

C8a	-0.0139 (4)	0.2437 (4)	-0.0641 (4)	0.0452 (1)
C8b	0.1161 (4)	0.1561 (4)	-0.4266 (4)	0.0470 (1)
C9a	0.0790 (4)	0.2244 (4)	0.0363 (4)	0.0447 (1)
C9b	0.2143 (4)	0.1434 (4)	-0.3250 (4)	0.0432 (1)
C10a	0.5026 (3)	0.2555 (3)	0.4382 (4)	0.0346 (1)
C10b	0.6352 (3)	0.0619 (3)	-0.0336 (4)	0.0311 (1)
C11a	-0.1979 (5)	0.2944 (5)	-0.2638 (6)	0.0650 (1)
C11b	-0.0782 (5)	0.1765 (5)	-0.6446 (7)	0.0681 (1)
O1W	0.0181 (3)	0.4662 (3)	0.3309 (4)	0.0612 (1)

Table 2. Selected geometric parameters (\AA , $^\circ$)

O1a—C1a	1.260 (4)	C1a—C2a	1.424 (4)
O1b—C1b	1.249 (4)	C1b—C2b	1.427 (5)
O2a—C7a	1.378 (4)	C2a—C3a	1.396 (4)
O2b—C7b	1.365 (4)	C2b—C3b	1.398 (4)
O2a—C11a	1.433 (5)	C2a—C10a	1.405 (5)
O2b—C11b	1.418 (6)	C2b—C10b	1.412 (5)
N1a—N2a	1.397 (4)	C4a—C5a	1.373 (5)
N1b—N2b	1.412 (4)	C4b—C5b	1.378 (4)
N1a—C3a	1.343 (4)	C4a—C9a	1.371 (5)
N1b—C3b	1.348 (5)	C4b—C9b	1.373 (5)
N2a—C1a	1.357 (4)	C5a—C6a	1.374 (5)
N2b—C1b	1.380 (4)	C5b—C6b	1.372 (5)
N3a—C3a	1.341 (4)	C6a—C7a	1.383 (5)
N3b—C3b	1.345 (4)	C6b—C7b	1.380 (5)
N3a—C4a	1.441 (4)	C7a—C8a	1.367 (5)
N3b—C4b	1.432 (4)	C7b—C8b	1.375 (5)
N4a—C10a	1.146 (4)	C8a—C9a	1.388 (5)
N4b—C10b	1.134 (4)	C8b—C9b	1.388 (5)
C7a—O2a—C11a	118.4 (3)	C3b—N3b—C4b	124.3 (3)
C7b—O2b—C11b	118.5 (3)	N2a—C1a—C2a	105.3 (3)
N2a—N1a—C3a	107.1 (3)	N2b—C1b—C2b	106.1 (3)
N2b—N1b—C3b	107.9 (3)	C1a—C2a—C3a	107.6 (3)
N1a—N2a—C1a	110.7 (3)	C1b—C2b—C3b	107.4 (3)
N1b—N2b—C1b	108.7 (3)	N1b—C3b—C2b	109.1 (3)
C3a—N3a—C4a	121.6 (3)	N1a—C3a—C2a	108.9 (3)

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A
N1a—H1a...O1W	0.97 (4)	1.78 (4)	2.743 (6)
N1b—H1b...O1a ⁱ	0.97 (3)	1.81 (4)	2.752 (5)
N2a—H2a...O1b ⁱⁱ	0.85 (3)	1.96 (3)	2.794 (5)
N2b—H2b...O1a ⁱⁱ	0.93 (4)	1.90 (4)	2.820 (5)
N3a—H3a...N4b ⁱⁱⁱ	0.89 (4)	2.16 (4)	3.026 (7)
N3b—H3b...N4a ⁱⁱⁱ	0.93 (4)	2.16 (4)	3.041 (7)
O1W—H11W...O1b ^v	1.07 (7)	1.96 (7)	2.894 (6)
O1W—H12W...O2a ^v	0.88 (6)	1.97 (6)	2.828 (5)

