

Intramolecular hydrogen bonding in dibenzyl  
2,2'-(propane-1,3-diyl-diimino)bis(cyclopent-1-ene-  
1-carbodithioate)Ricardo R. Contreras,<sup>a</sup> Bernardo  
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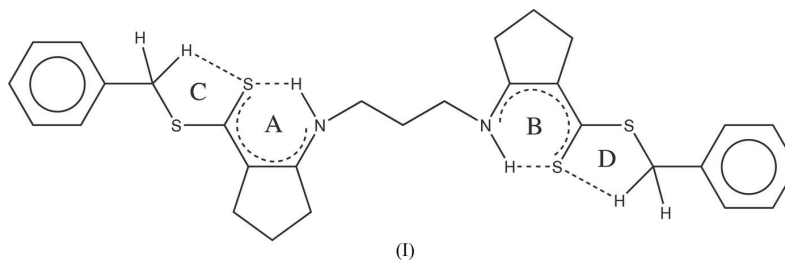
## Key indicators

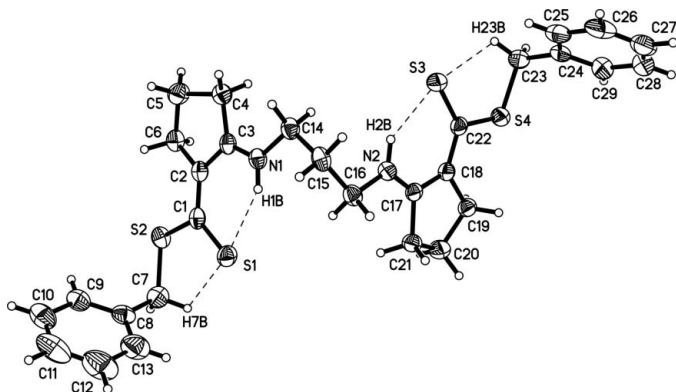
Single-crystal X-ray study  
 $T = 298\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$   
 $R$  factor = 0.041  
 $wR$  factor = 0.103  
Data-to-parameter ratio = 15.8For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title proligand,  $\text{C}_{29}\text{H}_{34}\text{N}_2\text{S}_4$ , exhibits two kinds of intramolecular hydrogen bonds,  $\text{N}-\text{H}\cdots\text{S}$  and  $\text{C}-\text{H}\cdots\text{S}$ , described by the graph-set symbols  $S(6)$  and  $S(5)$ , respectively. The structural parameters of the molecule suggest a partial electron delocalization involving the nitrogen lone pair, the cyclopentene ring and the carbodithioate group. In the crystal structure, the molecules are held together mainly by  $\text{C}-\text{H}\cdots\pi$  and van der Waals interactions.

## Comment

The development of nitrogen and sulfurated proligands are of great relevance for bioinorganic chemistry (Holm & Solomon, 2004). Frequently, the aim has been to synthesize low molecular weight model compounds in order to gain a better understanding of the role played by metal centres on the properties of metalloproteins (Ibers & Holm, 1980). There are a great variety of model complexes (Mandal *et al.*, 1997; Kim *et al.*, 2001; Anderson *et al.*, 1997), which involve pseudo-tetrahedral metal coordination with two N- and two S-donor atoms. From the biomimetic point of view, these molecular analogues with specific metal-coordination environments are very attractive, because of their similarity to biological systems found in nature. Among these can be mentioned those observed in (i) blue copper proteins (Gray & Solomon, 1981), (ii) carbon monoxide dehydrogenase (Diekert, 1988) and (iii) zinc finger proteins (Lipscomb & Sträter, 1996). Pioneering synthetic studies with such a family of proligands and their metal complexes were carried out by Nag & Joardar (1975, 1976) and Bereman *et al.* (1979, 1981). These authors focused their attention on ( $\text{N}_2\text{S}_2$ ) proligands derived from 2-amino-1-cyclopentene-1-dithiocarboxylic acid. More recently, we have developed the synthesis of several ligands of the class ethyl- $N,N'$ -alkyl-bis(2-amino-1-cyclopentenecarbodithioate) (Contreras *et al.*, 2005) and 2,4-bis-(cyclohexane)dispiro-1,2,3,4,4a,5,6,7-octahydro-(1*H*,3*H*)-quinazoline-8-carbodithioate (Contreras *et al.*, 2001).





