Crystal structure of 11-(3′-oxodihydro[1]benzothiophen-2′-ylidene)-cyclopenta[1,2-*b*:4,3-*b*′]di[1]benzothiophene, $C_{25}H_{12}OS_3$, *at 93K*

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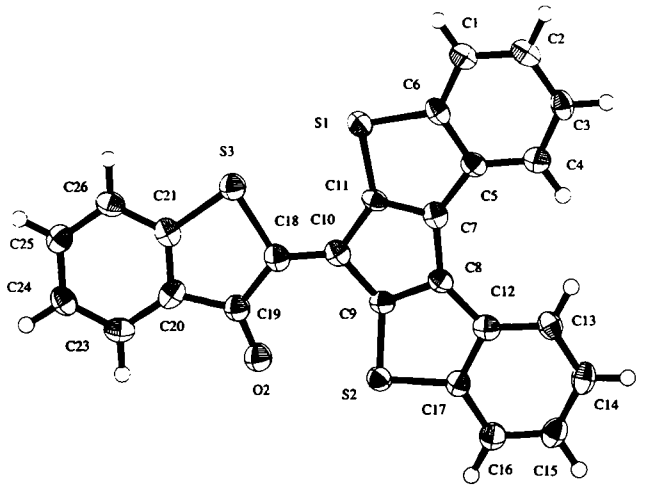
Received July 11, 2002, accepted and available on-line September 18, 2002; CCDC-No. 1267/898



Abstract

$C_{25}H_{12}OS_3$, triclinic, $P\bar{1}$ (No. 2), a = 3.8206(5) Å, b = 12.841(1) Å, c = 18.385(2) Å, α = 95.915(9)°, β = 92.55(1)°, γ = 94.07(1)°, V = 893.7 Å^3, Z = 2, $R_{gt}(F)$ = 0.057, $wR_{obs}(F^2)$ = 0.087, T = 93 K.

Source of material

The title compound was prepared by solid-state cogrinding of tri(benzo[*b*]thienyl)methyl alcohol with dichlorodicyanobenzoquinone [1]. The product was then purified by sublimation at about 625 K, using a two-zone furnace [2]. The single crystals were grown from the vapor phase in a closed system. After 48 h, a number of black needle crystals was obtained.

Experimental details

The molecule is disordered around S3, C19 and O2 atoms. Considerable electron densities of the S, C and O atoms (i.e. S4, C22 and O1) are also found for the molecule of the inverted form. The isotropic refinement on these atoms based on the 1:1 site occupancy gave the minimal R value.

Discussion

The title compound, a novel thioindigoid, has been synthesized in the course of our studies on the solid-state reactions induced by charge-transfer interactions [3,4]. This compound undergoes a color change from red to black when a mechanical stress was imposed on powders in a mortar with a pestle. The effect is called "tribo- or piezochromism". The present structure analysis has been undertaken in order to clarify the mechanism of the color change due to mechanical stress.

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The molecule is entirely planar as shown in the figure. The molecule has a symmetry of C_1 as characterized by a dipole moment of about 1.56 *D*. As mentioned before, the molecule is disordered around S3, C19 and O2 atoms. The present molecular form and its inverted form exist equally in the crystal lattice according to the site occupancy analysis. This indicates that the two kinds of molecular arrangements are possible along the stacking *a*-axis. One possibility is that the molecule of the one form and its inverted molecule are stacked alternately, cancelling each other the dipole moment. Another possibility is that the molecules of the one form are stacked in one column while the inverted molecules are likewise stacked in the neighboring column. If the former is the case, the structure should be characterized by a double periodicity along the stacking *a*-axis. Since no double periodicity is observed in the present experiment, the latter arrangement is considered to be the most probable stacking structure. It is also to be noted that there is a marked difference in the C=O bond length between the disordered structures: 1.197(8) Å for the C19—O2 bond and 1.287(8) Å for the C22-O1 bond.

Table 1. Data collection and handling.