Symmetry codes: (i) $x, y, z - 1$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $1 - x, -y, -z$; (iv) $x - 1, y, z$; (v) $-x, 1 - y, -z$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993a). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993b). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1021). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4,5-Dicyano-4',5'-ethylenedithiotetrathiafulvalene (CNET)[†]: a New Unsymmetrical TTF Derivative

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Abstract

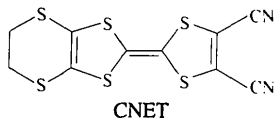
The molecule of the title compound, $\text{C}_{10}\text{H}_4\text{N}_2\text{S}_6$, is nearly planar except for the ethylene group. Intermolecular S...S interactions are found along the *a* axis in the crystal structure.

Comment

Various chemical modifications of TTF (tetrathiafulvalene) have been investigated because their radical-

[†] Alternative nomenclature: 2-(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]-dithiin-2-ylidene)-1,3-dithiole-4,5-dicarbonitrile.

cation salts show unique conducting properties. Since the discovery of superconductivity in DMET₂Au(CN)₂ [where DMET is dimethyl(ethylenedithio)diselenadithiafulvalene] (Kikuchi *et al.*, 1987), symmetrical and unsymmetrical donor molecules have attracted much attention. We report here a new unsymmetrical TTF derivative, CNET.



The molecular structure and the packing in the unit cell are illustrated in Figs. 1 and 2, respectively. Except for the ethylene moiety [—C(1)—C(2)—] the molecule is nearly planar. The bicyclic part of the molecule is similar to that of ET [bis(ethylenedithio)diselenadithiafulvalene] (Kobayashi, Kobayashi, Sasaki, Saito & Inokuchi, 1986). The average C—S bond length (1.758 Å) and the C(3)=C(4) length [1.334 (4) Å] in the five-membered ring are very close to those found in the neutral ET molecule (1.751 and 1.335 Å, respectively). The mean C—S bond length in the other five-membered ring, 1.751 Å, is similar. However, the C(7)=C(8) bond [1.357 (4) Å] and the central C(5)=C(6) bond [1.350 (3) Å] are longer than those found in neutral ET (1.312 and 1.332 Å, respectively), but close to

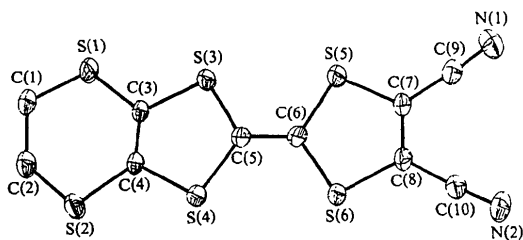


Fig. 1. Molecular structure of CNET. Displacement ellipsoids are plotted at the 30% probability level.

those found in the ET^{1/2+} salt (1.365 and 1.345 Å, respectively) (Kobayashi, Kobayashi, Sasaki, Saito & Inokuchi, 1984). These effects may be caused by the electron-withdrawing CN groups.

Close intermolecular S···S contacts are found along the *a* axis (Fig. 2). The distances S(3a)···S(2) (3.631 Å) and S(1a)···S(2) (3.573 Å) are shorter than the sum of the van der Waals radii (3.69 Å), suggesting the existence of S···S interactions. It is interesting to note that the neutral unsymmetrical CNET molecules adopt a side-by-side arrangement with close S···S contacts; this is a common structural feature of the symmetrical ET molecule and its cation salts.

Experimental

The title compound was prepared as dark purple crystals by (EtO)₃P mediated cross-coupling of 4,5-dicyano-1,3-dithiol-2-one (Klingsberg, 1964) and 4,5-ethylenedithio-1,3-dithiol-2-one (Varma, Bury, Harris & Underhill, 1987). Single crystals were obtained by slow evaporation of a dichloromethane solution of the compound.

