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# *trans,trans*-2-Cyano-5-(4-methoxyphenyl)penta-2,4-dienethioamide

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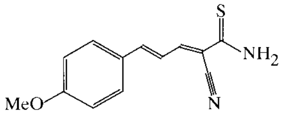
The title compound, $C_{13}H_{12}N_2OS$, was prepared by condensation of 4-methoxycinnamaldehyde and thioacetamide in ethanol at room temperature. Its investigation was undertaken as part of our search for new non-linear optical compounds. The $\pi$-conjugated title molecule is almost planar, the dihedral angle between the central planar 2-cyano-5-(4-methoxyphenyl)penta-2,4-diene fragment and the thioacetamide group being 9.2 (6)°. Molecules are linked by N—H···N and N—H···O hydrogen bonds forming a two-dimensional motif.

## Comment

Structural studies of polarized organic molecules as components for non-linear optical (NLO) and photorefractive materials have attracted a great deal of attention in the last two decades [see, for instance, Zyss (1994)]. The present work is part of a continuing project on the synthesis, structure investigation and property evaluation of potential NLO compounds. Recently, we investigated a series of polarized molecules having a dicyanovinyl acceptor part and various donors connected by $\pi$-conjugated chains of different lengths. There are derivatives of 2-aryl-1,1-dicyanovinyl and 4-aryl-1,1-dicyano-1,3-butadiene (Antipin *et al.*, 1997; Antipin, Clark *et al.*, 1998; Antipin, Timofeeva *et al.*, 1998; Timofeeva *et al.*, 1999). We present herein a structural investigation of the title compound, (I), whose molecules have another type of acceptor group.



(I)

According to our quantum-chemical calculations [using modified *MOPAC* and *HYPER* programs (Cardelino *et al.*, 1991, 1997)], the molecular hyperpolarizability of (I) is equal to 142 × $10^{-51}$ C $m^3$ $V^{-2}$. This is about 40% larger than for the dicyanovinyl analogues (Antipin, Clark *et al.*, 1998).

The molecule (Fig. 1) contains an almost planar fragment consisting of *p*-methoxyphenyl and 1-cyano-1,3-butadiene moieties, with a dihedral angle between them of 1.7 (2)°. The maximum deviation from the least-squares plane passing through all non-H atoms of this fragment is 0.031 (3) Å. The 1-cyano-1,3-butadiene fragment in (I) is planar despite the shortened H6*A*···H8*A* [2.196 (6) Å] and H8*A*···C12 [2.577 (6) Å] intramolecular contacts; the corresponding van der Waals radii sums are 2.20 and 2.87 Å, respectively (Rowland & Taylor, 1996). The thioacetamide group is slightly out of the above-mentioned planar fragment, with a dihedral angle of 9.2 (6)° between the two.

Bond lengths in (I) do not differ significantly from those of 4-aryl-1,1-dicyano-1,3-butadiene (Antipin, Clark *et al.*, 1998). In the 1,3-butadiene fragment, the observed bond length

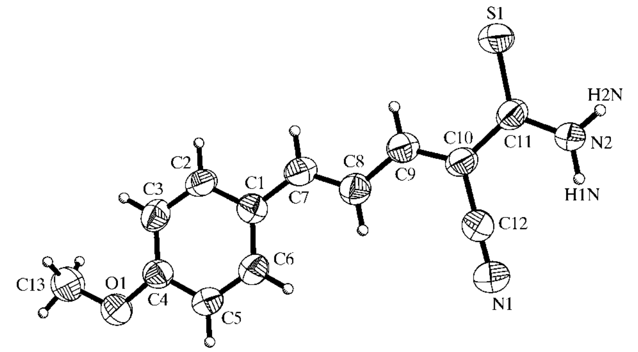


**Figure 1**
View of the title molecule with the atom-numbering scheme. The non-H atoms are shown with 50% probability displacement ellipsoids. H atoms are drawn as circles of small arbitrary radius for clarity.

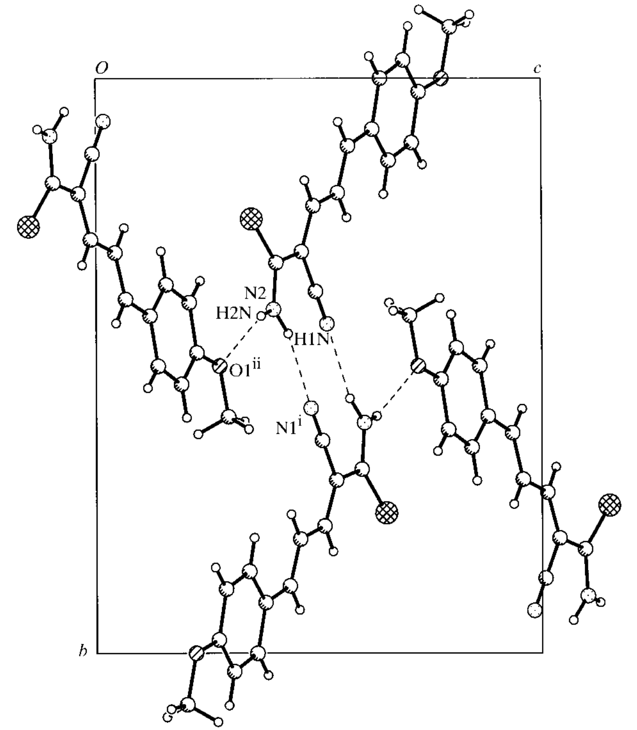


**Figure 2**
Projection onto the *bc* plane showing the hydrogen-bonding scheme. [Symmetry codes: (i) $1 - x, 2 - y, -z$; (ii) $x - \frac{3}{2}, \frac{3}{2} - y, \frac{1}{2} + z$.]

alternation [for standard bond lengths see Allen *et al.* (1987)] indicates $\pi$-conjugation in this system.

