7 (6)°]. This latter could be simply a packing effect, resulting in a more linear molecular shape.

## Experimental

The preparation of compounds (1) and (2) will be described elsewhere (Centore, Panunzi, Roviello & Sirigu, 1996)

## Compound (1)

### *Crystal data*

$C_{29}H_{26}N_2O_8$
$M_r = 530.54$
Triclinic
$P\bar{1}$
$a = 8.744\,(2)$ Å
$b = 11.087\,(2)$ Å
$c = 14.511\,(3)$ Å
$\alpha = 106.16\,(2)°$
$\beta = 102.98\,(2)°$
$\gamma = 75.31\,(2)°$
$V = 1288.9\,(5)$ Å$^3$
$Z = 2$
$D_x = 1.367$ Mg m$^{-3}$
$D_m$ not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 15.02–24.77°$
$\mu = 0.797$ mm$^{-1}$
$T = 295$ K
Platelet
0.43 × 0.17 × 0.036 mm
Yellow

### *Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega/\theta$ scans
Absorption correction: none
5292 measured reflections
5292 independent reflections
3362 observed reflections $[I > 3\sigma(I)]$

$\theta_{max} = 75.0°$
$h = -10 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = 0 \rightarrow 18$
1 standard reflection
frequency: 120 min
intensity decay: 0.5%

### *Refinement*

Refinement on $F$
$R = 0.049$
$wR = 0.064$
$S = 1.758$
3362 reflections
457 parameters
All H-atom parameters refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$(\Delta/\sigma)_{max} = 0.01$

$\Delta\rho_{max} = 0.347$ e Å$^{-3}$
$\Delta\rho_{min} = -0.174$ e Å$^{-3}$
Extinction correction: Stout & Jensen (1989)
Extinction coefficient: $1.3\,(4) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$) for (1)*

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

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| O1 | 1.3245 (3) | 1.0517 (2) | −0.0910 (1) | 0.1091 (6) |
| O2 | 1.2266 (2) | 1.0825 (1) | 0.0444 (1) | 0.0745 (5) |
| O3 | 1.0695 (2) | 0.4466 (1) | 0.2117 (1) | 0.0747 (5) |
| O4 | 0.7984 (2) | 0.2622 (2) | 0.5121 (1) | 0.0913 (6) |
| O5 | 0.8475 (2) | 0.0867 (1) | 0.3912 (1) | 0.0734 (5) |
| O6 | 0.6602 (2) | −0.1035 (1) | 0.6025 (1) | 0.0621 (5) |
| O7 | 0.3476 (2) | −0.3506 (2) | 0.8965 (1) | 0.1064 (6) |
| O8 | 0.4195 (2) | −0.5397 (2) | 0.8101 (1) | 0.1078 (6) |
| N1 | 0.6215 (2) | −0.2771 (2) | 0.4820 (1) | 0.0666 (6) |
| N2 | 0.4063 (2) | −0.4236 (2) | 0.8280 (1) | 0.0735 (6) |
| C1 | 1.2995 (4) | 1.3221 (2) | −0.0494 (2) | 0.0936 (9) |
| C2 | 1.2487 (3) | 1.2639 (2) | 0.0023 (2) | 0.0730 (7) |
| C3 | 1.2710 (3) | 1.1231 (2) | −0.0218 (2) | 0.0695 (7) |
| C4 | 1.2488 (3) | 0.9446 (2) | 0.0306 (2) | 0.0766 (6) |
| C5 | 1.1902 (3) | 0.9221 (2) | 0.1131 (2) | 0.0773 (6) |
| C6 | 1.2002 (3) | 0.7796 (2) | 0.1014 (2) | 0.0786 (6) |
| C7 | 1.1368 (3) | 0.7520 (2) | 0.1811 (2) | 0.0776 (6) |
| C8 | 1.1357 (3) | 0.6102 (2) | 0.1625 (2) | 0.0704 (6) |
| C9 | 1.0637 (3) | 0.5823 (2) | 0.2378 (2) | 0.0725 (6) |
| C10 | 1.0133 (3) | 0.3962 (2) | 0.2701 (2) | 0.0612 (6) |
| C11 | 0.9494 (3) | 0.4663 (2) | 0.3520 (2) | 0.0684 (6) |
| C12 | 0.8961 (3) | 0.4038 (2) | 0.4055 (2) | 0.0654 (6) |
| C13 | 0.9069 (3) | 0.2729 (2) | 0.3780 (2) | 0.0654 (6) |
| C14 | 0.9704 (3) | 0.2036 (2) | 0.2948 (2) | 0.0671 (6) |
| C15 | 1.0236 (3) | 0.2647 (2) | 0.2413 (2) | 0.0711 (6) |
| C16 | 0.8452 (3) | 0.2116 (2) | 0.4368 (2) | 0.0618 (6) |
| C17 | 0.7821 (3) | 0.0024 (2) | 0.4187 (2) | 0.0601 (6) |
| C18 | 0.7544 (3) | 0.0148 (2) | 0.5113 (2) | 0.0618 (6) |
| C19 | 0.6975 (3) | −0.0873 (2) | 0.5199 (1) | 0.0560 (6) |
| C20 | 0.6712 (3) | −0.1919 (2) | 0.4460 (2) | 0.0613 (6) |
| C21 | 0.6959 (3) | −0.1992 (2) | 0.3534 (2) | 0.0734 (7) |
| C22 | 0.7516 (3) | −0.0998 (2) | 0.3407 (2) | 0.0699 (7) |
| C23 | 0.6178 (3) | −0.2217 (2) | 0.5719 (2) | 0.0583 (6) |
| C24 | 0.5699 (3) | −0.2709 (2) | 0.6426 (2) | 0.0563 (2) |
| C25 | 0.5213 (3) | −0.1919 (2) | 0.7277 (2) | 0.0605 (6) |
| C26 | 0.4670 (3) | −0.2414 (2) | 0.7890 (2) | 0.0628 (7) |
| C27 | 0.4652 (3) | −0.3705 (2) | 0.7642 (2) | 0.0596 (6) |
| C28 | 0.5156 (3) | −0.4521 (2) | 0.6808 (2) | 0.0663 (6) |
| C29 | 0.5687 (3) | −0.4016 (2) | 0.6202 (2) | 0.0641 (6) |

