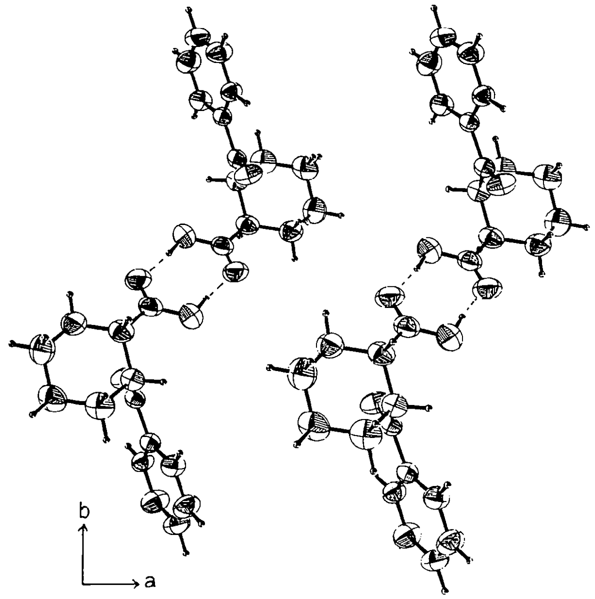

Fig. 2. Projection of the unit cell (*ab* plane) showing molecules in symmetry modifications x,y,z; $\frac{1}{2}-x,-\frac{1}{2}-y,-z$; $-x,-y,-z$; and $-\frac{1}{2}+x,\frac{1}{2}+y,z$. Dashed lines are intermolecular hydrogen bonds.

The eight molecules of 2-benzoylcyclohexanecarboxylic acid exist in pairs (Fig. 2) bonded together with two intermolecular hydrogen bonds involving the carboxylic groups [O(2)—H(1), 1·00 (4); H(1)···O(3′), 1·65 (4) Å, ∠O(2)—H(1)···O(3′), 173 (4)°]. The benzoyl oxygen atom, O(1), is not involved in hydrogen bonding and does not show the intramolecular hydrogen bonding postulated [O(2)—H(1)···O(1)] for the molecule in solution. [All O(1) intermolecular distances exceed 3·0 Å.] The cyclohexane ring exists in the chair form with the benzoyl group in the axial position and the carboxylic substituent in the equatorial position as predicted by conformational theory. All angles and distances are normal. There are no other significant intermolecular contact distances.

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Structure of 5,6,7,8-Tetrahydro-4*H*-3,1-benzothiazine-2(1*H*)-spirocyclohexane-4-thione, $C_{13}H_{19}NS_2$

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Abstract. $M_r = 253·42$, orthorhombic, *Pcab*, $a = 11·059\,(1)$, $b = 20·348\,(1)$, $c = 11·578\,(1)$ Å, $V = 2605·3\,(3)$ Å^3, $Z = 8$, $D_m = 1·31$, $D_x = 1·29$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0·7107$ Å, $\mu = 0·367$ mm^{-1}, $F(000) = 1088$, $T = 293$ K. Final $R = 0·034$ for 1734 observed reflections. The conformational parameters of the title compound are compared with those of other compounds. The deformation energies related to real chair form and real half-chair form in cyclohexane and cyclohexene rings are 0·14 (1) and 1·45 (1) kJ mol^{-1} respectively. The amount of double-bond character in the exocyclic C=S bond is about 75%.

Introduction. A great deal of research in the field of coordination chemistry has centred on complexes with ligands in which sulphur is the donor atom, or metallic chelates with ligands containing nitrogen and sulphur donors. Metallic complexes involving ligands with a

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sulphur donor are of considerable interest for many reasons, among them being the nature of the metal–sulphur interaction and the importance of sulphur in many molecules of biological interest (*Metal Ions in Biological Systems*, 1974–1981; Hughes, 1981).

