Acta Cryst. (1995). C**51**, 2323–2325

1-(Morpholinothiocarbonyl)-3,3-(oxydiethyl)-1,2-diphenylguanidine

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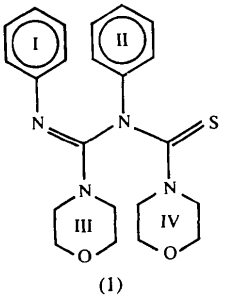
(*Received* 10 *March* 1995; *accepted* 30 *May* 1995)

Abstract

Two amidine groups (guanidine and thiourea) form the backbone of the title compound, 1,3-dimorpholino-2-phenyl-3-phenylimino-2-azapropane-1-thione, $C_{22}H_{26}N_4O_2S$, which carries two morpholino rings and two phenyl rings. The morpholine rings adopt chair conformations. The thiourea moiety and all substituent rings are twisted out of the guanidine plane.

Comment

The title compound, (1), is widely used as an accelerator in the curing of rubber. Since there is a scarcity of structural data for guanidine compounds, the crystal structure was determined to improve our understanding of this industrial process. A number of related structures have been published previously (*e.g.* Brown, 1967; Brown & Gash, 1984; Brown & Sengier, 1984).



(1)

The molecular conformation of (1) (synthesized at the SPIC Science Foundation, Madras) is shown in Fig. 1. Two amidine groups (guanidine around C8, thiourea around C16) form a backbone which carries two morpholino and two phenyl rings. The mean guanidine C—N bond length is 1.354 (7) Å and the mean thiourea C—N bond length is 1.382 (7) Å. The morpholino rings adopt chair conformations.

The guanidine and the thiourea moieties are almost perpendicular to each other [the dihedral angle between the least-squares planes is 88.3 (2)°]. All substituent rings are twisted out of the guanidine plane and the dihedral angles relative to the guanidine moiety are 95.4 (2), 98.4 (2), 21.6 (2) and 76.7 (2)° for rings I, II, III and IV, respectively. The two aromatic rings are almost perpendicular to each other [the dihedral angle between rings I and II is 103.1 (2)°].

The intermolecular cohesive forces are dominated by van der Waals interactions with some additional weak C—H···O and C—H···N hydrogen bonding.

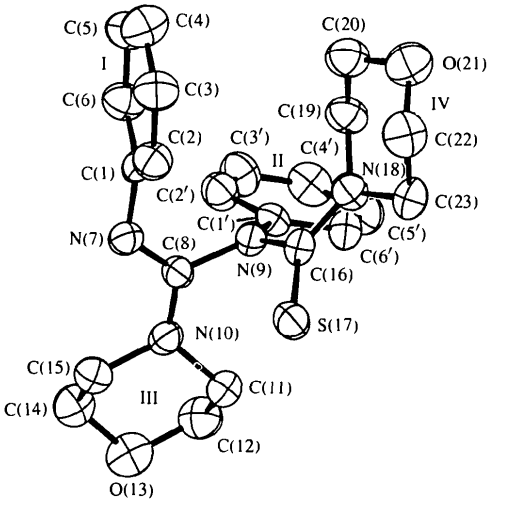


Fig. 1. Molecular structure and atomic numbering scheme with 50% probability ellipsoids.

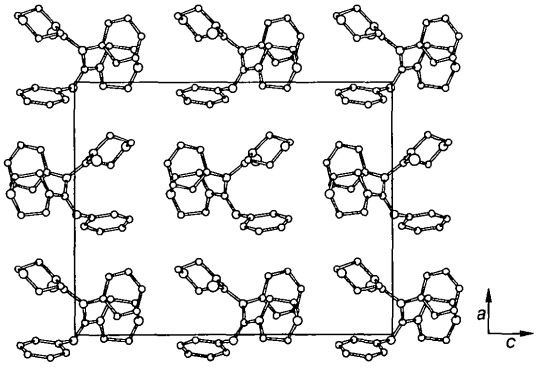


Fig. 2. Crystal-packing scheme projected on the *ac* plane. For clarity, only the section between $y = 0$ and $y = \frac{1}{2}$ is shown.

Experimental

The compound was synthesized and supplied by SPIC Science Foundation, Madras. D_m was measured by flotation in KI + water.