Table 2. *Selected geometric parameters (Å, °) for (1)*

| | | | |
|---|---|---|---|
| O1—C3 | 1.198 (3) | N1—C23 | 1.282 (3) |
| O2—C4 | 1.454 (3) | N2—C27 | 1.464 (4) |
| O3—C9 | 1.435 (3) | C1—C2 | 1.319 (4) |
| O3—C10 | 1.365 (3) | C2—C3 | 1.473 (3) |
| O4—C16 | 1.192 (3) | C17—C18 | 1.381 (3) |
| O5—C16 | 1.355 (2) | C17—C22 | 1.393 (3) |
| O5—C17 | 1.393 (3) | C18—C19 | 1.391 (4) |
| O6—C19 | 1.379 (3) | C19—C20 | 1.372 (3) |
| O6—C23 | 1.378 (3) | C20—C21 | 1.385 (4) |
| O7—N2 | 1.215 (2) | C21—C22 | 1.382 (4) |
| O8—N2 | 1.220 (3) | C23—C24 | 1.464 (4) |
| N1—C20 | 1.392 (3) | | |
| C3—O2—C4 | 116.8 (2) | O4—C16—C13 | 126.4 (2) |
| C9—O3—C10 | 118.0 (2) | O5—C16—C13 | 109.6 (2) |
| C16—O5—C17 | 126.0 (1) | O5—C17—C18 | 125.3 (1) |
| C19—O6—C23 | 103.1 (2) | O5—C17—C22 | 111.1 (2) |
| C20—N1—C23 | 104.3 (2) | C18—C17—C22 | 123.6 (2) |
| O7—N2—O8 | 123.0 (2) | C17—C18—C19 | 113.3 (1) |
| C1—C2—C3 | 120.9 (3) | O6—C19—C20 | 107.8 (3) |
| O1—C3—O2 | 123.0 (2) | C18—C19—C20 | 125.0 (2) |
| O1—C3—C2 | 125.3 (3) | N1—C20—C19 | 109.2 (2) |
| O2—C3—C2 | 111.6 (2) | C19—C20—C21 | 120.0 (2) |
| O3—C9—C8 | 106.4 (2) | C20—C21—C22 | 117.2 (2) |
| O3—C10—C11 | 124.7 (2) | C17—C22—C21 | 120.7 (3) |
| O3—C10—C15 | 115.1 (2) | O6—C23—N1 | 115.6 (2) |
| C12—C13—C16 | 118.7 (1) | N1—C23—C24 | 126.2 (2) |
| C14—C13—C16 | 122.2 (2) | C23—C24—C25 | 122.3 (2) |
| C17—O5—C16—C13 | −172.3 (2) | C12—C13—C16—O5 | 172.1 (2) |
| C16—O5—C17—C22 | 158.0 (2) | O6—C23—C24—C29 | −163.2 (2) |
| O7—N2—C27—C26 | 6.4 (4) | | |

