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Structure of 2-[α-(Methylthio)benzylideneamino]-2-phenyl-1,1-ethylenedicarbonitrile

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Abstract. $C_{18}H_{13}N_3S$, $M_r = 303{\cdot}4$, triclinic, $P\bar{1}$, $a = 18{\cdot}853$ (2), $b = 8{\cdot}843$ (2), $c = 10{\cdot}545$ (2) Å, $\alpha = 111{\cdot}39$ (1), $\beta = 83{\cdot}77$ (1), $\gamma = 102{\cdot}05$ (1)°, $V = 1599{\cdot}9$ (5) Å^3, $Z = 4$, $D_x = 1{\cdot}260$ (6) Mg m^{-3}, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $\mu = 1{\cdot}737$ mm^{-1}, $F(000) = 632$, room temperature, final $R = 0{\cdot}057$ for 4093 observed reflections. There is no electronic conjugation in the molecular chain [torsion angles C=N—C=C 68·8 (6) and 81·3 (5)°] in the two independent molecules. The arrangement about the C=N double bond is *E*, torsion angles S—C=N—C −171·5 (3) and −178·0 (3)° in the two molecules.

Introduction. The title compound was synthesized by Dr Lorente (Department of Organic Chemistry, University of Alcalá de Henares, Spain), from reaction of 2-methoxy-2-phenyl-1,1-ethylenedicarbonitrile and thiobenzamide in 2-propenol/sodium 2-propoxide followed by methylation with methyl iodide.

The determination of configuration in the *S*-methylthioimidates is not always possible by ^{1}H NMR methods (Yeh, Moriarty, Yeh & Ramey, 1972). In this case, the X-ray diffraction study was necessary to determine the configuration about the $\gt$C=N— bond of the molecule.

Experimental. Crystal 0·4 × 0·4 × 0·5 mm. Philips 1100 automatic diffractometer, 23 reflections used in determination of lattice parameters; no absorption correction. Data collection, Cu $K\alpha$, $2 < \theta < 60°$, h (−22 to 21), k (−10 to 9), l (0 to 12). Two check reflections measured every 100 reflections showed no significant variation; 5449 unique reflections, 4093 observed with $I \geq 2\sigma(I)$. Structure solved by direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), refined by full-matrix least squares, $\sum w(|F_o| - |F_c|)^2$ minimized, unit weights, anisotropic thermal parameters for non-H atoms. All H atoms located in difference Fourier synthesis, positional parameters included in further refinement with fixed isotropic temperature factor. Final $R = 0{\cdot}057$, $wR = 0{\cdot}057$. Residual peaks in final ΔF synthesis: max. positive 0·28 e Å^{-3}, max. negative −0·26 e Å^{-3}. Max. Δ/σ in final LS cycle 0·05. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations performed with *XRAY*70 (Stewart, Kundell & Baldwin, 1970), *PARST* (Nardelli, 1982) and *PESOS* (Martinez-Ripoll & Cano, 1975) on a UNIVAC 1108 computer.

Discussion. The structure of the title compound with the atomic numbering is shown in Fig. 1 (*ORTEP*; Johnson, 1965). Positional parameters and the equivalent U values of the anisotropic temperature factors are given in Table 1.* Bond lengths and angles and selected torsion angles are in Table 2.

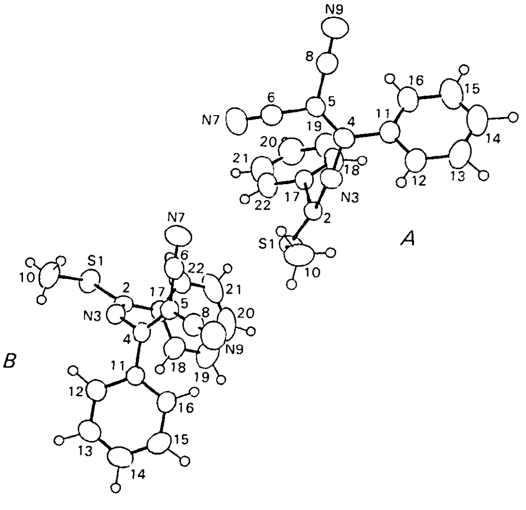

Fig. 1. The structures of the two independent molecules showing the atom numbering.