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Crystal data

$C_{22}H_{26}N_4O_2S$
$M_r = 410.5$
Orthorhombic
Pbca
$a = 14.928\ (3)$ Å
$b = 14.999\ (2)$ Å
$c = 18.952\ (2)$ Å
$V = 4243.5\ (1)$ Å^3
$Z = 8$
$D_x = 1.29$ Mg m^{-3}
$D_m = 1.30$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 18 reflections
$\theta = 16$–$33°$
$\mu = 1.52$ mm^{-1}
$T = 294$ K
Needle
$1.5 \times 0.2 \times 0.1$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–θ scans
Absorption correction: none
3134 measured reflections
2650 independent reflections
2041 observed reflections $[F > 3\sigma(F)]$

$R_{int} = 0.011$
$\theta_{max} = 60°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 21$
3 standard reflections frequency: 60 min intensity decay: 6.6%

Refinement

Refinement on F
$R = 0.068$
$wR = 0.073$
$S = 1.8$
2041 reflections
366 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.075614F^2]$

$(\Delta/\sigma)_{max} = 0.008$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
C(1)	−0.0343 (3)	0.2485 (4)	0.4483 (3)	3.3 (2)
C(2)	−0.0215 (4)	0.2612 (4)	0.3766 (3)	4.0 (2)
C(3)	−0.0411 (5)	0.1935 (5)	0.3290 (3)	4.7 (2)
C(4)	−0.0746 (5)	0.1146 (5)	0.3520 (4)	0.4 (2)
C(5)	−0.0889 (5)	0.1014 (5)	0.4226 (4)	5.3 (2)
C(6)	−0.0694 (5)	0.1698 (4)	0.4715 (3)	4.5 (2)
C(1′)	0.1442 (4)	0.2205 (3)	0.5874 (3)	3.1 (1)
C(2′)	0.0761 (4)	0.1907 (4)	0.6306 (3)	4.0 (2)
C(3′)	0.0955 (5)	0.1442 (5)	0.6916 (3)	4.7 (2)
C(4′)	0.1812 (5)	0.1260 (5)	0.7091 (3)	4.8 (2)
C(5′)	0.2509 (4)	0.1554 (5)	0.6679 (3)	4.6 (2)
C(6′)	0.2327 (4)	0.2021 (4)	0.6065 (3)	4.1 (2)
N(7)	−0.0230 (3)	0.3225 (3)	0.4947 (2)	3.4 (1)
C(8)	0.0489 (4)	0.3325 (3)	0.5306 (3)	2.9 (1)
N(9)	0.1227 (3)	0.2708 (3)	0.5254 (2)	3.0 (1)
N(10)	0.0574 (3)	0.3977 (3)	0.5785 (2)	3.4 (1)
C(11)	0.1420 (4)	0.4273 (4)	0.6101 (3)	4.0 (2)
C(12)	0.1266 (4)	0.4443 (5)	0.6873 (3)	4.8 (2)
O(13)	0.0566 (3)	0.5076 (3)	0.6990 (2)	4.9 (1)
C(14)	−0.0241 (4)	0.4784 (4)	0.6678 (3)	4.5 (2)
C(15)	−0.0147 (4)	0.4619 (4)	0.5900 (3)	3.6 (1)
C(16)	0.1796 (3)	0.2830 (4)	0.4667 (3)	3.2 (2)
S(17)	0.1920 (1)	0.3831 (1)	0.4316 (1)	4.0 (1)
N(18)	0.2201 (3)	0.2086 (3)	0.4423 (2)	3.7 (1)
C(19)	0.1929 (4)	0.1158 (4)	0.4558 (4)	4.3 (2)
C(20)	0.1728 (5)	0.0704 (4)	0.3878 (4)	5.0 (2)
O(21)	0.2443 (3)	0.0734 (3)	0.3393 (3)	5.4 (2)
C(22)	0.2611 (5)	0.1629 (5)	0.3235 (4)	5.2 (2)
C(23)	0.2902 (4)	0.2147 (5)	0.3886 (3)	4.3 (2)

Table 2. *Selected geometric parameters* (Å, °)

