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Structure of N-[Bis(methylthio)methylene]cinnamamide, C₁₂H₁₃NOS₂

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Abstract. $M_r = 251 \cdot 34$, monoclinic, $P2_1/n$, $a = 14 \cdot 626$ (3), $b = 7 \cdot 144$ (1), $c = 11 \cdot 996$ (2) Å, $\beta = 90 \cdot 03$ (2)°, $V = 1253 \cdot 4$ (6) Å³, $Z = 4$, $D_m = 1 \cdot 326$ (3), $D_x = 1 \cdot 331$ (3) g cm⁻³, Mo $K\alpha$, $\lambda = 0 \cdot 7107$ Å, $\mu = 3 \cdot 51$ cm⁻¹, $F(000) = 528 \cdot 0$, $T = 293$ K, $R = 3 \cdot 5\%$ for 1455 significant reflections. Of particular interest is an intramolecular attractive interaction between the sulphur and oxygen atoms with an S⋯O distance of $2 \cdot 658$ (3) Å, in which the oxygen atom appears to act as a nucleophile.

Introduction. The existing programme in our laboratory to study the molecular geometry of push–pull ethylenes by X-ray structural analysis (Adhikesavalu, Kamath & Venkatesan, 1983) included a study of 3,3-bis(methylthio)-2-nitro-2-propene-1-nitrile (Kamath & Venkatesan, 1984) where we observed that even with a combination of weak donors [bis(methylthio) group] and weak acceptors (nitro and cyano groups) the C=C double-bond length [$1 \cdot 377$ (3) Å] indicated a small degree of polarization. Interested in the possible push–pull character of the C=N double bond we decided to study the title compound where the donor groups remain the same, but the acceptor groups are replaced by a cinnamoyl group. Another point of interest is the synthetic potential of this compound and those of other N-[bis(alkylthio)methylene]acylamides which react with a wide range of nucleophilic compounds and therefore present new possibilities in the synthesis of heterocycles (Augustin, Richter & Salas, 1980).

The X-ray crystallographic investigations revealed a noteworthy structural feature in the geometry of this molecule which has a bivalent S atom as part of a five-membered hetero ring closed by an intramolecular S⋯O interaction. The compound was kindly provided by Dr Monica Richter, Martin-Luther University, Halle-Wittenberg.

Experimental. Single crystals grown from methanol by slow evaporation. D_m by flotation in KI solution. Crystal approximately $0 \cdot 6 \times 0 \cdot 3 \times 0 \cdot 5$ mm. Preliminary Weissenberg photographs indicated crystal to be monoclinic. Nonius CAD-4 diffractometer; lattice parameters refined by least-squares fit to settings of 23 accurately centred reflections. Intensity data collected using monochromated Mo $K\alpha$ radiation, scan speed 1° min⁻¹, $\theta_{max} = 23°$. Three standard reflections ($9\bar{1}0$, 060, $5\bar{2}4$) showed only statistical variation within ±2%. 1891 reflections collected, 1455 significant, $|F_o| \geq 3\sigma(|F_o|)$. No correction for absorption. h −15–16, k 0–7, l 0–13. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix refinement of scale factor, positional and anisotropic thermal parameters (isotropic for H, located from difference map), $R = 0 \cdot 035$, $R_w = 0 \cdot 041$, $S = 3 \cdot 42$; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 3 \cdot 981/\sigma^2(F)$. *SHELX*76 (Sheldrick, 1976) used for full-matrix refinement. Δ/σ for non-hydrogen atoms ~0·005; final difference Fourier synthesis featureless. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).*

Discussion. Positional coordinates are given in Table 1. A perspective view of the molecule viewed down the a axis is shown in Fig. 1. Bond lengths and angles involving non-hydrogen atoms are given in Fig. 2. Table 2 gives some of the important torsion angles.

The presence of the bis(methylthio) group as a donor and the cinnamoyl moiety as an acceptor about the C(3)=N(4) double bond was expected to induce a 'weak' push–pull character. The C(3)=N(4) distance of 1·289 (4) Å is comparable to 1·2849 (8) Å in glyoxime (Jeffrey, Ruble & Pople, 1982) and 1·278 (2)– 1·288 (4) Å in the three oximes examined by Bertolasi, Gilli & Veronese (1982), indicating the absence of any push–pull effect in this system.