Crystal data

C₁₀H₄N₂S₆
M_r = 344
 Triclinic
*P*1̄
a = 6.855 (2) Å
b = 7.606 (2) Å
c = 13.587 (3) Å
 α = 75.01 (2)°
 β = 87.88 (2)°
 γ = 70.56 (2)°
V = 644.3 (3) Å³
Z = 2
D_x = 1.789 Mg m⁻³

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 23 reflections
 θ = 3.52–12.1°
 μ = 1.039 mm⁻¹
T = 295 (1.5) K
 Needle
 0.48 × 0.34 × 0.30 mm
 Dark purple

Data collection

*R*3m/*E* diffractometer
 $\theta/2\theta$ scans
 Absorption correction: none
 2831 measured reflections
 2773 independent reflections
 2242 observed reflections
 $[I \geq 3\sigma(I)]$
R_{int} = 0.0112

θ_{\max} = 26°
h = 0 → 9
k = -10 → 10
l = -17 → 17
 2 standard reflections monitored every 98 reflections
 intensity decay: <1.7%

Refinement

Refinement on *F*
R = 0.0367
wR = 0.0350
S = 1.433
 2242 reflections
 180 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o) + 0.0001F_o^2] \times \{1 - \exp[-5(\sin\theta/\lambda)^2]\}$

$(\Delta/\sigma)_{\max}$ = 0.071
 $\Delta\rho_{\max}$ = 0.453 e Å⁻³
 $\Delta\rho_{\min}$ = -0.278 e Å⁻³
 Extinction correction: none
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

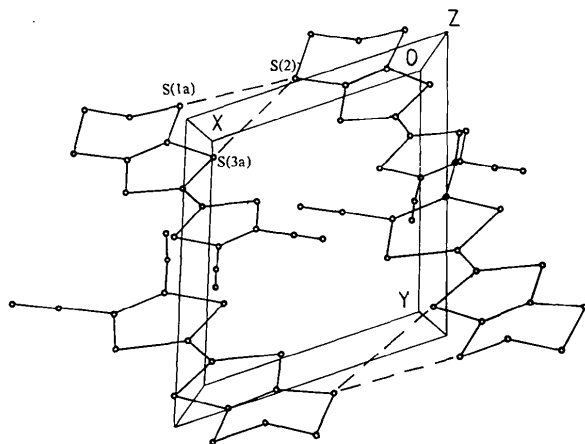


Fig. 2. Molecular packing in the title crystal.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
S(1)	0.1076 (1)	-0.1427 (1)	1.3884 (1)	0.041 (1)
S(2)	0.5952 (1)	-0.1049 (1)	1.3180 (1)	0.046 (1)
S(3)	-0.0274 (1)	0.0863 (1)	1.1767 (1)	0.037 (1)
S(4)	0.3841 (1)	0.1086 (1)	1.1168 (1)	0.034 (1)
S(5)	-0.2257 (1)	0.3177 (1)	0.9555 (1)	0.039 (1)
S(6)	0.1808 (1)	0.3495 (1)	0.8836 (1)	0.036 (1)
N(1)	-0.5495 (4)	0.5706 (4)	0.7156 (2)	0.054 (1)
N(2)	-0.0050 (4)	0.6262 (4)	0.6095 (2)	0.050 (1)
C(1)	0.3162 (4)	-0.1507 (5)	1.4683 (2)	0.040 (1)
C(2)	0.5285 (4)	-0.2472 (4)	1.4340 (2)	0.040 (1)
C(3)	0.1778 (4)	-0.0299 (4)	1.2701 (2)	0.029 (1)
C(4)	0.3630 (4)	-0.0176 (4)	1.2432 (2)	0.030 (1)
C(5)	0.1232 (4)	0.1653 (4)	1.0797 (2)	0.028 (1)
C(6)	0.0395 (4)	0.2638 (4)	0.9848 (2)	0.029 (1)
C(7)	-0.2142 (4)	0.4343 (4)	0.8283 (2)	0.030 (1)
C(8)	-0.0297 (4)	0.4493 (3)	0.7953 (2)	0.028 (1)
C(9)	-0.3984 (4)	0.5105 (4)	0.7643 (2)	0.035 (1)
C(10)	-0.0095 (4)	0.5468 (4)	0.6923 (2)	0.033 (1)

Table 2. Selected geometric parameters (\AA , $^\circ$)

