1,3-Di(2-thienyl)propen-1-one

LI ZHENGDONG AND SU GENBO

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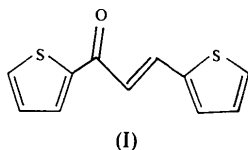
Abstract

In the title compound, $C_{11}H_8OS_2$, there are two molecules in the asymmetric unit. The torsion angles O(1A)—C(1A)—C(2A)—C(3A) and O(1B)—C(1B)—C(2B)—C(3B) of the C_2H_2CO moieties are -3.5 (7) and 2.0 (7)°, respectively. The H atoms are *trans* in C_2H_2CO. The dihedral angles between the thienyl rings are 10.28 and 1.49° for molecule A and B of the asymmetric unit, respectively.

Comment

The chalcone derivatives constitute newly developed organic crystals with non-linear optical properties (Fichou, Watanabe, Takeda, Miyata, Goto & Nakayama, 1988). In order to explore the relationship between their structure and non-linear optical properties, we have synthesized a series of substituted chalcones. The title compound, (I), is one of them, although it crystallizes in a centrosymmetric space group and therefore has no non-linear optical properties. This has been confirmed by SHG efficiency measurements on a powder sample using the method of Kurtz & Perry (1968). The result is different from that of Goto, Hayashi, Kimura & Nakayama (1991), who reported that the compound has an SHG activity which is 52 times larger than that of urea. These contradictory results suggest that the compound has a variable crystal form.

(I)

There are two molecules in the asymmetric unit and their molecular configurations are shown in Fig. 1. Least-squares-planes calculations showed that they are almost planar, the torsion angles O(1A)—C(1A)—C(2A)—C(3A) and O(1B)—C(1B)—C(2B)—C(3B) of the C_2H_2CO group being -3.5 (7) and 2.0 (7)°, respectively. The H atoms are *trans* in the C_2H_2CO moiety. The dihedral angles between the thienyl rings and between each thienyl ring and the C_2H_2CO moiety are 10.28, 8.79 and 1.68°, respectively, for molecule A, and

1.49, 2.42 and 2.52°, respectively, for molecule B. The angles for corresponding planes of the thienyl chalcone 1-(2-thienyl)-3-(4-methylphenyl)propen-1-one are 12.42, 11.48 and 8.79° for one molecule and 17.86, 15.66 and 6.79° for the other (Goto, Hayashi, Kimura & Nakayama, 1991). It is significant that conjugacy in the title molecule is better than in this thienyl chalcone. The UV spectra of the two compounds indicate that the above is correct, the values of λ_{max} being 349 and
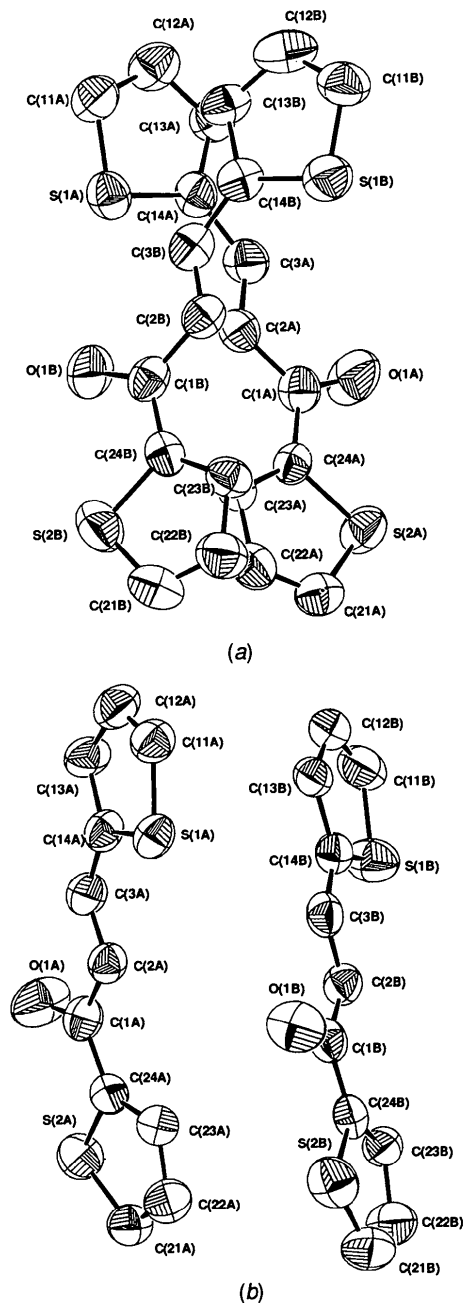