The title compound is an organic molecule containing two S atoms and one N atom as potential donors. It therefore offers itself as a ligand for the synthesis of coordination compounds which might in some way be applied in fields such as that mentioned above or serve as a starting point for the study of the possible employment of $C_{13}H_{19}NS_2$ to sequester toxic metals (Sanchez-Díaz, Casas & Gayoso, 1982). As a preliminary step towards the study of the behaviour of $C_{13}H_{19}NS_2$ as a ligand, the present paper reports an X-ray diffraction study of its structure.

Experimental. Samples provided by Drs Sanchez-Díaz, Casas and Gayoso (Department of Inorganic Chemistry, Universidad de Santiago, Spain). D_m measured by pycnometry. Transparent orange crystal, 0·4 × 0·4 × 0·1 mm, mounted along **b**. Enraf–Nonius CAD-4 automatic diffractometer, $\omega/2\theta$ scan, graphite-monochromated Mo $K\alpha$. 30 reflections used for measuring lattice parameters. 2913 reflections up to $\theta = 30°$, 1734 with $I > 2\sigma(I)$. Range of *hkl* 14,26,15. Absorption ignored. Two standard reflections monitored during data collection, intensity variation normal. Structure solved by *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1980). H (from ΔF) included in one cycle of refinement with isotropic temperature factors. Anisotropic full-matrix least-squares refinement on F until changes <0·25. 326 parameters refined. $w = K/\sigma^2$, $\sigma = a + b|F_o|$ (Martínez-Ripoll & Cano, 1975), with $a = 2·257$ and $b = -0·171$ for $F_o < 8·670$ and $a = 0·400$ and $b = 0·122$ for $F_o > 8·670$ and $K = 0·573$; final $R = 0·034$, $R_w = 0·038$. No correction made for secondary extinction. Scattering factors from *International Tables for X-ray Crystallography* (1974). Final difference Fourier maps showed no distinguishing features. All refinement performed with XRAY (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Discussion. The molecular structure and atom numbering are given in Fig. 1, positional parameters in Table 1. Table 2 shows bond distances and angles and torsion angles are given in Table 3.*

The molecule is formed by three six-membered rings. Ring *A* is a cyclohexene disubstituted at the unsaturated C atoms which belong to ring *B*, which is a six-membered heterocycle with an S atom attached to C(15) and a cyclohexane ring (*C*) substituted at the spiranic atom C(8).

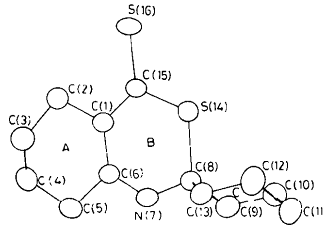

Fig. 1. Perspective view and labelling of the molecule without H atoms.

Table 1. *Atomic coordinates* (×10⁵) *and equivalent isotropic thermal parameters* (× 10⁴)

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j\cos(\mathbf{a}_i,\mathbf{a}_j).$$

	x	y	z	U_{eq} (Å²)
C(1)	63028 (19)	25762 (11)	49335 (18)	378 (6)
C(2)	58327 (22)	19069 (12)	45614 (19)	460 (7)
C(3)	62620 (25)	13473 (12)	53251 (19)	486 (7)
C(4)	76058 (25)	13980 (13)	55314 (23)	553 (9)
C(5)	79010 (24)	20287 (13)	61663 (23)	546 (9)
C(6)	72504 (19)	26256 (11)	57146 (18)	385 (7)
N(7)	76843 (17)	31978 (10)	61177 (16)	461 (6)
C(8)	69901 (19)	38053 (11)	61508 (17)	357 (6)
C(9)	78287 (21)	43898 (13)	63852 (22)	509 (8)
C(10)	71295 (25)	50255 (14)	65504 (26)	610 (10)
C(11)	61970 (29)	49703 (14)	75002 (26)	632 (9)
C(12)	53436 (23)	44023 (14)	72527 (24)	561 (9)
C(13)	60241 (22)	37622 (12)	70899 (20)	409 (7)
S(14)	63219 (6)	39228 (3)	47162 (4)	464 (2)
C(15)	58715 (19)	31324 (11)	43390 (17)	381 (6)
S(16)	49735 (7)	31044 (3)	31650 (4)	504 (2)