The S(1)–C(3) and the S(2)–C(3) bond distances are 1·746 (3) and 1·753 (3) Å, respectively; the value reported for an S–C_{sp^2} bond is 1·762 (5) Å (Jandal, Seip & Torgrimsen, 1976).

In the cinnamoyl part of the molecule, atoms C(5) to C(14), the C(8)–C(9) and C(5)–C(7) bond distances are 1·479 (4) and 1·459 (5) Å, respectively. In co-planar conjugated double bonds the C_{sp^2}–C_{sp^2} single-bond distance lies between 1·47 and 1·50 Å (Allen, Trotter & Rogers, 1970; Briansó, Miravitlles, Plana & Font-Altaba, 1973; Braibanti, Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1973; Saarinen, Korvenranta & Näsäkkälä, 1977). Gas electron diffraction studies on planar substituted butadienes or hexatrienes have also failed to find significant shrinkages of the C_{sp^2}–C_{sp^2} single bond (Trætteberg, 1968; Aten, Hedberg & Hedberg, 1968).

Table 1. *Final positional parameters for nonhydrogen atoms* ($\times 10^4$) *with equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^2$)

E.s.d.'s are given in parentheses.

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
S(1)	478 (1)	4236 (1)	3708 (1)	4·65 (3)
S(2)	624 (1)	4292 (1)	1240 (1)	4·74 (3)
C(3)	1181 (2)	4320 (4)	2533 (3)	3·77 (10)
N(4)	2062 (2)	4379 (4)	2539 (2)	4·09 (9)
C(5)	2538 (2)	4475 (5)	3550 (3)	4·74 (12)
O(6)	2179 (2)	4611 (5)	4457 (2)	8·22 (12)
C(7)	3532 (2)	4423 (5)	3449 (3)	4·68 (12)
C(8)	3993 (2)	4236 (4)	2520 (3)	4·06 (11)
C(9)	4999 (2)	4195 (4)	2396 (3)	3·78 (10)
C(10)	5596 (2)	4415 (5)	3282 (3)	4·93 (12)
C(11)	6530 (3)	4377 (6)	3118 (4)	5·70 (14)
C(12)	6877 (3)	4146 (6)	2073 (3)	5·89 (14)
C(13)	6292 (2)	3919 (6)	1176 (3)	5·68 (13)
C(14)	5363 (2)	3953 (5)	1338 (3)	4·68 (12)
C(15)	−662 (2)	4136 (6)	3142 (4)	5·44 (14)
C(16)	1571 (3)	4503 (7)	304 (3)	6·01 (15)

Table 2. *Some important torsion angles* (°)

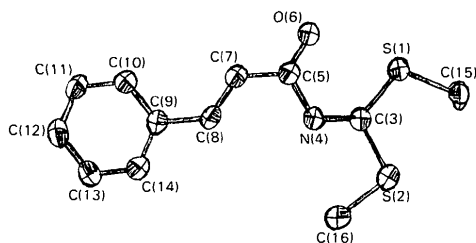|	
C(15)–S(1)–C(3)–S(2)	0·2 (2)
C(15)–S(1)–C(3)–N(4)	−179·0 (3)
C(16)–S(2)–C(3)–S(1)	177·4 (2)
S(1)–C(3)–N(4)–C(5)	−3·2 (5)
S(2)–C(3)–N(4)–C(5)	177·6 (2)
C(3)–N(4)–C(5)–O(6)	−4·2 (5)
C(3)–N(4)–C(5)–C(7)	176·5 (3)
N(4)–C(5)–C(7)–C(8)	−2·4 (5)
O(6)–C(5)–C(7)–C(8)	178·3 (4)
C(5)–C(7)–C(8)–C(9)	179·5 (3)
C(7)–C(8)–C(9)–C(10)	−2·1 (5)
C(7)–C(8)–C(9)–C(14)	178·9 (3)
C(8)–C(9)–C(10)–C(11)	−179·6 (3)
C(14)–C(9)–C(10)–C(11)	−0·6 (5)
C(8)–C(9)–C(14)–C(13)	179·5 (3)
C(9)–C(10)–C(11)–C(12)	0·9 (6)
C(10)–C(11)–C(12)–C(13)	−1·0 (6)
C(11)–C(12)–C(13)–C(14)	0·9 (6)
C(12)–C(13)–C(14)–C(9)	−0·6 (5)

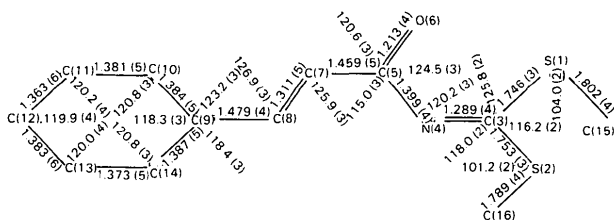Fig. 1. A perspective view of the molecule viewed down the a axis with the numbering scheme.