Fig. 1. The molecular structure of the title compound for (*a*) molecule A and (*b*) molecule B viewed from two directions. Displacement ellipsoids are drawn at the 50% probability level.

331 nm for 1,3-dithienylpropenone and the thienyl chal-
cone, respectively. The absorption wavelength of the
former compound is around 18 nm longer than the latter
(Goto, Hayashi, Kimura & Nakayama, 1991).

Experimental

The title compound was prepared by the acyloin condensation
method from 2-thiophenealdehyde and 2-acetylthiophene at
room temperature (Migrdichian, 1957). Crystals were obtained
from an ethanol solution.

Crystal data

$C_{11}H_8OS_2$	Mo $K\alpha$ radiation
$M_r = 220.30$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 20
$P2_1/n$	reflections
$a = 8.938\ (3)$ Å	$\theta = 9-11°$
$b = 17.109\ (5)$ Å	$\mu = 0.445$ mm^{-1}
$c = 14.272\ (3)$ Å	$T = 294$ K
$\beta = 104.21°$	Block
$V = 2116\ (1)$ Å^3	$1.0 \times 0.5 \times 0.5$ mm
$Z = 8$	Colorless
$D_x = 1.38$ Mg m^{-3}	

Data collection

Rigaku AFC-5R diffractom-	$R_{int} = 0.1373$
eter	$\theta_{max} = 25°$
ω–2θ scans	$h = 0 \rightarrow 11$
Absorption correction:	$k = 0 \rightarrow 20$
refined from ΔF	$l = -17 \rightarrow 17$
($DIFABS$; Walker &	3 standard reflections
Stuart, 1983)	monitored every 250
4125 measured reflections	reflections
3863 independent reflections	intensity decay: 0.3%
2196 observed reflections	
[$I > 3\sigma(I)$]	

Refinement

Refinement on F	$\Delta\rho_{max} = 0.23$ e Å^{-3}
$R = 0.054$	$\Delta\rho_{min} = -0.24$ e Å^{-3}
$wR = 0.066$	Extinction coefficient:
$S = 1.68$	0.70723×10^{-7}
2196 reflections	Atomic scattering factors
254 parameters	from International Tables
H-atom sites fixed	for X-ray Crystallography
$w = 1/\sigma^2(F_o)$	(1974, Vol. IV)
$(\Delta/\sigma)_{max} = 0.0057$	

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

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
S(1A)	−0.3240 (1)	0.12920 (8)	0.38144 (9)	5.00 (5)
S(2A)	0.3387 (1)	0.16954 (9)	0.1717 (1)	5.75 (6)
O(1A)	0.2734 (4)	0.1338 (3)	0.3563 (3)	8.1 (2)
C(1A)	0.1543 (5)	0.1445 (3)	0.2949 (3)	4.7 (2)
C(2A)	0.0032 (5)	0.1389 (3)	0.3183 (3)	4.3 (2)
C(3A)	−0.0054 (5)	0.1180 (3)	0.4062 (3)	4.9 (2)
C(11A)	−0.3986 (5)	0.0957 (3)	0.4726 (4)	5.5 (2)
C(12A)	−0.2894 (6)	0.0693 (3)	0.5475 (4)	6.0 (3)