## Compound (2)

### *Crystal data*

$C_{29}H_{26}N_2O_8$
$M_r = 530.54$
Triclinic
$P\bar{1}$
$a = 11.477\,(1)$ Å
$b = 15.123\,(2)$ Å
$c = 17.242\,(2)$ Å
$\alpha = 105.78\,(1)°$
$\beta = 99.22\,(1)°$
$\gamma = 107.83\,(1)°$
$V = 2643\,(20)$ Å$^3$
$Z = 4$
$D_x = 1.333$ Mg m$^{-3}$
$D_m$ not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 15.16–25.46°$
$\mu = 0.777$ mm$^{-1}$
$T = 295$ K
Platelet
0.43 × 0.17 × 0.05 mm
Pale yellow

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega/\theta$ scans
Absorption correction: none
10 501 measured reflections
10 501 independent reflections
4575 observed reflections $[I > 3\sigma(I)]$
$\theta_{\max} = 73°$
$h = -14 \rightarrow 14$
$k = -18 \rightarrow 18$
$l = 0 \rightarrow 21$
1 standard reflection
frequency: 120 min
intensity decay: 0.4%

*Refinement*

Refinement on $F$
$R = 0.069$
$wR = 0.093$
$S = 2.505$
4575 reflections
703 parameters
H-atom parameters not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.02$
$\Delta\rho_{\max} = 0.715$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.273$ e Å$^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (2)*