S(1)—C(1)	1.802 (3)	S(1)—C(3)	1.749 (2)
S(2)—C(2)	1.805 (3)	S(2)—C(4)	1.754 (2)
S(3)—C(3)	1.759 (2)	S(3)—C(5)	1.752 (2)
S(4)—C(4)	1.765 (2)	S(4)—C(5)	1.755 (2)
S(5)—C(6)	1.761 (3)	S(5)—C(7)	1.740 (2)
S(6)—C(6)	1.764 (2)	S(6)—C(8)	1.739 (2)
N(1)—C(9)	1.140 (4)	N(2)—C(10)	1.137 (3)
C(1)—C(2)	1.513 (4)	C(3)—C(4)	1.334 (4)
C(5)—C(6)	1.350 (3)	C(7)—C(8)	1.357 (4)
C(7)—C(9)	1.421 (3)	C(8)—C(10)	1.429 (3)
C(1)—S(1)—C(3)	99.3 (1)	N(1)—C(9)—C(7)	177.9 (3)
C(3)—S(3)—C(5)	95.5 (1)	C(2)—S(2)—C(4)	101.7 (1)
C(6)—S(5)—C(7)	94.2 (1)	C(4)—S(4)—C(5)	94.9 (1)
S(1)—C(1)—C(2)	113.3 (2)	C(6)—S(6)—C(8)	94.4 (1)
S(2)—C(2)—C(1)	113.6 (2)	S(1)—C(3)—C(4)	128.5 (2)
S(1)—C(3)—S(3)	114.4 (1)	S(2)—C(4)—S(4)	113.3 (1)
S(3)—C(3)—C(4)	117.0 (2)	S(4)—C(4)—C(3)	117.7 (2)
S(2)—C(4)—C(3)	129.0 (2)	S(3)—C(5)—C(6)	121.2 (2)
S(3)—C(5)—S(4)	114.8 (1)	S(5)—C(6)—S(6)	115.6 (1)
S(4)—C(5)—C(6)	124.0 (2)	S(6)—C(6)—C(5)	123.7 (2)
S(5)—C(6)—C(5)	120.7 (2)	S(5)—C(7)—C(9)	118.5 (2)
S(5)—C(7)—C(8)	118.2 (2)	S(6)—C(8)—C(7)	117.5 (2)
C(8)—C(7)—C(9)	123.3 (2)	C(7)—C(8)—C(10)	121.4 (2)
S(6)—C(8)—C(10)	121.1 (2)	N(2)—C(10)—C(8)	176.1 (3)

The structure was solved by direct methods and subsequent difference Fourier techniques, and refined by full-matrix least-squares methods with anisotropic displacement parameters for all non-H atoms. H atoms were found by difference Fourier techniques. All calculations were performed using the *SHELXTL/PC* system of computer programs (Sheldrick, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1079). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4-Chloro-7-(iodoacetyl)amino-3-methoxyisocoumarin

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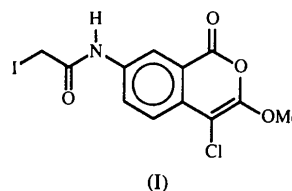
(Received 25 July 1994; accepted 24 July 1995)

Abstract

The crystal structure of the iodo analog of 7-(bromoacetyl)amino-4-chloro-3-methoxyisocoumarin, an inhibitor of human neutrophil elastase (HNE), $\text{C}_{12}\text{H}_9\text{ClINO}_4$, has been determined. The isocoumarin ring system is highly planar, with the carbonyl group of the amide function being coplanar with the isocoumarin ring.

Comment

The title compound, (I), was synthesized from 7-amino-4-chloro-3-methoxyisocoumarin by known methods (Harper & Powers, 1985) using iodoacetic anhydride as the acylating agent. The bromo analog is an effective *in vitro* inhibitor of human neutrophil elastase (HNE) (Kerrigan, Oleksyszyn, Kam, Selzler & Powers, 1995). The title compound was synthesized to obtain a precise structure of an isocoumarin for future modeling studies in order to investigate further the inhibitory activity of the isocoumarins.



The isocoumarin ring system is planar [maximum displacement 0.024(10) \AA] with the carbonyl O(11) atom positioned slightly out-of-plane. The acetyl amide