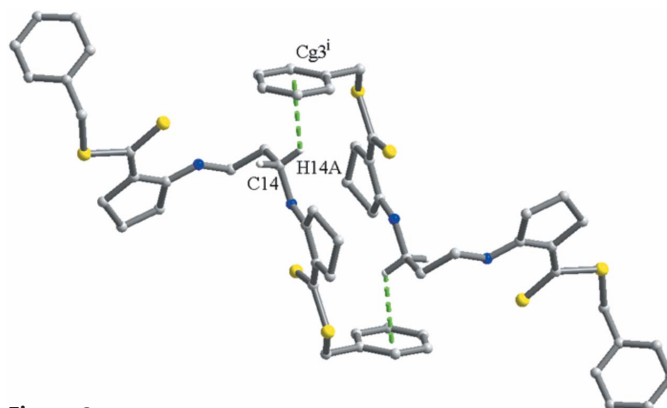
**Figure 1**

Molecular structure of the title compound, showing the atom-labelling scheme and intramolecular hydrogen bonds (dashed lines). Displacement ellipsoids are drawn at the 30% probability level. H atoms are shown as small spheres of arbitrary radii.

cyclopentencarbodithioate), (I), and its crystal structure are reported. This proligand has been successfully used as a chelating agent for  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Cu}^{\text{II}}$  (Contreras, Fontal *et al.*, 2004; Contreras, Suárez *et al.*, 2004).

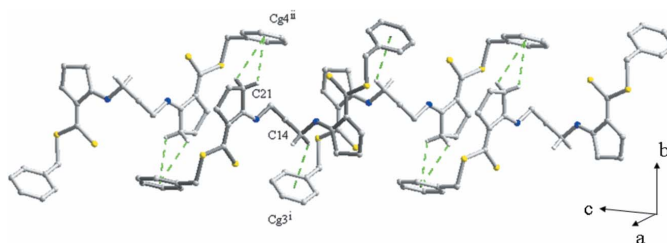
The molecule adopts pseudo- $C_2$  symmetry about atom C15 (Fig. 1). This molecular conformation is determined by the formation of pairs of intramolecular  $\text{N}-\text{H}\cdots\text{S}$  and  $\text{C}-\text{H}\cdots\text{S}$  hydrogen bonds. These interactions lead to the formation of six- and five-membered rings (see scheme), described by graph-set symbols  $S(6)$  and  $S(5)$ , respectively (Bernstein *et al.*, 1995). Details of the hydrogen-bonding geometry are given in Table 2. Each of these hydrogen-bonded rings (rings *A–D*) adopts a nearly planar conformation. In the six-membered rings *A* and *B*, the maximum deviation from the mean planes are 0.005 Å for C1 and 0.013 Å for C22. In the five-membered rings *C* and *D*, larger deviations are observed, *viz.* 0.045 Å for C1 and 0.062 Å for C22. Rings *A* and *C* are essentially coplanar, as are rings *B* and *D*, the dihedral angles between them being 3.73 (9) and 7.06 (8)°, respectively. The phenyl groups are twisted with respect to the mean plane of the hydrogen-bonded ring to which they are directly attached [dihedral angle between phenyl ring C8–C13 and ring *C* is 80.37 (11)°; that between phenyl ring C24–C29 and ring *D* is 75.32 (11)°]. The C2–C6 and C17–C21 rings adopt envelope conformations; the flap atoms C5 and C20 deviate from the respective planes by 0.168 (2) and 0.103 (2) Å.

The bond lengths in the  $S(6)$  rings have values (Table 1) typical of a conjugated system [average C–C = 1.39 Å and C–N = 1.320 Å] (Cambridge Structural Database; Version 5.25; Allen, 2002). These structural features suggest electron delocalization involving the nitrogen lone pair, the cyclopentene ring and the carbodithioate group. These distances agree with values previously reported in analogous compounds, such as methyl-*N,N'*-propyl-bis(2-amino-1-cyclopentencarbodithioate), methyl-*N,N'*-(3,6-diazaoctane)-bis(2-amino-1-cyclopentencarbodithioate), methyl-*N,N'*-diethyl-amino-bis(2-amino-1-cyclopentencarbodithioate) (Sarkar & Gupta, 1981, 1982*a,b*, respectively) and (*R*)-bis(*N*-phenylethyl-2-amino-1-cyclopentenemercaptomethyl)disulfide (Cea-



**Figure 2**

Ball-and-stick representation, showing the centrosymmetric dimer generated by  $\text{C}-\text{H}\cdots\pi$  interactions (dashed lines). [Symmetry code: (i)  $1-x, 1-y, 2-z$ .] Most H atoms have been omitted.