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

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| O1A | 0.7788 (4) | 0.3012 (3) | 1.2781 (3) | 0.165 (2) |
| O2A | 0.6087 (3) | 0.2405 (3) | 1.1712 (2) | 0.100 (1) |
| O3A | 0.5386 (3) | 0.0098 (2) | 0.7013 (2) | 0.092 (1) |
| O4A | 0.2285 (3) | −0.2336 (2) | 0.3255 (2) | 0.089 (1) |
| O5A | 0.1922 (3) | −0.0928 (2) | 0.3401 (2) | 0.103 (1) |
| O6A | −0.1413 (3) | −0.4119 (2) | −0.0426 (2) | 0.083 (1) |
| O7A | −0.4095 (4) | −0.5880 (4) | −0.4032 (2) | 0.164 (2) |
| O8A | −0.5040 (4) | −0.5579 (4) | −0.3081 (3) | 0.155 (2) |
| N1A | 0.0414 (3) | −0.4021 (3) | −0.0792 (2) | 0.080 (1) |
| N2A | −0.4086 (4) | −0.5580 (3) | −0.3304 (3) | 0.114 (2) |
| C1A | 0.6382 (7) | 0.3716 (5) | 1.3929 (5) | 0.145 (4) |
| C2A | 0.5921 (5) | 0.3303 (4) | 1.3035 (4) | 0.119 (3) |
| C3A | 0.6709 (5) | 0.2899 (4) | 1.2519 (3) | 0.100 (2) |
| C4A | 0.6829 (4) | 0.2039 (4) | 1.1179 (3) | 0.094 (2) |
| C5A | 0.5987 (5) | 0.1538 (4) | 1.0307 (3) | 0.095 (2) |
| C6A | 0.6745 (5) | 0.1139 (4) | 0.9730 (3) | 0.092 (2) |
| C7A | 0.5960 (5) | 0.0585 (4) | 0.8820 (3) | 0.095 (2) |
| C8A | 0.6751 (5) | 0.0217 (4) | 0.8261 (3) | 0.099 (2) |
| C9A | 0.5963 (5) | −0.0475 (4) | 0.7374 (3) | 0.106 (2) |
| C10A | 0.4631 (4) | −0.0365 (4) | 0.6213 (3) | 0.082 (2) |
| C11A | 0.4323 (5) | −0.1339 (3) | 0.5739 (3) | 0.089 (2) |
| C12A | 0.3562 (5) | −0.1711 (4) | 0.4919 (3) | 0.087 (2) |
| C13A | 0.3111 (4) | −0.1093 (3) | 0.4589 (3) | 0.077 (2) |
| C14A | 0.3416 (4) | −0.0114 (3) | 0.5079 (3) | 0.081 (2) |
| C15A | 0.4177 (4) | 0.0250 (3) | 0.5891 (3) | 0.082 (2) |
| C16A | 0.2366 (4) | −0.1413 (3) | 0.3710 (3) | 0.081 (2) |
| C17A | 0.1661 (4) | −0.2698 (3) | 0.2401 (3) | 0.082 (2) |
| C18A | 0.2371 (4) | −0.2857 (3) | 0.1847 (3) | 0.085 (2) |
| C19A | 0.1781 (4) | −0.3242 (3) | 0.1001 (3) | 0.081 (2) |
| C20A | 0.0482 (4) | −0.3459 (3) | 0.0715 (3) | 0.075 (2) |
| C21A | −0.0203 (4) | −0.3301 (4) | 0.1288 (3) | 0.094 (2) |
| C22A | 0.0395 (4) | −0.2913 (4) | 0.2138 (3) | 0.103 (2) |
| C23A | −0.0121 (4) | −0.3867 (3) | −0.0186 (3) | 0.079 (2) |
| C24A | −0.0588 (4) | −0.4418 (3) | −0.1508 (3) | 0.076 (2) |
| C25A | −0.0612 (4) | −0.4744 (4) | −0.2350 (3) | 0.093 (2) |
| C26A | −0.1790 (4) | −0.5143 (4) | −0.2935 (3) | 0.089 (2) |
| C27A | −0.2872 (4) | −0.5172 (3) | −0.2663 (3) | 0.082 (2) |
| C28A | −0.2893 (4) | −0.4831 (4) | −0.1832 (3) | 0.084 (2) |