C(1)—C(2)	1.385 (8)	C(8)—N(10)	1.340 (7)
C(1)—C(6)	1.364 (9)	N(9)—C(16)	1.412 (7)
C(1)—N(7)	1.426 (7)	N(10)—C(11)	1.467 (7)
C(2)—C(3)	1.389 (9)	N(10)—C(15)	1.461 (8)
C(3)—C(4)	1.357 (11)	C(11)—C(12)	1.503 (8)
C(4)—C(5)	1.369 (11)	C(12)—O(13)	1.429 (8)
C(5)—C(6)	1.413 (10)	O(13)—C(14)	1.412 (7)
C(1′)—C(2′)	1.380 (8)	C(14)—C(15)	1.502 (8)
C(1′)—C(6′)	1.397 (8)	C(16)—S(17)	1.653 (6)
C(1′)—N(9)	1.433 (7)	C(16)—N(18)	1.351 (7)
C(2′)—C(3′)	1.381 (9)	N(18)—C(19)	1.472 (8)
C(3′)—C(4′)	1.350 (10)	N(18)—C(23)	1.463 (7)
C(4′)—C(5′)	1.374 (9)	C(19)—C(20)	1.488 (10)
C(5′)—C(6′)	1.385 (9)	C(20)—O(21)	1.409 (9)
N(7)—C(8)	1.280 (7)	O(21)—C(22)	1.398 (9)
C(8)—N(9)	1.442 (7)	C(22)—C(23)	1.521 (10)
C(6)—C(1)—N(7)	121.3 (5)	C(8)—N(9)—C(16)	115.5 (4)
C(2)—C(1)—N(7)	118.8 (5)	C(1′)—N(9)—C(16)	125.4 (4)
C(2)—C(1)—C(6)	119.2 (5)	C(8)—N(10)—C(15)	120.8 (5)
C(1)—C(2)—C(3)	120.5 (6)	C(8)—N(10)—C(11)	125.4 (5)
C(2)—C(3)—C(4)	120.4 (6)	C(11)—N(10)—C(15)	112.0 (4)
C(3)—C(4)—C(5)	119.8 (7)	N(10)—C(11)—C(12)	108.5 (5)
C(4)—C(5)—C(6)	120.3 (7)	C(11)—C(12)—O(13)	112.1 (5)
C(1)—C(6)—C(5)	119.7 (6)	C(12)—O(13)—C(14)	110.7 (5)
C(6′)—C(1′)—N(9)	121.9 (5)	O(13)—C(14)—C(15)	112.5 (5)
C(2′)—C(1′)—N(9)	119.5 (5)	N(10)—C(15)—C(14)	108.9 (5)
C(2′)—C(1′)—C(6′)	118.6 (5)	N(9)—C(16)—N(18)	115.6 (5)
C(1′)—C(2′)—C(3′)	120.4 (6)	N(9)—C(16)—S(17)	120.2 (4)
C(2′)—C(3′)—C(4′)	120.5 (6)	S(17)—C(16)—N(18)	124.2 (4)
C(3′)—C(4′)—C(5′)	120.9 (6)	C(16)—N(18)—C(23)	120.5 (5)
C(4′)—C(5′)—C(6′)	119.4 (6)	C(16)—N(18)—C(19)	126.7 (5)
C(1′)—C(6′)—C(5′)	120.2 (5)	C(19)—N(18)—C(23)	112.2 (5)
C(1)—N(7)—C(8)	121.2 (4)	N(18)—C(19)—C(20)	109.7 (5)
N(7)—C(8)—N(10)	121.7 (5)	C(19)—C(20)—O(21)	113.4 (6)
N(7)—C(8)—N(9)	122.0 (5)	C(20)—O(21)—C(22)	107.8 (5)
N(9)—C(8)—N(10)	116.2 (5)	O(21)—C(22)—C(23)	111.6 (6)
C(1′)—N(9)—C(8)	116.9 (4)	N(18)—C(23)—C(22)	109.2 (5)