**Figure 3**

View of the one-dimensional ribbon along the *c* axis, generated by  $\text{C}-\text{H}\cdots\pi$  interactions (dashed lines). [Symmetry code: (i)  $1-x, 1-y, 2-z$ ; (ii)  $-x, 1-y, 1-z$ .] Most H atoms have been omitted.

Olivares *et al.*, 1999). This electronic behaviour is consistent with the bathochromic shift observed in the absorption spectrum (see *Experimental*).

The crystal structure of (I) consists of dimers linked by self-complementary  $\text{C}-\text{H}\cdots\pi$  interactions [ $\text{C}14\cdots\text{C}g3$ ] related by an inversion centre (Fig. 2;  $\text{C}g3$  is the centroid of the C8–C13 phenyl ring). The other  $\text{C}-\text{H}\cdots\pi$  interactions,  $\text{C}21\cdots\text{C}g4$ , lead to the formation, along the *c* axis, of ribbons built up from neighbouring dimers (Fig. 3;  $\text{C}g4$  is the centroid of the C24–C29 phenyl ring). Finally, the stacking of adjacent ribbons is sustained by weak van der Waals interactions.

## Experimental

The reagents and solvents (Aldrich Chemical, Merck Co., Baker Analyzed and Eastman Co.) were used without further purification. Carbon disulfide was purified as described in the literature (Gordon & Ford, 1972). Proligand (I) was prepared by modifying the reaction conditions reported by Bordás *et al.* (1972), according to the method of Contreras *et al.* (2005). The reaction between cyclopentanone and carbon disulfide in ammonium hydroxide yielded 2-amino-1-cyclopentene-1-dithiocarboxylic acid, which was esterified with a mixture of benzyl chloride dissolved in an aqueous suspension of NaI. The product was synthesized via a Schiff base reaction with 1,3-diaminopropane. Yellow crystals, suitable for X-ray analysis, were obtained by recrystallization from toluene. Precaution: All handling and reactions must be carried out in a well ventilated fume hood and the residues properly disposed of. Analysis calculated for  $\text{C}_{29}\text{H}_{32}\text{N}_2\text{S}_4$ : C 64.88, H 6.01, N 5.22, S 23.89%; found: C 64.63, H 5.78, N 5.19, S 23.75%. Electronic spectral data,  $\lambda$  ( $\text{cm}^{-1}$ ) ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ):

44,050 (10,800), 31,550 (10,900), 25,690 (16,400), 25,000 (14,600). The electronic absorption spectrum shows bands in the ultraviolet region assigned as  $\pi \rightarrow \pi^*$  or  $n \rightarrow \pi^*$  transitions of the chromophoric groups present:  $-\text{C}=\text{C}- + K(\text{benzene})$ ,  $\text{C}-\text{S} + B(\text{benzene})$ ;  $-\text{C}=\text{N}- + -\text{C}=\text{S}-$ . These bands displayed a bathochromic effect. IR ( $\text{cm}^{-1}$ ): 3452 (*m*), 1590 (*s*), 1485 (*m*), 1324 (*m*), 1269 (*m*), 950 (*m*), 914 (*m*), 702 (*w*).  $^1\text{H}$  NMR spectrum shows the following results:  $\delta$  12.4 (2H, *s*), 7.78 (4H, *d*,  $J = 7.6$  Hz), 7.27 (4H, *t*,  $J = 7.6$  Hz), 7.24 (2H, *d*,  $J = 7.6$  Hz), 4.52 (4H, *s*), 3.48 (2H, *t*,  $J = 6.4$  Hz), 2.77 (2H, *d*,  $J = 7.6$  Hz), 2.68 (4H, *t*,  $J = 7.4$  Hz), 1.86 (4H, *m*), 1.80 (4H, *m*). The  $^{13}\text{C}$  NMR spectra show the following values:  $\delta$  202.7 ( $-\text{CS}_2\text{C}_7\text{H}_7$ ), 169.8 (N=C), 137.4, 129.3, 128.4, 127.1, 117.8, 42.9, 37.9, 33.3, 32.8, 20.6.

