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2-[Bis(methoxycarbonyl)methylene]-3-phenyl-1,3-thiazolidine

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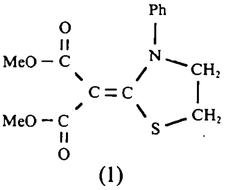
Abstract

The molecular structure of the title compound [dimethyl 2-(3-phenyltetrahydrothiazol-2-ylidene)-malonate, $C_{14}H_{15}NO_4S$], is characterized by a short intramolecular S···O interaction [2.679 (2) Å] leading to a conjugation effect in which one of the two carboxyl groups is involved. This is confirmed by the dihedral angles between the carboxyl groups and the roughly planar 1,3-thiazolidine ring of 18.8 and 50.2°. The dihedral angle between the 1,3-thiazolidine and the phenyl ring is 60.8°. The slight deviation of the 1,3-thiazolidine moiety from planarity can be described in terms of a half-chair conformation.

Comment

An *ORTEP*II drawing (Johnson, 1976) of the title compound, (1), is shown in Fig. 1. The 1,3-thiazolidine ring is approximately planar with only moderate deviations from the best plane through its five atoms [largest deviation 0.083 (3) Å observed for C4]. Considering this deviation from exact planarity, the conformation can be described as half chair. This is derived from the torsion angles of the ring (*cf.* Table 2) and by the analysis of ring-puckering parameters according to Cremer & Pople (1975). The ring puckering analysis gives $\varphi = 92\,(1)°$ and $q = 0.115\,(2)$, whereas the ideal value for a half-chair conformation of a five-membered ring is $\varphi = 90°$.



(1)

Similar conformational behaviour of 1,3-thiazolidine ring systems is observed in a series of 2-amino-1,3-thiazolidine derivatives (Cohen-Addad, 1982). However, the five ring atoms in those compounds show larger deviations from planarity, ranging from 0.18 to 0.49 Å. The dihedral angle between the 1,3-thiazolidine ring plane and the least-squares plane of the phenyl ring in (1) is 60.8°.

An essential structural feature of (1) is a short intramolecular S···O interaction, characterized by an S1···O2 distance of 2.679 (2) Å, which is considerably shorter than the sum of the corresponding van der Waals radii (3.25 Å) given by Bondi (1964). The observed S1···O2 distance and the C3—S1···O2 angle of 168.3 (8)° are in the usual range for intramolecular S···O interactions, as given in the literature (Kucsman & Kapovits, 1985; Rosenfield, Parthasarathy & Dunitz, 1977).

The observed close S···O contact in (1) is connected to an approximately planar arrangement of the five-atom fragment S1—C1=C2—C12=O2 [largest deviation of an atom from the corresponding least-squares plane is 0.109 (2) Å for atom C12]. The aforementioned 2-amino-1,3-thiazolidine derivatives (Cohen-Addad, 1982) show similar S···O interactions (S···O distances ranging from 2.66 to 2.74 Å, C—S···O angles ranging from 162.2 to 164.3°), accompanied by an almost planar arrangement of the corresponding atoms with all deviations from the least-squares plane less than 0.1 Å. In (1), this planar arrangement leads to improved resonance possibilities along the N1—C1—C2—C12 bonds. This is confirmed by a shortening of the C1—N1 bond to 1.352 (2) Å and an elongation of the C1—C2 bond to 1.385 (2) Å compared with the corresponding standard values of 1.416 and 1.331 Å for a single and double bond, respectively (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). Moreover, the structurally equivalent bonds C2—C11 [1.482 (2) Å]