Crystal:	black needle, size 0.050 × 0.050 × 0.250 mm
Wavelength:	Cu K_α radiation (1.5419 Å)
μ:	39.08 cm^{-1}
Diffractometer, scan mode:	Rigaku RAXIS-RAPID, 60 frames, $\Delta\omega$ = 15°
$2\theta_{max}$:	136.8°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8814, 2941
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 0\ \sigma(I_{obs})$, 2829
$N(param)_{refined}$:	259
Programs:	SHELXS-86 [5], teXsan [6], ABSCOR [7], ORTEPII [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ	*x*	*y*	*z*	U_{iso}
S(3)	2*i*	0.50	0.6073(6)	0.3613(2)	0.4293(1)	0.0358(5)
S(4)	2*i*	0.50	0.6710(5)	0.1114(2)	0.4373(1)	0.0273(5)
O(1)	2*i*	0.50	0.532(1)	0.4056(4)	0.4173(2)	0.033(1)
O(2)	2*i*	0.50	0.650(1)	0.0610(4)	0.4236(3)	0.040(1)
C(19)	2*i*	0.50	0.676(2)	0.1541(6)	0.4400(4)	0.034(2)
C(22)	2*i*	0.50	0.615(2)	0.3172(6)	0.4375(4)	0.031(2)
H(1)	2*i*		0.0033	0.5588	0.1776	0.041
H(2)	2*i*		−0.2502	0.5267	0.0567	0.043

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(3)	2*i*	–0.358	0.3491	0.0017	0.040
H(4)	2*i*	–0.2068	0.2083	0.0643	0.040
H(5)	2*i*	–0.1991	0.0459	0.0709	0.038
H(6)	2*i*	–0.2897	–0.1328	0.0218	0.045
H(7)	2*i*	–0.1034	–0.2672	0.0871	0.047

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(8)	2*i*	0.1853	–0.2296	0.2043	0.042
H(9)	2*i*	1.0233	0.0926	0.5731	0.042
H(10)	2*i*	1.2370	0.2181	0.6719	0.036
H(11)	2*i*	1.1729	0.3991	0.6676	0.038
H(12)	2*i*	0.8855	0.4590	0.5643	0.042