In the crystalline phase, molecules of (I) are linked by hydrogen bonds forming a two-dimensional motif (Fig. 2). Both H atoms of the amino group are involved in hydrogen bond formation, one with the O atom of the methoxy group and the other with the N atom of the cyano group of a neighboring molecule.

Compound (I) crystallizes in a centrosymmetric space group and this phase therefore cannot exhibit second-order NLO effects, but the compound may do so when incorporated into a suitable liquid crystalline or polymer matrix.

## Experimental

The title compound was obtained by the reaction of 4-methoxycinnamaldehyde (0.81 g, 5 mmol) with thioacetamide (0.50 g, 5 mmol) in the presence of a catalytic amount of morpholine (0.1 ml) in ethanol (20 ml) at room temperature. The precipitate which separated from the solution was recrystallized from ethanol (30 ml) (m.p. 458–459 K; yield 0.93 g, 76%). Yellow crystals were obtained by isothermal evaporation from a solution of (I) in ethanol.

*Crystal data*

$C_{13}H_{12}N_2OS$
$M_r = 244.31$
Monoclinic, $P2_1/n$
$a = 6.4590$ (13) Å
$b = 15.662$ (3) Å
$c = 12.276$ (3) Å
$\beta = 95.51$ (3)°
$V = 1236.1$ (4) Å$^3$
$Z = 4$

$D_x = 1.313$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 11$–12°
$\mu = 0.246$ mm$^{-1}$
$T = 295$ (2) K
Prism, yellow
0.45 × 0.30 × 0.25 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
2922 measured reflections
2688 independent reflections
1283 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.112$

$\theta_{\max} = 26.96°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 19$
$l = -15 \rightarrow 15$
3 standard reflections every 97 reflections intensity decay: 5%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.076$
$wR(F^2) = 0.201$
$S = 1.334$
2655 reflections
162 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1213P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.32$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.30$ e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| S1—C11 | 1.653 (4) | C7—C8 | 1.344 (6) |
| O1—C4 | 1.361 (5) | C8—C9 | 1.424 (6) |
| O1—C13 | 1.425 (6) | C9—C10 | 1.351 (6) |
| N1—C12 | 1.143 (6) | C10—C12 | 1.425 (6) |
| N2—C11 | 1.312 (5) | C10—C11 | 1.483 (6) |
| C1—C7 | 1.435 (6) | | |
| C4—O1—C13 | 117.5 (4) | C7—C8—C9 | 122.7 (4) |
| C11—N2—H1N | 123 (3) | C10—C9—C8 | 126.2 (4) |
| C11—N2—H2N | 117 (3) | C9—C10—C12 | 118.2 (4) |
| H1N—N2—H2N | 120 (4) | C9—C10—C11 | 123.4 (4) |
| C6—C1—C2 | 117.1 (4) | C12—C10—C11 | 118.4 (4) |
| C6—C1—C7 | 123.6 (4) | N2—C11—C10 | 115.5 (4) |
| C2—C1—C7 | 119.3 (4) | N2—C11—S1 | 122.7 (3) |
| O1—C4—C3 | 125.5 (4) | C10—C11—S1 | 121.8 (3) |
| O1—C4—C5 | 115.2 (4) | N1—C12—C10 | 179.3 (5) |
| C8—C7—C1 | 126.6 (4) | | |
| C13—O1—C4—C3 | 0.1 (6) | C8—C9—C10—C11 | 179.9 (4) |
| C13—O1—C4—C5 | −179.6 (4) | C9—C10—C11—N2 | −170.5 (4) |
| C2—C1—C7—C8 | −179.9 (4) | C12—C10—C11—N2 | 7.1 (6) |
| C1—C7—C8—C9 | 180.0 (4) | C9—C10—C11—S1 | 11.0 (6) |
| C7—C8—C9—C10 | 179.6 (4) | C12—C10—C11—S1 | −171.4 (3) |
| C8—C9—C10—C12 | 2.2 (6) | | |

**Table 2**
Hydrogen-bonding geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H1N···N1$^{\rm i}$ | 0.92 (5) | 2.18 (5) | 3.042 (5) | 155 (4) |
| N2—H2N···O1$^{\rm ii}$ | 0.83 (5) | 2.27 (5) | 3.035 (5) | 153 (4) |

Symmetry codes: (i) $1 - x, 2 - y, -z$; (ii) $x - \frac{3}{2}, \frac{3}{2} - y, \frac{1}{2} + z$.

The two amino H atoms were located from a difference Fourier map and were refined isotropically. All other H atoms were positioned geometrically and thereafter refined using a riding model.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *SHELXTL-Plus* (Sheldrick, 1994); program(s) used to solve structure: *SHELXTL-Plus*; program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1375). Services for accessing these data are described at the back of the journal.

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