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* Lists of structure amplitudes, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42360 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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There are two independent molecules (*A* and *B*) in the unit cell. The phenyl groups in each molecule are planar with average torsion angles 1·8 (8) and 0·4 (8)° for molecule *A*, 0·6 (7) and 0·5 (8)° for molecule *B* and the dihedral angles between the least-squares planes through the two phenyl rings are 32·7 (2) and 40·2 (2)° respectively for molecules *A* and *B*. The mean dihedral angle for the two independent molecules between the phenyl group C(11)–C(12)–C(13)–C(14)–C(15)–C(16) and the plane C(5)–C(4)–N(3) is 34 (4)° and that between the phenyl group C(17)–C(18)–C(19)–C(20)–C(21)–C(22) and the plane N(3)–C(2)–S(1) is 48 (7)°.

The geometry of the central chain, torsion angles 68·8 (6) and 81·3 (5)° in *A* and *B*, constrains the possible electron conjugation in this C(2)=N(3)–C(4)=C(5) group.

The C(2)–N(3) bond distance is the same in both molecules and the S(1)–C(2) bond is similar in both molecules and comparable with the value found in *N*-[bis(methylthio)methylene]cinnamide (Kamath & Venkatesan, 1984). The C(2)–S(1)–C(10) bond angles are also in good agreement with the values found in this compound.

The C(4)–C(5)(CN)$_2$ groups are nearly planar. The maximum deviations from the least-squares planes through these atoms involve C(5), which are 0·032 (4) and 0·031 (4) Å out of the plane for molecules *A* and *B* respectively. C(11) is also situated in the plane.

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2 × 10^4)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j \cos(\mathbf{a}_i.\mathbf{a}_j).$$

