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Key indicators

Single-crystal X-ray study

T = 150 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.039

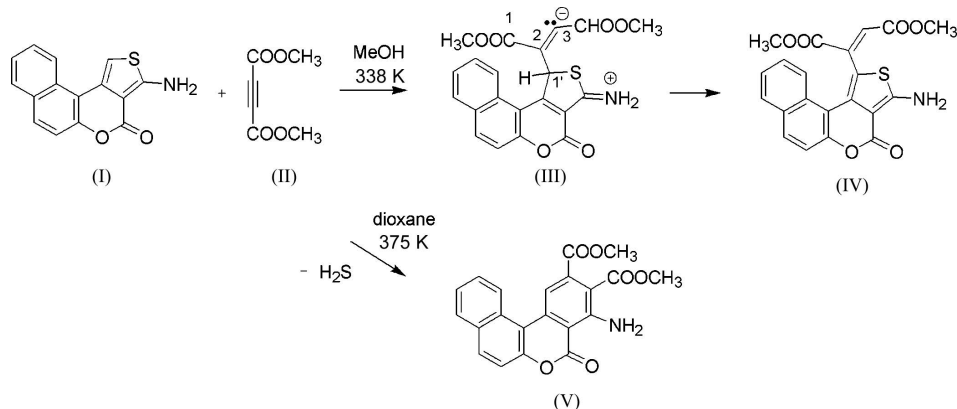
wR factor = 0.100

Data-to-parameter ratio = 14.7

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Dimethyl 2-(3-amino-4-oxo-4*H*-benzo[*f*]-
thieno[3,4-*c*]chromen-1-yl)fumarateThe title compound, $\text{C}_{21}\text{H}_{15}\text{NO}_6\text{S}$, shows a helical structure of the molecule. In the crystal packing, molecules are linked *via* intermolecular $\text{N}-\text{H}\cdots\text{O}$ interactions into infinite sheets that are stacked along [100].

Comment

2-Aminothiophenes, when [*c*]annelated to a mono- or oligocyclic π -system as in (I) (see scheme), undergo Diels–Alder additions with electron-poor alkenes across the dienoid system of the thiophene ring (Nyiondi-Bonguen *et al.*, 1994; Al-Omran *et al.*, 1996; Erian *et al.*, 1998; Sopbue Fondjo *et al.*, 2006) with subsequent loss of hydrogen sulfide from the 1:1 cycloadducts. In principle, the same reaction is possible with electron-poor alkynes. Under mild conditions, however, a Michael-type addition of the alkyne to C1 of (I) is the preferred mode of reaction (Al-Omran *et al.*, 1996; Sopbue Fondjo *et al.*, 2006). Thus, the reaction of (I) with dimethyl ethynedicarboxylate, (II), at 338 K in methanol [stabilizing intermediate (III)] gives a 64% yield of the title compound, (IV), while in refluxing dioxane (375 K) only 26% of (IV) is obtained, together with 58% of the fused phthalate (V). In (I), C1' (see scheme) is the doubly vinylene-homologous position of the 3'-NH₂ group. In other words, C1' is electron rich and a good nucleophile towards electron-poor multiple bonds. The conjugate addition to generate (III) obviously has a lower activation energy than the [4+2]-cycloaddition leading to (V) by loss of hydrogen sulfide. Intermediate (III) just requires a protonation at the fumarate C3 and a deprotonation at C1' to form (IV). All attempts to achieve a separation of the enantiomers by HPLC on chiral stationary phases have so far been unsuccessful however (Sopbue Fondjo *et al.*, 2006). We report here the crystal and molecular structure of (IV), whose crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 602732.



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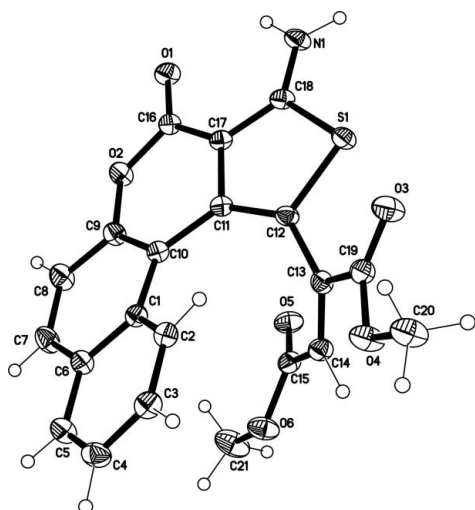


Figure 1
Molecular structure of (IV). Displacement ellipsoids are drawn at the 50% probability level.

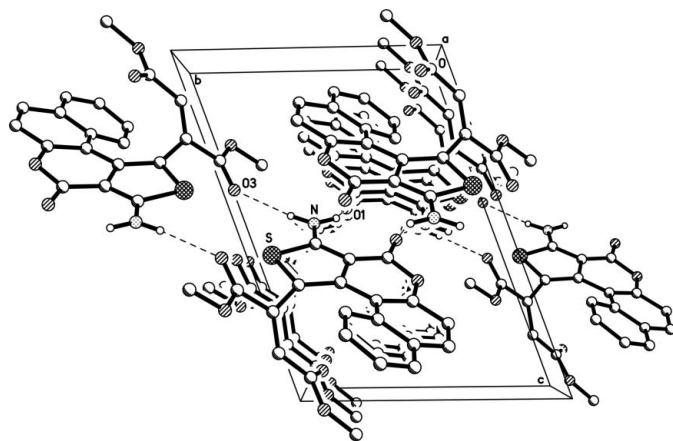


Figure 2
Crystal packing viewed along [100], with the intermolecular hydrogen-bonding pattern indicated as dashed lines. H atoms not involved in hydrogen bonding have been omitted.