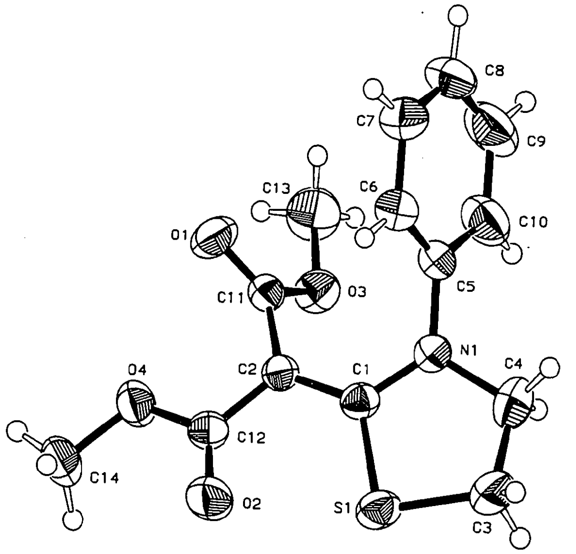


Fig. 1. Molecular structure and atomic numbering of (1). The displacement ellipsoids are drawn at the 50% probability level and the H atoms are shown as spheres of arbitrary radii.

and C2—C12 [1.452 (2) Å] differ significantly, yet, the observed bond lengths agree well with the standard values for a non-conjugated (1.484 Å) and a conjugated C—C bond (1.464 Å), respectively, in the corresponding chemical environment (Allen *et al.*, 1987).

The two acetyloxy groups (C2, C11, O1, O3 and C2, C12, O2, O4) show only minor deviations from planarity, the maximum deviation of an atom from the best plane through the four atoms being 0.018 (2) and 0.017 (2) Å for the two groups, respectively. The dihedral angles between these planes and the thiazolidine ring are 50.2 and 18.0°, respectively. The remarkable difference in the interplanar angles is again a consequence of the short S···O interaction.

Experimental

The title compound was prepared by thiocarbamoylation of diethyl malonate with phenyl isothiocyanate in the presence of sodium hydride, and subsequent alkylation using 1,2-dibromoethane. Recrystallization from methanol yielded suitable crystals with m.p. 423–424 K.

Crystal data

$C_{14}H_{15}NO_4S$
$M_r = 293.34$
Monoclinic
$P2_1/c$
$a = 15.224\ (2)$ Å
$b = 6.068\ (1)$ Å
$c = 14.968\ (1)$ Å
$\beta = 90.87\ (1)°$
$V = 1382.6$ Å^3
$Z = 4$
$D_x = 1.409$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 86 reflections
$\theta = 10.0–14.0°$
$\mu = 0.23$ mm^{-1}
$T = 293$ K
Prism
0.5 × 0.35 × 0.35 mm
White

Data collection

Stoe Stadi-4 diffractometer
ω/θ scans
Absorption correction: none
3638 measured reflections
2972 independent reflections
2531 observed reflections [$F_o > 4.0\sigma(F_o)$]

$R_{\rm int} = 0.034$
$\theta_{\rm max} = 27.5°$
$h = -19 \rightarrow 19$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity variation: ±3.5%

Refinement

Refinement on F
$R = 0.039$
$wR = 0.046$
$S = 4.63$
2531 reflections
242 parameters
$w = 3.19/[\sigma^2(F_o) + 0.00005F_o^2]$
$(\Delta/\sigma)_{\rm max} = 0.019$

$\Delta\rho_{\rm max} = 0.257$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.204$ e Å^{-3}
Extinction correction: empirical, $F_{\rm corr} = F_c(1 - 10^{-7}\chi F_c^2/\sin\theta)$
Extinction coefficient: $\chi = 1.38\ (5)$
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S1	0.91248 (3)	0.18160 (9)	0.48686 (3)	0.0484 (2)
O1	0.69535 (9)	0.0145 (2)	0.2314 (1)	0.0570 (5)
O2	0.92456 (9)	−0.1649 (2)	0.37684 (9)	0.0562 (5)
O3	0.75243 (8)	0.3516 (2)	0.24372 (8)	0.0484 (4)
O4	0.86288 (8)	−0.1800 (2)	0.24076 (8)	0.0479 (4)
N1	0.76648 (9)	0.3720 (3)	0.4440 (1)	0.0441 (5)
C1	0.8208 (1)	0.2113 (3)	0.4154 (1)	0.0361 (5)
C2	0.8096 (1)	0.0835 (3)	0.3395 (1)	0.0347 (5)
C3	0.8808 (2)	0.4108 (6)	0.5553 (2)	0.080 (1)
C4	0.8014 (2)	0.5147 (4)	0.5155 (1)	0.0542 (7)
C5	0.6761 (1)	0.3952 (3)	0.4180 (1)	0.0420 (5)
C6	0.6192 (1)	0.2213 (4)	0.4289 (1)	0.0484 (6)
C7	0.5314 (1)	0.2479 (5)	0.4064 (2)	0.0645 (8)
C8	0.5008 (2)	0.4455 (5)	0.3734 (2)	0.0748 (10)
C9	0.5582 (2)	0.6179 (5)	0.3632 (2)	0.078 (1)
C10	0.6460 (2)	0.5942 (4)	0.3863 (2)	0.0632 (8)
C11	0.7452 (1)	0.1395 (3)	0.2677 (1)	0.0373 (5)
C12	0.8699 (1)	−0.0972 (3)	0.3238 (1)	0.0375 (5)
C13	0.6902 (2)	0.4319 (5)	0.1776 (2)	0.0720 (10)
C14	0.9244 (2)	−0.3534 (4)	0.2197 (2)	0.0582 (8)