C(2)—C(1)—N(7)—C(8)	−100.8 (6)
C(6)—C(1)—N(7)—C(8)	88.6 (7)
C(1)—N(7)—C(8)—N(9)	1.0 (8)
C(1)—N(7)—C(8)—N(10)	−174.6 (5)
N(7)—C(8)—N(9)—C(1′)	−115.2 (6)
N(10)—C(8)—N(9)—C(1′)	60.6 (6)
C(8)—N(9)—C(1′)—C(2′)	37.2 (7)
C(8)—N(9)—C(1′)—C(6′)	−141.5 (5)
N(7)—C(8)—N(10)—C(11)	−165.2 (5)
N(7)—C(8)—N(10)—C(15)	−1.9 (8)
N(9)—C(8)—N(10)—C(11)	19.0 (8)
N(9)—C(8)—N(10)—C(15)	−177.7 (5)
C(8)—N(9)—C(16)—S(17)	28.5 (6)
C(1′)—N(9)—C(16)—S(17)	−134.3 (5)
C(8)—N(9)—C(16)—N(18)	−150.6 (5)
C(1′)—N(9)—C(16)—N(18)	46.6 (7)
N(9)—C(16)—N(18)—C(19)	18.9 (8)
N(9)—C(16)—N(18)—C(23)	−171.1 (5)
S(17)—C(16)—N(18)—C(19)	−160.2 (5)
S(17)—C(16)—N(18)—C(23)	9.9 (7)

The structure was solved by direct methods and refinement was by the full-matrix least-squares method. All H atoms were located from difference Fourier maps and refined isotropically.

Data collection: *SDP* (Frenz, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

KS thanks the Deutscher Akademischer Austauschdienst for a grant to stay in Berlin, and LS is grateful to CSIR, New Delhi, India, for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1128). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 2325–2327

Alkynyl Contacts in 1β-Hydroxy-1α-propargyl-2α-(2-ethoxycarbonylvinyl)-2,4,4-trimethylcyclopentane

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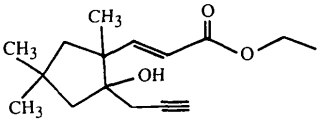
(*Received* 9 *March* 1995; *accepted* 6 *June* 1995)

Abstract

In the crystal structure of the title compound [ethyl 2-hydroxy-1,4,4-trimethyl-2-(2-propynyl)cyclopentane-1-propenoate, $C_{16}H_{24}O_3$] the propynyl residue only acts as a donor in a long and severely bent C—H···O interaction, with an H···O distance of 2.92 Å. It is engaged in a short alkyne–alkyne C—H···H—C contact, with an H···H distance of 2.38 Å; such a short contact distance is unprecedented (numerical values are for normalized H-atom positions).

Comment

Terminal alkynes of the type described here are used as starting materials in the syntheses of insect pheromones (Morrison & Boyd, 1989). The crystal structure of the title compound, (I), was determined in order to study the solid-state interactions of the propargyl residue. Normally, terminal alkynes act as weak hydrogen-bond donors with various acceptors such as O, N or even C (Desiraju, 1991; Steiner, 1994; Steiner, Starikov, Amado & Teixeira-Dias, 1995).



(I)

The molecular geometry of the title compound is shown in Fig. 1. The cyclopentane ring adopts an envelope conformation, with the *cis* torsion angle C2—C3—C4—C5 having a value of 3.2 (4)° (Table 2). The crystal packing arrangement is shown in Fig. 2. The hydrogen-bond pattern is not a favourable one as the O19—H hydroxy group donates an intermolecular hydrogen bond to the carbonyl O17 atom, which accepts an additional contact from the propargyl C—H group (Table 3). However, the latter contact is very long and bent (H···O 2.92 Å, angle at H 124°), so that its classification as a hydrogen bond is questionable. The resulting finite arrangement O—H···O···H—C≡C is a much weaker pattern than the cooperative hydrogen-bond chain C≡C—H···O—H···O=C, which was

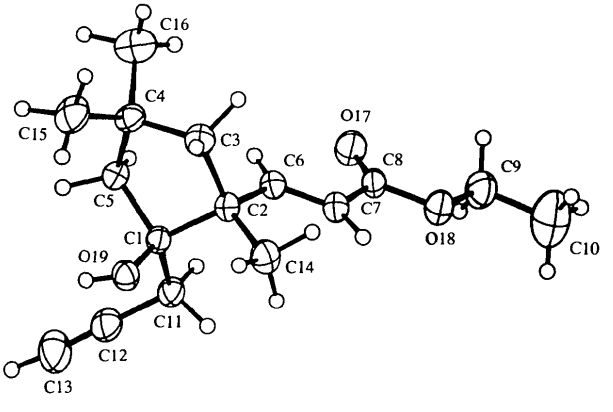


Fig. 1. Molecular structure and atomic numbering scheme of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

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