	x	y	z	B_{eq}
C(13A)	−0.1388 (5)	0.0768 (3)	0.5339 (3)	5.2 (2)
C(14A)	−0.1386 (5)	0.1079 (3)	0.4448 (3)	4.5 (2)
C(21A)	0.2589 (6)	0.1928 (3)	0.0545 (4)	5.5 (2)
C(22A)	0.1031 (6)	0.1953 (3)	0.0339 (4)	5.7 (2)
C(23A)	0.0434 (5)	0.1782 (3)	0.1147 (3)	4.3 (2)
C(24A)	0.1614 (4)	0.1644 (2)	0.1968 (3)	4.0 (2)
S(1B)	0.8064 (2)	−0.16053 (9)	0.2227 (1)	6.53 (7)
S(2B)	0.6807 (2)	0.16227 (8)	−0.1124 (1)	6.57 (7)
O(1B)	0.6112 (4)	0.1236 (2)	0.0713 (3)	7.1 (2)
C(1B)	0.6784 (5)	0.0695 (3)	0.0437 (3)	4.6 (2)
C(2B)	0.7163 (5)	−0.0026 (3)	0.0983 (3)	4.5 (2)
C(3B)	0.6753 (5)	−0.0141 (3)	0.1803 (3)	4.8 (2)
C(11B)	0.7894 (6)	−0.2053 (3)	0.3253 (4)	6.4 (3)
C(12B)	0.7092 (7)	−0.1618 (4)	0.3744 (4)	6.5 (3)
C(13B)	0.6605 (5)	−0.0900 (3)	0.3330 (3)	4.8 (2)
C(14B)	0.7058 (5)	−0.0802 (3)	0.2437 (3)	4.6 (2)
C(21B)	0.7711 (7)	0.1313 (4)	−0.1964 (4)	7.0 (3)
C(22B)	0.8346 (7)	0.0602 (3)	−0.1778 (4)	6.4 (3)
C(23B)	0.8096 (5)	0.0270 (3)	−0.0917 (3)	4.7 (2)
C(24B)	0.7250 (5)	0.0777 (2)	−0.0483 (3)	4.3 (2)

Table 2. Selected geometric parameters (Å, °)

S(1A)—C(11A)	1.700 (5)	S(1B)—C(11B)	1.692 (5)
S(1A)—C(14A)	1.721 (4)	S(1B)—C(14B)	1.708 (5)
S(2A)—C(21A)	1.697 (5)	S(2B)—C(21B)	1.688 (6)
S(2A)—C(24A)	1.710 (4)	S(2B)—C(24B)	1.706 (5)
O(1A)—C(1A)	1.215 (5)	O(1B)—C(1B)	1.220 (5)
C(1A)—C(2A)	1.473 (6)	C(1B)—C(2B)	1.453 (6)
C(1A)—C(24A)	1.457 (6)	C(1B)—C(24B)	1.479 (6)
C(2A)—C(3A)	1.325 (6)	C(2B)—C(3B)	1.325 (6)
C(3A)—C(14A)	1.440 (6)	C(3B)—C(14B)	1.433 (6)
C(11A)—C(12A)	1.337 (7)	C(11B)—C(12B)	1.344 (7)
C(12A)—C(13A)	1.413 (6)	C(12B)—C(13B)	1.386 (7)
C(13A)—C(14A)	1.379 (6)	C(13B)—C(14B)	1.439 (6)
C(21A)—C(22A)	1.352 (6)	C(21B)—C(22B)	1.342 (7)
C(22A)—C(23A)	1.414 (6)	C(22B)—C(23B)	1.420 (6)
C(23A)—C(24A)	1.391 (6)	C(23B)—C(24B)	1.392 (6)
C(11A)—S(1A)—C(14A)	92.0 (2)	C(11B)—S(1B)—C(14B)	92.8 (2)
C(21A)—S(2A)—C(24A)	91.8 (2)	C(21B)—S(2B)—C(24B)	91.5 (3)
O(1A)—C(1A)—C(24A)	119.4 (4)	O(1B)—C(1B)—C(24B)	118.9 (4)
O(1A)—C(1A)—C(2A)	121.1 (4)	O(1B)—C(1B)—C(2B)	122.6 (4)
C(24A)—C(1A)—C(2A)	119.5 (4)	C(24B)—C(1B)—C(2B)	118.5 (4)
C(3A)—C(2A)—C(1A)	120.1 (4)	C(3B)—C(2B)—C(1B)	121.4 (4)
C(2A)—C(3A)—C(14A)	129.8 (4)	C(2B)—C(3B)—C(14B)	128.6 (4)
C(12A)—C(11A)—S(1A)	112.3 (4)	C(12B)—C(11B)—S(1B)	111.9 (4)
C(11A)—C(12A)—C(13A)	113.1 (4)	C(11B)—C(12B)—C(13B)	114.9 (5)
C(14A)—C(13A)—C(12A)	112.3 (4)	C(14B)—C(13B)—C(12B)	110.6 (4)
C(13A)—C(14A)—C(3A)	126.0 (4)	C(13B)—C(14B)—C(3B)	126.8 (4)
C(13A)—C(14A)—S(1A)	110.3 (3)	C(13B)—C(14B)—S(1B)	109.7 (4)
C(3A)—C(14A)—S(1A)	123.6 (3)	C(3B)—C(14B)—S(1B)	123.5 (3)
C(22A)—C(21A)—S(2A)	112.5 (4)	C(22B)—C(21B)—S(2B)	113.4 (4)
C(21A)—C(22A)—C(23A)	113.0 (4)	C(21B)—C(22B)—C(23B)	112.7 (5)
C(24A)—C(23A)—C(22A)	111.2 (4)	C(24B)—C(23B)—C(22B)	110.7 (4)
C(23A)—C(24A)—C(1A)	130.3 (4)	C(23B)—C(24B)—C(1B)	129.7 (4)
C(23A)—C(24A)—S(2A)	111.4 (3)	C(23B)—C(24B)—S(2B)	111.7 (3)
C(1A)—C(24A)—S(2A)	118.3 (3)	C(1B)—C(24B)—S(2B)	118.6 (3)