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	2*i*	0.2482(2)	0.41337(7)	0.27926(4)	0.0314(5)	0.0353(5)	0.0336(5)	0.0046(4)	–0.0023(4)	0.0065(4)
S(2)	2*i*	0.3610(2)	–0.02659(6)	0.29221(4)	0.0289(5)	0.0314(5)	0.0342(5)	0.0037(4)	–0.0014(4)	0.0051(4)
C(1)	2*i*	–0.0374(8)	0.4868(3)	0.1541(2)	0.034(2)	0.038(2)	0.036(2)	0.007(2)	0.003(2)	0.009(2)
C(2)	2*i*	–0.1876(8)	0.4671(3)	0.0842(2)	0.032(2)	0.042(2)	0.043(2)	0.009(2)	0.004(2)	0.015(2)
C(3)	2*i*	–0.2496(8)	0.3630(3)	0.0514(2)	0.023(2)	0.050(2)	0.031(2)	0.004(2)	–0.003(1)	0.004(2)
C(4)	2*i*	–0.1605(8)	0.2798(3)	0.0879(2)	0.030(2)	0.034(2)	0.038(2)	0.003(2)	0.004(2)	0.006(2)
C(5)	2*i*	–0.0072(8)	0.2976(3)	0.1588(2)	0.024(2)	0.034(2)	0.033(2)	0.008(2)	0.005(1)	0.005(2)
C(6)	2*i*	0.0526(8)	0.4034(3)	0.1912(2)	0.019(2)	0.043(2)	0.029(2)	0.007(2)	0.004(1)	0.009(2)
C(7)	2*i*	0.1149(8)	0.2275(3)	0.2087(2)	0.017(2)	0.038(2)	0.032(2)	0.002(2)	0.004(1)	0.005(2)
C(8)	2*i*	0.1420(8)	0.1136(2)	0.2116(2)	0.020(2)	0.032(2)	0.032(2)	0.006(2)	0.004(1)	0.005(2)
C(9)	2*i*	0.3034(7)	0.1019(2)	0.2786(2)	0.018(2)	0.027(2)	0.037(2)	0.001(1)	0.002(1)	0.004(2)
C(10)	2*i*	0.3827(8)	0.2039(3)	0.3217(2)	0.016(2)	0.038(2)	0.035(2)	0.005(1)	0.006(1)	0.005(2)
C(11)	2*i*	0.2561(8)	0.2784(2)	0.2734(2)	0.019(2)	0.027(2)	0.036(2)	0.003(1)	0.002(1)	0.009(2)
C(12)	2*i*	0.0527(8)	0.0144(3)	0.1678(2)	0.017(2)	0.036(2)	0.038(2)	0.004(2)	0.007(1)	0.004(2)
C(13)	2*i*	–0.1160(8)	–0.0098(3)	0.0987(2)	0.024(2)	0.041(2)	0.037(2)	0.001(2)	–0.002(2)	0.006(2)
C(14)	2*i*	–0.1722(8)	–0.1139(3)	0.0695(2)	0.030(2)	0.047(2)	0.034(2)	–0.007(2)	–0.001(2)	–0.002(2)
C(15)	2*i*	–0.0619(8)	–0.1939(3)	0.1087(2)	0.030(2)	0.043(2)	0.037(2)	0.003(2)	0.005(2)	–0.007(2)
C(16)	2*i*	0.1023(8)	–0.1727(3)	0.1764(2)	0.030(2)	0.040(2)	0.035(2)	0.005(2)	0.003(2)	0.000(2)
C(17)	2*i*	0.1601(8)	–0.0681(2)	0.2066(2)	0.021(2)	0.034(2)	0.032(2)	0.001(2)	0.002(1)	0.001(2)
C(18)	2*i*	0.5369(8)	0.2222(3)	0.3899(2)	0.022(2)	0.043(2)	0.034(2)	0.007(2)	0.005(2)	0.003(2)
C(20)	2*i*	0.8354(8)	0.2051(3)	0.5105(2)	0.024(2)	0.037(2)	0.034(2)	–0.002(2)	0.011(2)	–0.004(2)
C(21)	2*i*	0.7999(8)	0.3114(3)	0.5080(2)	0.026(2)	0.045(2)	0.031(2)	0.004(2)	0.005(2)	0.007(2)
C(23)	2*i*	0.9996(9)	0.1685(3)	0.5707(2)	0.034(2)	0.032(2)	0.043(2)	0.007(2)	0.011(2)	0.009(2)
C(24)	2*i*	1.1180(8)	0.2410(3)	0.6285(2)	0.026(2)	0.048(2)	0.035(2)	0.007(2)	0.003(2)	0.009(2)
C(25)	2*i*	1.0833(8)	0.3478(3)	0.6263(2)	0.029(2)	0.037(2)	0.039(2)	–0.002(2)	0.002(2)	0.001(2)
C(26)	2*i*	0.9223(8)	0.3841(3)	0.5661(2)	0.031(2)	0.034(2)	0.042(2)	0.004(2)	0.005(2)	0.009(2)

References

1. Tanifuji, N.; Kobayashi, K.: Unpublished results, The University of Tokio, 2002.
2. Mizuguchi, J.: An improved method for purification of β-copperphthalocyanine. Cryst. Res. Tech. **16** (1981) 695-700.
3. Tanaka, M.; Tanifuji, N.; Hatada, S.; Kobayayshi, K.: Solid-state solvolysis of thiophene-substituted trityl-type alcohols: Nucleophilic substitution induced by gas-solid contact. J. Org. Chem. **66** (2001) 803-808.
4. Tanaka, M.; Kobayashi, K.: Solid-state solvolysis induced via charge-transfer complexation by solid-state grinding followed by contact with solvent vapor. Chem. Commun. (1998) 1965-1966.
5. Sheldrick, G. M.: Phase Annealing in SHELX-90: Direct methods for Larger Structure. Acta Crystallogr. A**46** (1990) 467-473.
6. teXsan: Single Crystal Structure Analysis Software. Version 1.11, Molecular Structure Corporation; 3200 Research Forest Drive, The Woodlands, TX 77381, USA 2000.
7. Higashi, T.: ABSCOR. Empirical Absorption Correction, Rigaku Corporation, Japan 1995.
8. Johnson, C. K.: ORTEPII, Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA 1976.