Fig. 2. Bond lengths (Å) and angles (°) involving the non-hydrogen atoms. E.s.d.'s are given in parentheses.

The C(7)=C(8) bond of 1·311 (5) Å is significantly different from 1·336 (2) Å in ethylene (Bartell, Roth, Hollowell, Kuchitsu & Young, 1965) and is comparable to the values of 1·324 (4) Å in (+)-2,4:3,5-di-O-methylene-D-mannitol 1,6-di-*trans*-cinnamate (Bernstein, Green & Rejtö, 1980).

The bis(methylthio) group defined by atoms C(16), S(2), C(3), S(1) and C(15) has a *syn–anti* conformation as already observed in 3,3-bis(methylthio)-2-nitro-2-propene-1-nitrile (Kamath & Venkatesan, 1984), although electron diffraction studies of 1,1-bis-(methylthio)ethylene (Jandal, Seip & Torgrimsen, 1976) show that this group is not in a *syn–anti* conformation.

The observed intramolecular distance of 2·658 (3) Å between S(1) and O(6) is shorter than the sum of the van der Waals radii of 3·32 Å [r(O) = 1·52, r(S)
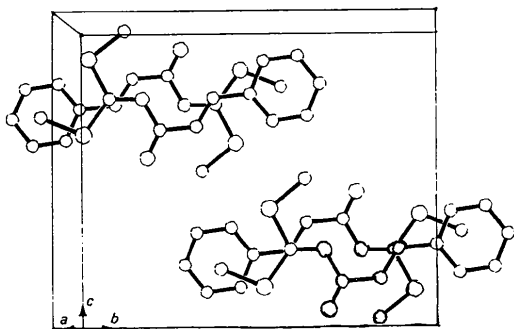
Fig. 3. Packing of the molecules viewed down the a axis.

$= 1\cdot80$ Å (Bondi, 1964)]. A similar observation has been made in the structure of 3,3-bis(methylthio)-2-nitro-2-propene-1-nitrile (Kamath & Venkatesan, 1984).

On the basis of the results reported on the directional preferences for the approach of electrophiles and nucleophiles to the divalent sulphur atom (Rosenfield, Parthasarathy & Dunitz, 1977) it appears that, in the present structure, O(6) acts as a nucleophile as it approaches the sulphur atom along the LUMO orbital of S. The oxygen atom is $34\cdot8°$ out of the plane defined by atoms C(15), S(1) and C(3) and the C(15)—S(1)$\cdots$O(6) angle is approximately linear [$175\cdot8$ (3)°].

The packing of the molecule viewed down the a axis is displayed in Fig. 3. There are no intermolecular short contacts of special significance. The illustrations were made with ORTEP II (Johnson, 1976).

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Structure of exo-(8bRS,8cSR,12aRS,12bSR)-8b,8c,9,10,12a,12b-Hexahydrobenzocyclobuta[1,2-e]pyrene, C22H18

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Abstract. $M_r = 282\cdot38$, monoclinic, $P2_1/a$, $a = 21\cdot698$ (2), $b = 13\cdot240$ (1), $c = 5\cdot1026$ (4) Å, $\beta = 93\cdot802$ (7)°, $V = 1462\cdot7$ (2) Å^3, $Z = 4$, $D_m = 1\cdot26$, $D_x = 1\cdot282$ Mg m^{-3}, λ(Cu $K\alpha$) $= 1\cdot5418$ Å, $\mu = 0\cdot51$ mm^{-1}, m.p. $404\cdot5$–$405\cdot5$ K, $T = 300$ K, $F(000) = 600$, final $R = 0\cdot050$ for 2044 reflexions above $1\cdot0\sigma(F)$. The structure of one of the photocycloaddition products of pyrene and 1,3-cyclohexadiene has been determined. The configuration of the H atoms in the cyclobutane ring was confirmed to be cis–anti, leading to the conclusion that the title compound was formed by $2\pi s + 2\pi s$ photocycloaddition in solution.