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

S1—C1	1.754 (2)	N1—C4	1.470 (3)
S1—C3	1.797 (3)	N1—C5	1.431 (2)
O1—C11	1.198 (2)	C1—C2	1.385 (2)
O2—C12	1.213 (2)	C2—C11	1.482 (2)
O3—C11	1.341 (2)	C2—C12	1.452 (2)
O4—C12	1.343 (2)	C3—C4	1.480 (4)
N1—C1	1.352 (2)		
C1—S1—C3	92.87 (11)	C1—C2—C11	122.57 (15)
C1—N1—C4	115.99 (15)	C1—C2—C12	119.04 (14)
C1—N1—C5	125.15 (15)	C11—C2—C12	117.98 (14)
C4—N1—C5	118.39 (16)	S1—C3—C4	108.95 (19)
S1—C1—N1	111.50 (12)	N1—C4—C3	109.05 (20)
S1—C1—C2	121.99 (13)	C11—O3—C13	116.86 (17)
N1—C1—C2	126.50 (15)		
C3—S1—C1—N1	−4.0 (2)	N1—C1—C2—C11	13.8 (3)
C1—S1—C3—C4	−4.0 (2)	S1—C1—C2—C11	−165.2 (1)
C3—S1—C1—C2	175.1 (2)	N1—C1—C2—C12	−173.7 (2)
C4—N1—C1—S1	11.5 (2)	S1—C1—C2—C12	7.3 (2)
C5—N1—C1—S1	−160.6 (1)	C1—C2—C11—O1	−134.7 (2)
C4—N1—C1—C2	−167.6 (2)	C1—C2—C11—O3	48.7 (2)
C5—N1—C1—C2	20.4 (3)	C12—C2—C11—O1	52.8 (2)
C1—N1—C4—C3	−14.4 (2)	C12—C2—C11—O3	−123.8 (2)
C5—N1—C4—C3	158.2 (3)	C1—C2—C12—O2	9.1 (3)
C13—O3—C11—O1	6.6 (3)	C1—C2—C12—O4	−167.8 (2)
C13—O3—C11—C2	−176.7 (2)	C11—C2—C12—O2	−178.2 (2)
C14—O4—C12—O2	0.0 (2)	C11—C2—C12—O4	4.9 (2)
C14—O4—C12—C2	177.0 (2)	S1—C3—C4—N1	10.4 (2)

Data collection: *DIF*4 (Stoe & Cie, 1991*a*) using the learnt-profile method (Clegg, 1981). Data reduction: *REDU*4 (Stoe & Cie, 1991*b*). Program used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to perform geometrical calculations: *EDIT* (Jaskólski, 1982). The structure was solved by direct methods. Refinement was by full-matrix least-squares methods. All H atoms were localized in a difference Fourier map and refined isotropically.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SH1096). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Clegg, W. (1981). *Acta Cryst.* **A37**, 22–28.