| C29A | −0.1718 (4) | −0.4479 (3) | −0.1289 (3) | 0.075 (2) |
| O1B | −0.4643 (4) | −0.4258 (4) | −1.0710 (3) | 0.160 (2) |
| O2B | −0.5310 (3) | −0.3532 (3) | −0.9676 (2) | 0.109 (1) |
| O3B | −0.0038 (3) | −0.1371 (2) | −0.4843 (2) | 0.094 (1) |
| O4B | 0.1047 (3) | 0.0831 (2) | −0.0998 (2) | 0.099 (1) |
| O5B | 0.2591 (3) | 0.0218 (3) | −0.0965 (2) | 0.121 (1) |
| O6B | 0.0609 (3) | 0.2683 (2) | 0.2662 (2) | 0.081 (1) |
| O7B | 0.0871 (4) | 0.4263 (4) | 0.6252 (2) | 0.152 (2) |
| O8B | −0.0740 (4) | 0.3985 (3) | 0.5275 (2) | 0.157 (2) |
| N1B | 0.2633 (3) | 0.2798 (3) | 0.3055 (2) | 0.092 (2) |
| N2B | 0.0333 (4) | 0.4021 (3) | 0.5528 (2) | 0.116 (2) |
| C1B | −0.7120 (5) | −0.4897 (4) | −1.1851 (4) | 0.132 (3) |
| C2B | −0.6777 (5) | −0.4410 (4) | −1.0977 (4) | 0.115 (3) |
| C3B | −0.5494 (5) | −0.4080 (4) | −1.0474 (3) | 0.105 (2) |
| C4B | −0.4044 (5) | −0.3195 (4) | −0.9144 (3) | 0.111 (3) |
| C5B | −0.4019 (5) | −0.2705 (4) | −0.8275 (3) | 0.106 (2) |
| C6B | −0.2710 (5) | −0.2473 (4) | −0.7687 (3) | 0.093 (2) |
| C7B | −0.2582 (4) | −0.1957 (4) | −0.6773 (3) | 0.094 (2) |
| C8B | −0.1341 (4) | −0.1876 (3) | −0.6217 (3) | 0.088 (2) |
| C9B | −0.1199 (4) | −0.1366 (4) | −0.5307 (3) | 0.085 (2) |
| C10B | 0.0314 (4) | −0.0945 (3) | −0.3993 (3) | 0.078 (2) |
| C11B | −0.0387 (4) | −0.0502 (3) | −0.3546 (3) | 0.085 (2) |
| C12B | 0.0069 (4) | −0.0090 (3) | −0.2682 (3) | 0.084 (2) |
| C13B | 0.1187 (4) | −0.0123 (3) | −0.2273 (3) | 0.077 (2) |
| C14B | 0.1863 (4) | −0.0588 (3) | −0.2742 (3) | 0.084 (2) |
| C15B | 0.1419 (4) | −0.0992 (3) | −0.3595 (3) | 0.080 (2) |
| C16B | 0.1703 (4) | 0.0304 (3) | −0.1367 (3) | 0.085 (2) |
| C17B | 0.1273 (4) | 0.1251 (3) | −0.0131 (3) | 0.084 (2) |
| C18B | 0.0230 (4) | 0.1335 (4) | 0.0135 (3) | 0.093 (2) |
| C19B | 0.0332 (4) | 0.1758 (4) | 0.0965 (3) | 0.089 (2) |
| C20B | 0.1495 (4) | 0.2092 (3) | 0.1539 (3) | 0.073 (2) |
| C21B | 0.2542 (4) | 0.2017 (4) | 0.1266 (3) | 0.094 (2) |
| C22B | 0.2455 (4) | 0.1606 (4) | 0.0434 (3) | 0.100 (2) |
| C23B | 0.1640 (4) | 0.2526 (3) | 0.2431 (3) | 0.080 (2) |
| C24B | 0.2253 (4) | 0.3158 (4) | 0.3767 (3) | 0.082 (2) |
| C25B | 0.2910 (5) | 0.3516 (4) | 0.4613 (3) | 0.100 (2) |
| C26B | 0.2248 (5) | 0.3802 (4) | 0.5175 (3) | 0.102 (2) |
| C27B | 0.1012 (5) | 0.3725 (4) | 0.4889 (3) | 0.090 (2) |
| C28B | 0.0331 (4) | 0.3369 (4) | 0.4056 (3) | 0.087 (2) |
| C29B | 0.1011 (4) | 0.3082 (3) | 0.3523 (3) | 0.074 (2) |