	x	*y*	*z*	$U_{\rm eq}$
S(1*A*)	0·8740 (1)	0·6274 (1)	0·6596 (1)	542 (5)
C(2*A*)	0·9036 (2)	0·6048 (5)	0·4914 (4)	447 (16)
N(3*A*)	0·9461 (2)	0·7232 (4)	0·4654 (3)	500 (14)
C(4*A*)	0·9665 (2)	0·7309 (4)	0·3380 (4)	440 (15)
C(5*A*)	0·9174 (2)	0·7456 (5)	0·2610 (4)	454 (15)
C(6*A*)	0·8426 (2)	0·7424 (5)	0·3050 (4)	525 (18)
N(7*A*)	0·7840 (2)	0·7447 (6)	0·3408 (4)	795 (21)
C(8*A*)	0·9366 (2)	0·7780 (5)	0·1362 (4)	544 (18)
N(9*A*)	0·9496 (2)	0·8014 (6)	0·0360 (4)	820 (22)
C(10*A*)	0·9054 (3)	0·8435 (6)	0·7474 (5)	701 (23)
C(11*A*)	1·0452 (2)	0·7450 (5)	0·3040 (4)	470 (16)
C(12*A*)	1·0949 (2)	0·8291 (5)	0·4069 (5)	553 (18)
C(13*A*)	1·1689 (3)	0·8473 (6)	0·3753 (6)	709 (24)
C(14*A*)	1·1936 (3)	0·7790 (6)	0·2419 (7)	744 (26)
C(15*A*)	1·1449 (3)	0·6904 (7)	0·1413 (6)	769 (26)
C(16*A*)	1·0708 (2)	0·6723 (6)	0·1705 (5)	613 (20)
C(17*A*)	0·8776 (2)	0·4383 (5)	0·3906 (4)	441 (15)
C(18*A*)	0·9243 (2)	0·3595 (5)	0·2865 (5)	568 (19)
C(19*A*)	0·8997 (3)	0·2045 (6)	0·1930 (5)	680 (22)
C(20*A*)	0·8286 (3)	0·1273 (6)	0·2025 (6)	793 (25)
C(21*A*)	0·7826 (3)	0·2050 (7)	0·3049 (6)	785 (25)
C(22*A*)	0·8065 (2)	0·3604 (6)	0·4005 (5)	603 (20)
S(1*B*)	0·4456 (1)	0·0007 (1)	0·7003 (1)	568 (4)
C(2*B*)	0·5250 (2)	0·1082 (5)	0·7863 (4)	421 (15)
N(3*B*)	0·5298 (2)	0·2600 (4)	0·8613 (3)	437 (12)
C(4*B*)	0·5902 (2)	0·3584 (4)	0·9306 (4)	403 (14)
C(5*B*)	0·6461 (2)	0·4290 (5)	0·8642 (4)	441 (15)
C(6*B*)	0·6466 (2)	0·3814 (5)	0·7181 (4)	557 (18)
N(7*B*)	0·6473 (2)	0·3425 (6)	0·6027 (4)	825 (21)
C(8*B*)	0·7037 (2)	0·5597 (5)	0·9314 (4)	517 (17)
N(9*B*)	0·7500 (2)	0·6651 (5)	0·9799 (4)	736 (19)
C(10*B*)	0·3931 (3)	0·1624 (6)	0·7435 (6)	667 (22)
C(11*B*)	0·5852 (2)	0·3929 (4)	1·0789 (4)	390 (13)
C(12*B*)	0·5161 (2)	0·3856 (5)	1·1425 (4)	475 (16)
C(13*B*)	0·5089 (2)	0·4065 (5)	1·2805 (4)	576 (18)
C(14*B*)	0·5687 (3)	0·4329 (6)	1·3534 (5)	614 (20)
C(15*B*)	0·6374 (3)	0·4405 (5)	1·2912 (5)	597 (19)
C(16*B*)	0·6460 (2)	0·4218 (5)	1·1540 (4)	498 (17)
C(17*B*)	0·5821 (2)	0·0086 (5)	0·7670 (4)	466 (15)
C(18*B*)	0·6105 (2)	0·0001 (5)	0·8805 (5)	570 (18)
C(19*B*)	0·6645 (3)	−0·0929 (6)	0·8617 (7)	765 (26)
C(20*B*)	0·6904 (3)	−0·1743 (6)	0·7313 (7)	825 (28)
C(21*B*)	0·6618 (3)	−0·1649 (6)	0·6197 (7)	790 (25)
C(22*B*)	0·6077 (3)	−0·0738 (6)	0·6368 (5)	647 (20)

Table 2. *Bond lengths* (Å), *angles* (°) *and selected torsion angles* (°)