The data were corrected for Lorentz and polarization factors
and the structure was solved by direct methods. H-atom
coordinates were added according to theoretical models and
were included in the structure-factor calculations. The scale
factor, positional and anisotropic displacement parameters
for non-H atoms were refined by full-matrix least-squares
methods.

All calculations were performed on a VAX computer with
programs from the TEXSAN crystallographic software package
(Molecular Structure Corporation, 1985).

References

Fichou, D., Watanabe, T., Takeda, T., Miyata, S., Goto, Y. & Nakayama, M. (1988). Jpn. J. Appl. Phys. 27, L429–L430.

Goto, Y., Hayashi, A., Kimura, Y. & Nakayama, M. (1991). J. Cryst. Growth, 108, 688–698.

Kurtz, S. K. & Perry, T. T. (1968). J. Appl. Phys. 39, 3798–3813.

Migrdichian, V. (1957). Organic Synthesis, Vol. 1, pp. 171–176. New York: Reinhold.

Molecular Structure Corporation (1985). TEXSAN. TEXRAY Structure Analysis Package. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Walker, N. & Stuart, D. (1983). Acta Cryst. A39, 158–166.

Acta Cryst. (1995). C51, 683–685

1:1 Molecular Complex of 2,3,4,5,6-Pentafluoro-*trans*-cinnamic Acid and 4-(*N*,*N*-Dimethylamino)-*trans*-cinnamic Acid

B. Satish Goud, P. Krishna Reddy, Kaliyamoorthy Panneerselvam and Gautam R. Desiraju

School of Chemistry, University of Hyderabad, PO Central University, Hyderabad 500134, India

Abstract

The donor–acceptor complex $C_9H_3F_5O_2 \cdot C_{11}H_{13}NO_2$ crystallizes as carboxy-hetero dimers which are stacked to optimize $\pi \cdots \pi$ interactions. Additionally C—H···O, C—H···F, O···F and F···F interactions are important.