Table 2. *Bond distances* (Å) *and angles* (°)

C(1)–C(2)	1·520 (3)	C(8)–C(9)	1·532 (3)
C(1)–C(6)	1·388 (3)	C(8)–C(13)	1·527 (3)
C(1)–C(15)	1·408 (3)	C(8)–S(14)	1·834 (2)
C(2)–C(3)	1·518 (3)	C(9)–C(10)	1·519 (4)
C(3)–C(4)	1·508 (4)	C(10)–C(11)	1·512 (4)
C(4)–C(5)	1·515 (4)	C(11)–C(12)	1·519 (4)
C(5)–C(6)	1·505 (3)	C(12)–C(13)	1·516 (4)
C(6)–N(7)	1·343 (3)	S(14)–C(15)	1·739 (3)
N(7)–C(8)	1·456 (3)	C(15)–S(16)	1·684 (2)
C(6)–C(1)–C(15)	121·1 (2)	N(7)–C(8)–C(9)	110·2 (2)
C(2)–C(1)–C(15)	117·8 (2)	C(13)–C(8)–S(14)	111·8 (2)
C(2)–C(1)–C(6)	120·5 (2)	C(9)–C(8)–S(14)	107·6 (2)
C(1)–C(2)–C(3)	113·6 (2)	C(9)–C(8)–C(13)	110·0 (2)
C(2)–C(3)–C(4)	110·4 (2)	C(8)–C(9)–C(10)	112·0 (2)
C(3)–C(4)–C(5)	110·3 (2)	C(9)–C(10)–C(11)	112·1 (2)
C(4)–C(5)–C(6)	114·3 (2)	C(10)–C(11)–C(12)	110·1 (2)
C(1)–C(6)–C(5)	121·9 (2)	C(11)–C(12)–C(13)	111·6 (2)
C(5)–C(6)–N(7)	114·1 (2)	C(8)–C(13)–C(12)	112·7 (2)
C(1)–C(6)–N(7)	124·0 (2)	C(8)–S(14)–C(15)	102·8 (1)
C(6)–N(7)–C(8)	123·9 (2)	C(1)–C(15)–S(14)	121·6 (2)
N(7)–C(8)–S(14)	107·4 (2)	S(14)–C(15)–S(16)	113·8 (1)
N(7)–C(8)–C(13)	109·8 (2)	C(1)–C(15)–S(16)	124·5 (2)

Table 3. *Torsion angles* (°)

Ring *A* (cyclohexene)			
C(1)–C(2)–C(3)–C(4)	−47·3 (3)	C(4)–C(5)–C(6)–C(1)	11·4 (3)
C(2)–C(3)–C(4)–C(5)	62·4 (3)	C(5)–C(6)–C(1)–C(2)	3·9 (3)
C(3)–C(4)–C(5)–C(6)	−44·1 (3)	C(6)–C(1)–C(2)–C(3)	14·4 (3)
Ring *B* (six-membered)			
C(1)–C(6)–N(7)–C(8)	23·6 (3)	C(8)–S(14)–C(15)–C(1)	−15·5 (2)
C(6)–N(7)–C(8)–S(14)	49·7 (2)	S(14)–C(15)–C(1)–C(6)	10·7 (3)
N(7)–C(8)–S(14)–C(15)	40·5 (2)	C(15)–C(1)–C(6)–N(7)	12·1 (3)
Ring *C* (cyclohexane)			
C(8)–C(9)–C(10)–C(11)	55·8 (3)	C(11)–C(12)–C(13)–C(8)	55·4 (3)
C(9)–C(10)–C(11)–C(12)	−56·2 (3)	C(12)–C(13)–C(8)–C(9)	53·1 (3)
C(10)–C(11)–C(12)–C(13)	55·7 (3)	C(13)–C(8)–C(9)–C(10)	52·9 (3)

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38503 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The cyclohexene ring *A* adopts a distorted C(2)—C(3) 'half-chair' conformation. The values of the asymmetry parameters (Duax & Norton, 1975) are $\Delta C_2^{3,4} = 3{\cdot}1\ (3)$, $\Delta C_s^3 = 21{\cdot}2\ (3)$ and $\Delta C_s^2 = 46{\cdot}7\ (2)°$.