### Crystal data

$\text{C}_{29}\text{H}_{34}\text{N}_2\text{S}_4$	$Z = 2$
$M_r = 538.82$	$D_x = 1.266 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.8860$ (3) Å	Cell parameters from 25 reflections
$b = 12.427$ (3) Å	$\theta = 32.4\text{--}37.2^\circ$
$c = 14.752$ (3) Å	$\mu = 0.36 \text{ mm}^{-1}$
$\alpha = 90.62$ (3) $^\circ$	$T = 298$ (2) K
$\beta = 94.24$ (3) $^\circ$	Prism, yellow
$\gamma = 101.25$ (3) $^\circ$	$0.60 \times 0.24 \times 0.22 \text{ mm}$
$V = 1413.6$ (5) Å $^3$	

### Data collection

Rigaku AFC-7S diffractometer	$R_{\text{int}} = 0.038$
$\omega$ - $2\theta$ scans	$\theta_{\text{max}} = 25.0^\circ$
Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968)	$h = -9 \rightarrow 9$
$T_{\text{min}} = 0.861$ , $T_{\text{max}} = 0.921$	$k = 0 \rightarrow 14$
5320 measured reflections	$l = -17 \rightarrow 17$
4986 independent reflections	3 standard reflections
3374 reflections with $I > 2\sigma(I)$	every 150 reflections
	intensity decay: none

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2 + 0.4751P]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.103$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.20 \text{ e } \text{Å}^{-3}$
4986 reflections	$\Delta\rho_{\text{min}} = -0.19 \text{ e } \text{Å}^{-3}$
316 parameters	
H-atom parameters constrained	

**Table 1**

Selected geometric parameters (Å,  $^\circ$ ).

S1—C1	1.695 (3)	N2—C17	1.320 (3)
S2—C1	1.771 (3)	N2—C16	1.461 (3)
S2—C7	1.805 (3)	C1—C2	1.385 (4)
S3—C22	1.683 (3)	C2—C3	1.409 (4)
S4—C22	1.780 (3)	C3—C4	1.489 (4)
S4—C23	1.814 (3)	C17—C18	1.400 (4)
N1—C3	1.315 (3)	C18—C22	1.390 (4)
N1—C14	1.459 (3)		
C1—S2—C7	105.12 (14)	C8—C7—S2	114.6 (2)
C22—S4—C23	105.38 (14)	N1—C14—C15	110.2 (2)
C3—N1—C14	125.1 (2)	C16—C15—C14	115.0 (2)
C17—N2—C16	124.8 (2)	N2—C16—C15	111.0 (2)
C2—C1—S1	126.2 (2)	N2—C17—C18	127.1 (2)
C2—C1—S2	112.62 (19)	N2—C17—C21	121.4 (2)
S1—C1—S2	121.15 (17)	C18—C17—C21	111.4 (2)
C1—C2—C3	126.9 (2)	C22—C18—C17	126.0 (2)
C1—C2—C6	125.2 (2)	C22—C18—C19	124.9 (2)
C3—C2—C6	107.8 (2)	C17—C18—C19	108.9 (2)
N1—C3—C2	125.8 (3)	C18—C22—S3	126.8 (2)
N1—C3—C4	122.8 (2)	C18—C22—S4	111.27 (19)
C2—C3—C4	111.4 (2)	S3—C22—S4	121.87 (16)
C6—C5—C4	105.2 (2)	C24—C23—S4	112.7 (2)
C5—C6—C2	104.4 (2)		

**Table 2**

Hydrogen-bond geometry (Å,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ S1	0.86	2.29	3.018 (3)	142
N2—H2 $\cdots$ S3	0.90	2.29	3.030 (2)	138
C7—H7B $\cdots$ S1	0.97	2.66	3.140 (3)	111
C23—H23B $\cdots$ S3	0.97	2.62	3.179 (3)	117
C14—H14A $\cdots$ Cg3 <sup>i</sup>	0.97	2.99	3.637 (51)	125
C21—H21A $\cdots$ Cg4 <sup>ii</sup>	0.97	3.13	3.583 (38)	110
C21—H21B $\cdots$ Cg4 <sup>ii</sup>	0.97	3.13	3.583 (38)	110

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 2$ ; (ii)  $-x, -y + 1, -z + 1$ . Cg3 and Cg4 are the centroids of the C8—C13 and C24—C29 phenyl rings.

All H atoms bound to C atoms were included in calculated positions. The H atoms bonded to N (Table 2) were located in a Fourier difference map. All H atoms were refined using a riding model, with  $\text{C}-\text{H} = 0.93\text{--}0.97$  Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ .

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXLTL-NT* (Bruker, 1998); program(s) used to refine structure: *SHELXLTL-NT*; molecular graphics: *SHELXLTL-NT* and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXLTL-NT* and *PLATON* (Spek, 2003).

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