	A	*B*	Average
S(1)–C(10)	1·793 (5)	1·802 (6)	1·798
S(1)–C(2)	1·751 (4)	1·742 (4)	1·747
C(2)–N(3)	1·275 (5)	1·275 (4)	1·275
C(2)–C(17)	1·486 (5)	1·482 (6)	1·484
N(3)–C(4)	1·379 (5)	1·376 (4)	1·377
C(4)–C(5)	1·352 (6)	1·370 (5)	1·361
C(4)–C(11)	1·478 (5)	1·476 (5)	1·477
C(5)–C(6)	1·432 (6)	1·440 (5)	1·436
C(5)–C(8)	1·440 (7)	1·436 (6)	1·438
C(6)–N(7)	1·131 (6)	1·137 (5)	1·134
C(8)–N(9)	1·141 (7)	1·140 (6)	1·141
C(11)–C(12)	1·396 (6)	1·400 (5)	1·398
C(12)–C(13)	1·388 (6)	1·394 (6)	1·391
C(13)–C(14)	1·384 (8)	1·366 (6)	1·375
C(14)–C(15)	1·375 (8)	1·387 (7)	1·381
C(15)–C(16)	1·386 (7)	1·391 (7)	1·388
C(16)–C(11)	1·396 (6)	1·389 (6)	1·393
C(17)–C(18)	1·398 (5)	1·395 (7)	1·396
C(18)–C(19)	1·384 (6)	1·392 (8)	1·388
C(19)–C(20)	1·383 (7)	1·389 (9)	1·386
C(20)–C(21)	1·376 (7)	1·382 (11)	1·379
C(21)–C(22)	1·392 (6)	1·384 (8)	1·388
C(22)–C(17)	1·386 (5)	1·386 (6)	1·386
C(2)–S(1)–C(10)	101·9 (2)	101·3 (2)	101·6
S(1)–C(2)–C(17)	114·0 (3)	114·9 (3)	114·5
S(1)–C(2)–N(3)	120·2 (3)	120·0 (3)	120·1
N(3)–C(2)–C(17)	125·8 (4)	125·1 (4)	125·4
C(2) N(3) C(4)	126·5 (4)	125·2 (3)	125·9
N(3)–C(4)–C(11)	115·3 (3)	114·9 (3)	115·1
N(3)–C(4)–C(5)	119·9 (4)	120·1 (3)	120·0
C(5)–C(4)–C(11)	124·3 (4)	124·7 (4)	124·5
C(4)–C(5)–C(6)	121·3 (4)	119·9 (4)	120·7
C(4)–C(5)–C(8)	123·1 (4)	124·2 (4)	123·6
C(6)–C(5)–C(8)	115·4 (4)	115·8 (4)	115·6
C(5)–C(8)–N(9)	177·7 (5)	177·1 (4)	177·4
C(5)–C(6)–N(7)	178·0 (5)	179·3 (5)	178·7
C(4)–C(11)–C(16)	121·0 (4)	122·3 (3)	121·6
C(4)–C(11)–C(12)	119·8 (4)	117·9 (3)	118·9
C(12)–C(11)–C(16)	119·3 (4)	119·8 (4)	119·5
C(11)–C(12)–C(13)	120·2 (5)	119·6 (4)	119·9
C(12)–C(13)–C(14)	120·0 (5)	120·4 (4)	120·2
C(13)–C(14)–C(15)	119·9 (5)	120·4 (4)	120·2
C(14)–C(15)–C(16)	121·0 (5)	120·2 (4)	120·6
C(11)–C(16)–C(15)	119·6 (5)	119·6 (4)	119·6
C(2)–C(17)–C(22)	119·5 (4)	120·0 (4)	119·8
C(2)–C(17)–C(18)	120·7 (4)	119·6 (4)	120·2
C(18)–C(17)–C(22)	119·8 (4)	120·4 (4)	120·1
C(17)–C(18)–C(19)	120·3 (4)	119·3 (5)	119·7
C(18)–C(19)–C(20)	119·9 (5)	120·1 (5)	120·0
C(19)–C(20)–C(21)	119·8 (5)	119·9 (5)	119·9
C(20)–C(21)–C(22)	121·2 (5)	120·5 (6)	120·8
C(21)–C(22)–C(17)	119·0 (4)	119·7 (5)	119·4
C(10)–S(1)–C(2)–C(17)	−173·5 (3)	−177·9 (3)	−175·7
C(10)–S(1)–C(2)–N(3)	9·4 (4)	3·7 (4)	6·5
S(1)–C(2)–N(3)–C(4)	−171·5 (3)	−178·0 (3)	−174·8
C(2)–N(3)–C(4)–C(5)	68·8 (6)	81·3 (5)	75·1
C(2)–N(3)–C(4)–C(11)	−119·2 (5)	−104·7 (4)	−111·9
N(3)–C(4)–C(5)–C(6)	−4·2 (6)	−9·0 (6)	−6·6
N(3)–C(4)–C(5)–C(8)	170·9 (4)	166·2 (4)	168·6
N(3)–C(4)–C(11)–C(12)	−32·1 (6)	−25·5 (5)	−28·8
N(3)–C(4)–C(11)–C(16)	146·6 (4)	150·5 (4)	148·5
C(5)–C(4)–C(11)–C(12)	139·6 (4)	148·1 (4)	143·8
C(5)–C(4)–C(11)–C(16)	−41·8 (6)	−35·8 (6)	−38·8