Table 4. *Selected geometric parameters (Å, °) for (2)*

| | | | |
|---|---|---|---|
| O1A—C3A | 1.190 (7) | O1B—C3B | 1.191 (8) |
| O2A—C3A | 1.339 (5) | O2B—C3B | 1.343 (6) |
| C6A—C7A | 1.531 (6) | C6B—C7B | 1.517 (7) |
| O2A—C4A | 1.463 (7) | O2B—C4B | 1.442 (6) |
| O3A—C9A | 1.446 (8) | O3B—C9B | 1.444 (6) |
| O3A—C10A | 1.366 (5) | O3B—C10B | 1.365 (5) |
| O4A—C16A | 1.369 (6) | O4B—C16B | 1.361 (6) |
| O4A—C17A | 1.402 (5) | O4B—C17B | 1.400 (5) |
| O5A—C16A | 1.198 (7) | O5B—C16B | 1.200 (6) |
| O6A—C23A | 1.374 (5) | O6B—C23B | 1.374 (6) |
| O6A—C29A | 1.382 (5) | O6B—C29B | 1.378 (5) |
| O7A—N2A | 1.211 (6) | O7B—N2B | 1.200 (5) |
| O8A—N2A | 1.218 (6) | O8B—N2B | 1.218 (7) |
| N1A—C23A | 1.299 (6) | N1B—C23B | 1.306 (5) |
| N1A—C24A | 1.389 (5) | N1B—C24B | 1.395 (6) |
| N2A—C27A | 1.467 (6) | N2B—C27B | 1.497 (7) |
| C1A—C2A | 1.435 (9) | C1B—C2B | 1.413 (8) |
| C2A—C3A | 1.511 (9) | C2B—C3B | 1.441 (7) |
| C13A—C16A | 1.482 (6) | C13B—C16B | 1.459 (6) |
| C14A—C15A | 1.385 (6) | C14B—C15B | 1.369 (6) |
| C20A—C23A | 1.464 (6) | C20B—C23B | 1.458 (6) |
| C24A—C25A | 1.393 (6) | C24B—C25B | 1.399 (6) |
| C24A—C29A | 1.391 (7) | C24B—C29B | 1.381 (7) |
| C25A—C26A | 1.393 (6) | C25B—C26B | 1.382 (8) |
| C26A—C27A | 1.389 (7) | C26B—C27B | 1.382 (8) |
| C27A—C28A | 1.391 (7) | C27B—C28B | 1.388 (6) |
| C28A—C29A | 1.364 (6) | C28B—C29B | 1.365 (7) |
| C3A—O2A—C4A | 115.6 (4) | C3B—O2B—C4B | 115.8 (4) |
| C9A—O3A—C10A | 116.7 (4) | C9B—O3B—C10B | 118.5 (4) |
| C16A—O4A—C17A | 117.2 (4) | C16B—O4B—C17B | 123.9 (4) |
| C23A—O6A—C29A | 104.1 (3) | C23B—O6B—C29B | 104.3 (3) |
| C23A—N1A—C24A | 104.0 (4) | C23B—N1B—C24B | 104.8 (4) |
| O7A—N2A—O8A | 122.7 (4) | O7B—N2B—O8B | 124.3 (5) |
| O1A—C3A—C2A | 124.8 (5) | O1B—C3B—C2B | 125.7 (5) |
| O2A—C3A—C2A | 113.6 (4) | O2B—C3B—C2B | 113.6 (5) |
| O3A—C10A—C11A | 125.7 (5) | O3B—C10B—C11B | 123.6 (4) |

| | | | |
|---|---|---|---|
| O3A—C10A—C15A | 113.4 (4) | O3B—C10B—C15B | 115.2 (4) |
| C12A—C13A—C16A | 122.9 (4) | C12B—C13B—C16B | 122.7 (5) |
| C14A—C13A—C16A | 117.0 (5) | C14B—C13B—C16B | 118.0 (4) |
| O4A—C16A—C13A | 111.9 (5) | O4B—C16B—C13B | 112.1 (4) |
| O4A—C17A—C18A | 117.4 (4) | O4B—C17B—C18B | 115.0 (4) |
| O5A—C16A—C13A | 125.8 (4) | O5B—C16B—C13B | 126.3 (5) |
| O6A—C23A—N1A | 115.4 (3) | O6B—C23B—N1B | 114.3 (4) |
| N1A—C23A—C20A | 128.0 (4) | N1B—C23B—C20B | 128.7 (5) |
| N1A—C24A—C29A | 109.8 (4) | N1B—C24B—C29B | 108.7 (4) |
| C19A—C20A—C23A | 119.4 (4) | C19B—C20B—C23B | 121.0 (4) |
| C21A—C20A—C23A | 121.6 (4) | C21B—C20B—C23B | 119.3 (4) |
| C25A—C24A—C29A | 119.4 (4) | C25B—C24B—C29B | 121.1 (5) |
| C24A—C25A—C26A | 117.5 (4) | C24B—C25B—C26B | 116.0 (5) |
| C25A—C26A—C27A | 119.4 (4) | C25B—C26B—C27B | 120.2 (4) |
| C26A—C27A—C28A | 125.2 (4) | C26B—C27B—C28B | 125.4 (5) |
| C27A—C28A—C29A | 112.6 (4) | C27B—C28B—C29B | 112.6 (5) |
| O6A—C29A—C24A | 106.8 (3) | O6B—C29B—C24B | 107.9 (4) |
| C24A—C29A—C28A | 125.9 (4) | C24B—C29B—C28B | 124.7 (4) |