The deformation energy E_D (Bucourt, 1967) has been calculated for ring *A*. E_D is equal to $E_B + E_P + E_{VW}$ (E_B = tension energy of Bayer, E_P = torsion energy of Pitzer, and E_{VW} = interaction energy of van der Waals). The calculated values are $E_B = 3{\cdot}05\ (1)$, $E_P = 4{\cdot}94\ (1)$, $E_{VW} = 0{\cdot}42\ (1)$ and $E_D = 8{\cdot}40\ (1)$ kJ mol^{-1} for H atoms separated by two or more C atoms (Bucourt & Hainaut, 1964). E_D is 1·45 kJ mol^{-1} higher than the expected value for an 'ideal' half-chair conformation. This increase may be accounted for by the departure from ideal values of valence angles θ_1 and θ_6 (ideal value 123·5°) and θ_2 and θ_5 (ideal value 111·7°) leading to observed values of the torsion angles $\varphi_{5,6}$, $\varphi_{1,6}$ and $\varphi_{2,3}$ of 11·4 (3), 3·9 (3) and −47·3 (3)° instead of the ideal values 15·2, 0 and −44·9° respectively (Chaig & Bauer, 1969).

The observed values of θ_1 and θ_6 are expected by the presence of substituents on C(1) and C(6) (Karle, Britts & Brenner, 1964). The conjugation in ring *B* would reduce the partial double-bond character of C(1)—C(6) and, consequently, would also modify the remaining bond distances of the cyclohexene ring (Sutton, 1958, 1965).

The departures from ideality are no doubt due to the variety of atoms and bonds of which ring *B* is composed. It may be deduced that the π orbital of C(1)—C(6) has suffered delocalization in conjunction with the non-bonding electron pairs on the N and exocyclic S atoms. The endocyclic S atom is also affected *via* the bond nearest C=S. The difference in length between the two C—S bonds in the ring is in agreement with the difference found in similar compounds (Klewe & Seip, 1972).

The length of the exocyclic S—C bond is very close to that found in thiocarbonyl compounds (Warter, Harto & Voss, 1976), which lies between the values given by Pauling (1961) for single bonds (1·81 Å) and double bonds (1·61 Å). The value of 1·684 (2) Å, found by us, implies 75% double-bond character, calculated by rules proposed by Abrahams (1956).

Ring *C* is a cyclohexane which may be considered as disubstituted at C(8), where it is joined to ring *B*. Its conformation, as studied also by the method of Duax & Norton, is a 'chair' with values of the asymmetry parameters of: $\Delta C_s^8 = 0{\cdot}4\ (2)$, $\Delta C_2^{10-11} = 1{\cdot}8\ (3)$ and $\Delta C_2^{9-10} = 2{\cdot}9\ (3)°$.

The values found, in this ring, for E_B, E_P and E_{VW} are 0·54 (1), 1·35 (1) and 0·12 (1) kJ mol^{-1}, respectively. The E_{VW} is lower than that found in the 'ideal-chair' conformation (Bucourt & Hainaut, 1965). The calculated value of the deformation energy, E_D = 2·02 (1) kJ mol^{-1}, exceeds by 0·14 (1) kJ mol^{-1} that of the 'ideal-chair' conformation. This small increase can be attributed to the presence of substituents on spiranic C(8), which cause a decrease of the corresponding valence angle to 110·0° from the 'ideal' value of 111·1° and a change in $\varphi_{8,9}$ to −52·9 from −55·8° and in $\varphi_{13,8}$ to +53·1 from +55·8°. These values are expected when there exists a union of the cyclohexane ring in the 'chair' conformation with another ring (Bucourt, 1974).

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