Comment

Charge-transfer molecular complexes of cinnamic acids are of interest because of their possible solid-state reactivity (Sarma & Desiraju, 1985). The $\pi \cdots \pi$ interactions between two electronically different cinnamic acids have been exploited in the preparation of asymmetric truxinic acids in the solid state; these acids are good candidates for molecular recognition in host–guest complexes (Weber, Hecker, Csoregh & Czugler, 1989; Desiraju & Sharma, 1991; Sharma, Panneerselvam, Pilati & Desiraju, 1993). The title molecular complex (1) was prepared with the aim of engineering a solid-state reaction. Complex (1) is, however, unreactive upon photoirradiation in the solid state and this led us to study its structural features.

(1)
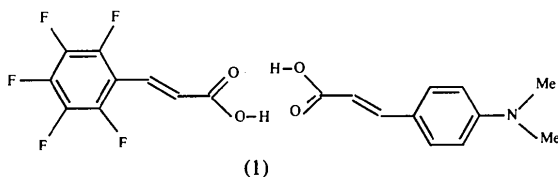
Acids *A* (2,3,4,5,6-pentafluoro-*trans*-cinnamic acid) and *B* [4-(*N*,*N*-dimethylamino)-*trans*-cinnamic acid] in (1) are hydrogen bonded through carboxyl groups to form a hetero dimer. The O···O distances are 2.61–2.62 Å. The carboxyl groups are partially disordered in the molecule of *A* with C(9)—O(2) 1.246 (2) Å, C(9)—O(1) 1.290 (2) Å, O(2)—C(9)—C(8) 121.6 (2)°, O(1)—C(9)—C(8) 114.9 (2)° and also in the molecule of *B* with C(9)—O(2) 1.251 (2) Å, C(9)—O(1) 1.293 (2) Å, O(2)—C(9)—C(8) 121.7 (2)°, O(1)—C(9)—C(8) 115.8 (2)°. This disorder is caused by the comparable crystal environments around the O(1) and O(2) atoms, especially with regard to their C—H···O hydrogen-bond forming ability (Leiserowitz, 1976; Goud, Pathaneni & Desiraju, 1993). These hetero dimers are stabilized by C—H···O and C—H···F interactions and form a sheet-like structure along (101) (Fig. 2). These sheets are stacked using $\pi \cdots \pi$ interactions (Fig. 3). Evidence for these interactions is obtained from the deeper colour of the complex (dark yellow) when compared with its constituents (acid *A* is white and *B* is light yellow). Interestingly, the donor–acceptor phenyl rings of the *A* and *B* molecules do not overlap but instead have a large lateral offset such that $\pi \cdots \pi$ interactions between the aromatic ring and the double bond are optimized. This is a rare occurrence (Sharma *et al.*, 1993).
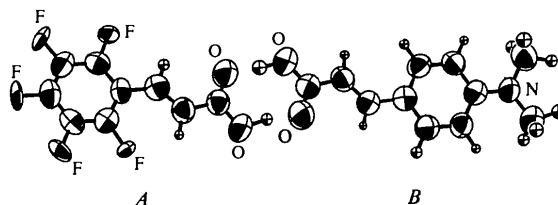

Fig. 1. *ORTEP*II (Johnson, 1976) view of complex (1) showing the atom-labelling scheme. Displacement ellipsoids are plotted at the 50% probability level.
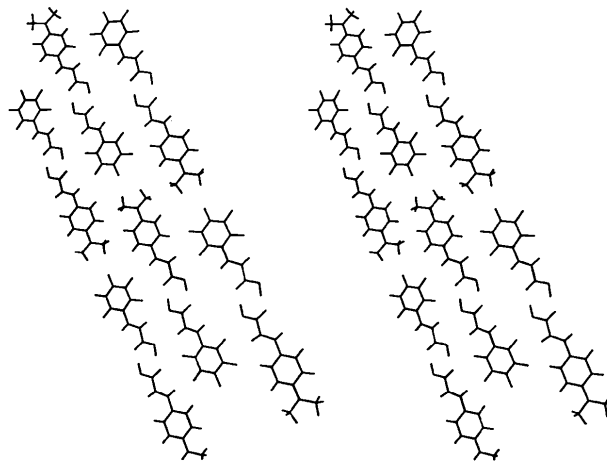

Fig. 2. Molecular complex (1) viewed along (101) to show the sheet structure.