| | |
|---|---|
| C17A—O4A—C16A—C13A | −176.6 (4) |
| C16A—O4A—C17A—C18A | 115.2 (5) |
| O8A—N2A—C27A—C26A | −177.4 (5) |
| C7A—C8A—C9A—O3A | 60.7 (6) |
| C14A—C13A—C16A—O4A | 170.8 (4) |
| C19A—C20A—C23A—O6A | 176.3 (4) |
| C17B—O4B—C16B—C13B | 174.6 (4) |
| C16B—O4B—C17B—C18B | −150.8 (5) |
| O8B—N2B—C27B—C26B | 177.5 (5) |
| C7B—C8B—C9B—O3B | 177.4 (4) |
| C14B—C13B—C16B—O4B | 172.7 (4) |
| C21B—C20B—C23B—O6B | 173.1 (5) |

For both compounds, data collection: *SDP* (Enraf–Nonius, 1985); cell refinement: *SDP*; data reduction: *SDP*. Program(s) used to solve structures: *RANTAN* in *MULTAN*11/82 (Main *et al.*, 1982) for (1); *SIR*92 (Altomare *et al.*, 1994) for (2). For both compounds, program(s) used to refine structures: *SDP*; molecular graphics: *ORTEP* (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1148). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# [1,3]Dithiolo[4,5-*b*][1]benzothiophene-2-thione

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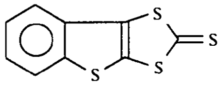
## Abstract

The crystals of the title compound, $C_9H_4S_4$, are composed of essentially planar molecules separated by normal van der Waals distances, with $S{=}C$ and $S{-}C_{sp^2}$(mean) bond distances of 1.641 (7) and 1.741 (11) Å, respectively.

## Comment

Recently, there has been considerable interest in the area of organic superconductors (Williams *et al.*, 1992). The majority of these incorporate a tetrathiafulvalene (TTF) unit as the electron donor in the conducting salt. Our goal was to a synthesize a novel TTF unit starting from benzo[*b*]thiophene. This was accomplished by a series of reactions starting with the reduction of 2,3-bis(methylthio)benzo[*b*]thiophene, (1) (Clark, Mesher & Primak, 1995). This reaction afforded a yellow oil, (2), that was not amenable to identification and which was reacted further with thiophosgene to afford a yellow solid, (3). Due to the ambiguous identification of (2), compound (3) could not be properly identified. Crystals were thus grown and an X-ray analysis performed, the results of which are described herein.



(3)

An *ORTEP*II (Johnson, 1976) drawing of the title compound, (3), is presented in Fig. 1, together with the atomic numbering scheme. The molecules are essentially planar, with a maximum deviation of 0.057 (9) Å (for atom C8) from the least-squares plane of the S and C atoms. The mean bond distances are: $S{=}C$ 1.641 (7), $S{-}C_{sp^2}$ 1.741 (11), $C{-}C_{\text{aromatic}}$ 1.386 (15), $C_{sp^2}{-}C_{sp^2}$ 1.458 (9) and $C{=}C$ 1.335 (8) Å. Similar $S{-}C_{sp^2}$ bond lengths have been reported for the crystal structures of both 2,3-bis(ethylsulfonyl)benzo-[*b*]thiophene [1.725 (1) Å; Parvez, Mesher & Clark, 1996*a*] and 2,3,6,7-tetrakis(methylthio)benzo[*b*]thiophene [1.741 (11) Å; Parvez, Mesher & Clark, 1996*b*].