The conformation is *E* with respect to the C(2)=N(3) bond; the methylthio methyl group is *cis* to N(3) in both molecules, torsion angles C(10)—S(1)—C(2)—N(3) 9·4 (4) and 3·7 (4)° in molecules *A* and *B*.

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Structure of 2,3-Dichloronaphthazarin

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Abstract. 2,3-Dichloro-5,8-dihydroxy-1,4-naphthoquinone, $C_{10}H_4Cl_2O_4$, $M_r = 259·0$, monoclinic, space group $P2_1/n$, $a = 14·110 (1)$, $b = 7·070 (1)$, $c = 9·810 (1)$ Å, $\beta = 102·09 (1)°$, $V = 956·9 (4)$ Å^3, $Z = 4$, $D_x = 1·798$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1·5418$ Å, $\mu = 62·174$ cm^{-1}, $F(000) = 520$, $T = 294$ K, $R = 0·058$ for 1531 observed reflections. The crystal is built up of molecules, possessing $2m$ symmetry, stacked along a diagonal axis; the molecules overlap to form a charge-transfer complex. The distance between the overlapping planes of neighbouring molecules is 3·40 (3) Å. There are intramolecular H bonds between the carbonyl and hydroxyl O atoms.

Introduction. According to the procedure previously described (Rodriguez, Vilches, Smith-Verdier & García-Blanco, 1983), the title compound was obtained by cycloaddition of 1,3-butadiene to 2,3-dichloro-*p*-benzoquinone and successive acetylation and oxidation of the adduct. Good crystals were obtained from an ethyl acetate solution by slow evaporation.

In chloroform solution, 2,3-dichloronaphthazarin shows absorption bands in the visible spectrum at 570 ($\varepsilon = 226$), 528 ($\varepsilon = 340$) and 496 nm ($\varepsilon = 284$ m^2 mol^{-1}) due to the annular chromophoric absorption of the carbonyl delocalization with the conjugated system and 468 nm ($\varepsilon = 178$ m^2 mol^{-1}) as a shoulder due to the charge-transfer complexation of the naphthazarin nucleus.

Analysis by ^{1}H NMR (200 MHz) in chloroform solution shows singlet signals at 12·34 (OH groups) and 7·33 (2 H aromatic or quinonoid protons). Chemical equivalence of the OH protons and also of the aromatic or quinonoid protons indicates that in solution the molecule has mirror symmetry.

The naphthazarin nucleus forms a charge-transfer self-complex (Rodriguez, Smith-Verdier, Florencio & García-Blanco, 1984). Verification of this fact and elucidation of the molecular stereochemistry requires determination of the structure.

Experimental. Crystal 0·02 × 0·15 × 0·30 mm, Philips 1100 automatic four-circle diffractometer, graphite monochromator, Cu $K\alpha$ radiation. Lattice parameters determined by least-squares refinement of θ values for 25 reflections; ω–2θ scan, $2 \le \theta \le 67°$; two reflections used as standard and remeasured after every 90 min, no decomposition observed. 1704 independent reflections ($-16 \le h \le 16$, $0 \le k \le 8$, $0 \le l \le 11$), 1531 observed with $I \ge 2\sigma(I)$, $\sigma(I)$ is the standard deviation based on

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