The molecular structure of (IV) (Fig. 1) shows a helical arrangement of the four fused rings *A* (C1–C6), *B* (C1/C6–C10), *C* (O2/C9–C11/C17/C16), *D* (C11/C12/S1/C18/C17) and the dicarboxylate unit. The dihedral angles between the rings are $A/B = 7.2(1)^\circ$, $B/C = 8.1(1)^\circ$ and $C/D = 8.8(1)^\circ$. The aromatic ring system (C1–C10) is puckered, with atom deviations of $-0.106(2)$ for C8 and $0.153(2)$ Å for C10 from the mean plane, and the associated C–C bond lengths lie between $1.358(3)$ and $1.447(3)$ Å (Table 1). Rings *C* and *D* are almost planar, with largest deviations of $0.077(2)$ for C10 and $0.034(2)$ Å for C12. Delocalization of the π system leads to a shortening of single C–C bonds [C10–C11 = $1.465(2)$ Å, C16–C17 = $1.429(3)$ Å and C11–C17 = $1.439(2)$ Å]. The thiophene ring has geometric parameters similar to those of other thiophene systems, e.g. JIGGIP (Joseph *et al.*, 1991; refcode in the Cambridge Structural Database; *MOGUL*, Version 1.0; Allen, 2002). The acetate group at C19 is almost coplanar with the C13=C14 bond, as shown by the

C14=C13–C19–O4 torsion angle of $-24.8(2)^\circ$, and is associated with an intramolecular C14–H···O4 interaction (Table 2). Another expected intramolecular hydrogen bond is N–H···O1. The crystal packing (Fig. 2) is stabilized by strong intermolecular hydrogen bonds (Table 2) N–H···O1 and N–H···O3 that link molecules into extended sheets which are stacked along [100].

Experimental

A sample of 3-amino-4*H*-benzo[*f*]thieno[3,4-*c*]-(*2H*)chromen-2-one, (I) (814 mg, 3.05 mmol) and an excess of dimethyl ethylenedicarboxylate, (II), in 10 ml of methanol was kept at reflux temperature for 10 h. The concentrated residue was stored in a freezer for several days. The precipitate was filtered off and crystallized from methanol to give 777 mg (62%) of (IV), m.p. 454–456 K. Single crystals of (IV) were grown from the same solvent. For spectroscopic and analytical details see Sopbue Fondjo *et al.* (2006).

Crystal data

$C_{21}H_{15}NO_6S$	$V = 895.4(17) \text{ \AA}^3$
$M_r = 409.40$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.519 \text{ Mg m}^{-3}$
$a = 7.718(8) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.451(11) \text{ \AA}$	$\mu = 0.22 \text{ mm}^{-1}$
$c = 13.058(13) \text{ \AA}$	$T = 150(2) \text{ K}$
$\alpha = 109.40(1)^\circ$	Prism, colourless
$\beta = 91.50(1)^\circ$	$0.47 \times 0.35 \times 0.34 \text{ mm}$
$\gamma = 93.71(1)^\circ$	

Data collection

Siemens P4 rotating anode diffractometer	3901 independent reflections
ω scans	3223 reflections with $I > 2\sigma(I)$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$R_{\text{int}} = 0.013$
$T_{\text{min}} = 0.903$, $T_{\text{max}} = 0.928$	$\theta_{\text{max}} = 27.0^\circ$
3903 measured reflections	3 standard reflections every 100 reflections
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2 + 0.3857P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.100$	$(\Delta/\sigma)_{\text{max}} = 0.003$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
3901 reflections	$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$
266 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: $0.004(1)$

Table 1
Selected geometric parameters (Å, °).

S1–C18	1.723(2)	C6–C7	1.421(3)
S1–C12	1.758(2)	C7–C8	1.358(3)
O1–C16	1.216(2)	C8–C9	1.406(3)
O2–C16	1.377(2)	C9–C10	1.388(3)
O2–C9	1.385(2)	C10–C11	1.465(3)
N1–C18	1.341(2)	C11–C12	1.383(3)
C1–C2	1.421(3)	C11–C17	1.439(2)
C1–C6	1.425(3)	C12–C13	1.469(2)
C1–C10	1.447(3)	C13–C14	1.342(3)
C2–C3	1.373(3)	C13–C19	1.510(2)
C3–C4	1.404(3)	C16–C17	1.429(3)
C4–C5	1.366(3)	C17–C18	1.393(3)
C5–C6	1.419(3)		
C18–S1–C12	92.48(10)	C16–O2–C9	122.10(14)

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C14—H14A \cdots O4	0.96	2.38	2.733 (3)	101
N1—H1B \cdots O1	0.90	2.26	2.854 (4)	124
N1—H1A \cdots O3 ⁱ	0.90	2.13	2.947 (3)	150
N1—H1B \cdots O1 ⁱⁱ	0.90	2.31	2.979 (3)	131

Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $-x + 2, -y + 1, -z + 1$.

H atoms were located in difference Fourier maps and refined at idealized positions riding on the C and N atoms with C—H = 0.96 Å, N—H = 0.90 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ and $1.5U_{\text{eq}}(\text{methyl C})$. Methyl H atoms were refined as rigid groups allowed to rotate but not tip.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Bruker, 2002); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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