Cohen-Addad, C. (1982). *Acta Cryst.* **B38**, 1753–1757.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Jaskólski, M. (1982). *EDIT. Program to Edit Atomic Information from Atom Data Files.* Univ. of Poznań, Poland.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kucsman, A. & Kapovits, I. (1985). *Organic Sulfur Chemistry*, edited by F. Bernardi, L. G. Csizmadia & A. Mangini, pp. 191–245. Amsterdam: Elsevier.

Rosenfield, E. R. Jr, Parthasarathy, R. & Dunitz, J. D. (1977). *J. Am. Chem. Soc.* **99**, 4860–4862.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.

Stoe & Cie (1991*a*). *DIF4. Stoe 4-Circle Diffractometer Control Program.* Version 7.08. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1991*b*). *REDU4. Stoe 4-Circle Data Reduction Program.* Version 7.08. Stoe & Cie, Darmstadt, Germany.

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Glycoluril

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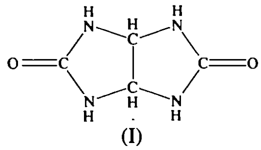
Abstract

The crystal structure of glycoluril [tetrahydroimidazo-[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione, $C_4H_6N_4O_2$] has been determined. The molecule has two equivalent planes containing urea moieties, and hence exhibits C_{2v} symmetry. The dihedral angle is found to be 124.1 (4)°.

Comment

Glycoluril (I) is a small molecule with relatively high symmetry and has a structure closely related to that of urea.



(I)

A recent study of the electronic spectrum of urea (Campbell & Clark, 1989) obtained experimental results that were contradictory to previous theoretical electronic structure calculations. In order to clarify the situation, polarized electronic spectra of single crystals of glycoluril have been measured (Xu & Clark, 1994). Interpretation of the polarized spectra requires a knowledge of the disposition of the molecules in the crystal. Although glycoluril has no important chemical applications except as a slow release fertilizer (Addiscott & Thomas, 1979; Shimizu, 1987), the fact that it is composed of two symmetrically disposed urea linkages is of significant value with respect to studies of the electronic structure of the basic chromophore. The structure of glycoluril has been investigated previously, but atomic co-

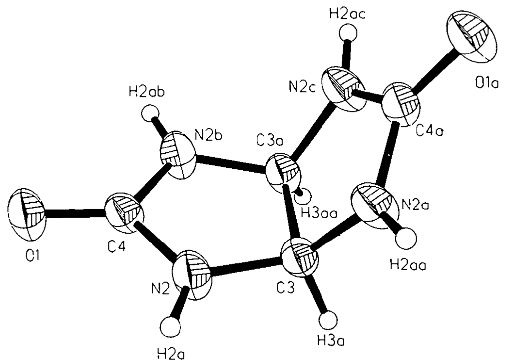


Fig. 1. A view of glycoluril with displacement ellipsoids at the 50% probability level. H atoms are drawn as small circles of arbitrary radii.

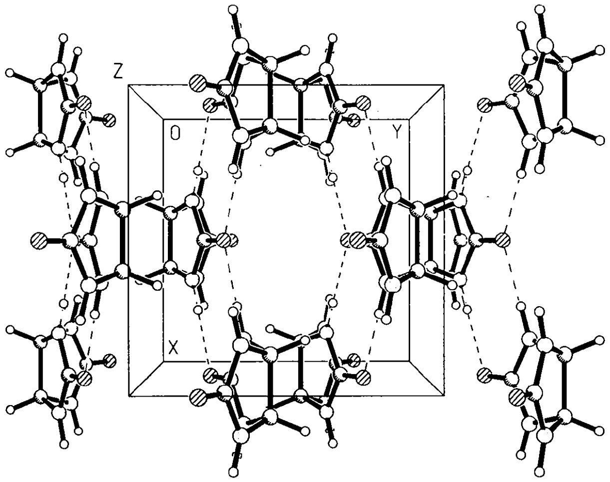


Fig. 2. A packing diagram viewed down the *c* axis showing the hydrogen bonding (O1···H2—N2 2.86 Å). The (010) face is determined to be a cleavage plane.

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