

The Structure of 2,3,8,8a-Tetrahydro-2-methyl-5,8a-diphenyl-1*H*-imidazo[2,1-*c*][1,4]thiazine

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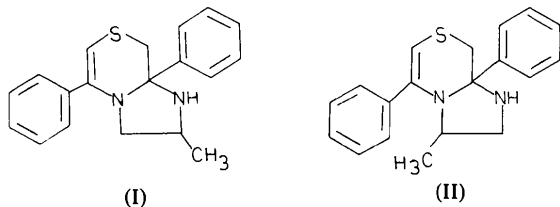
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Abstract. C₁₉H₂₀N₂S, monoclinic, $P2_1/n$, $a = 16.980$ (4), $b = 12.430$ (1), $c = 7.800$ (2) Å, $\beta = 101.48$ (2)°, $V = 1613.34$ Å³, $Z = 4$ and $\mu = 0.152$ mm⁻¹. The structure was solved by direct methods and refined by full-matrix least-squares methods to a conventional R value of 0.0859 for 1679 reflections. The H atoms were located geometrically and refined isotropically. All nonhydrogen atoms were allotted anisotropic thermal parameters. The S—C(sp^2) distance is 1.740 (9) Å and S—C(sp^3) distance 1.798 (9) Å. The C—S—C angle in the thiazine moiety is 97.6 (4)°.

Introduction. The crystal structure determination of 2,3,8,8a-tetrahydro-2-methyl-5,8a-diphenyl-1*H*-imidazo[2,1-*c*][1,4]thiazine (TDIT) was undertaken after its structural study by ¹³C NMR and IR spectroscopy (Sandhu, Tandon & Singh, 1980). The main interest of the crystal structure analysis was to confirm the formation of the imidazo[2,1-*c*][1,4]thiazine because very little is known about the structure of this moiety.

The title compound was obtained by the reaction of 2,2'-thiodiacetophenone with 1,2-diaminopropane. From spectroscopic data it was concluded that the structure can be either (I) or (II). The compound was obtained as elongated needles from an ethyl acetate/petroleum ether mixture. Preliminary Weissenberg photographs indicated the crystal to be monoclinic, space group $P2_1/n$.



The intensities of 2836 reflections were measured by the θ - 2θ scan on a computer-controlled Philips PW1100 diffractometer using Mo radiation [$\lambda(\text{Mo } K\alpha) = 0.7107$ Å]. All reflections with $I < 3\sigma(I)$ were considered to be unobserved and were not included in

refinements. Three reflections were measured every hour to check the stability of the crystal during intensity measurements.

Using *SHELX* (Sheldrick, 1976) the intensities were corrected for Lp effects. No absorption correction was applied.

The structure was solved using *MULTAN* 78 (Main, Lessinger, Woolfson, Germain & Declercq, 1978). In the first attempt E values were generated without using any information about the geometry of the molecule. The E map corresponding to the phase set having the highest figure of merit (FOM) revealed 20 nonhydrogen atoms. All attempts to refine this model were unsuccessful. Analysis of the convergence map revealed that the phase combinations involved near the end had $h + k$ odd for all reflections. Geometrical information generated in the first attempt was used in generating new E values. In the second attempt 173 reflections with E values > 1.43 were used in phase extension. The program gave 16 possible solutions. Out of these the phase set lying seventh in FOM revealed 20 nonhydrogen atoms. The remaining atoms were located by difference Fourier syntheses. The structure was refined by the full-matrix least-squares method to an R value of 0.0859 using *SHELX*. Unit weights were used. All nonhydrogen atoms were assigned anisotropic thermal parameters. H atoms were located geometrically and, during refinement, were constrained to a distance of 1.08 Å from the bonded atom. Complex neutral-atom scattering factors were used for nonhydrogen atoms (Cromer & Mann, 1968; Cromer & Liberman, 1970).†

All computations were performed on a DEC 20 Model 50 Computer of Regional Computer Centre, Chandigarh.

Discussion. The stereochemistry of the molecule is illustrated in Fig. 1, which also shows the numbering

† Lists of structure factors, anisotropic thermal parameters and H atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36382 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Final atomic parameters with e.s.d.'s in parentheses (fractional coordinates $\times 10^4$)

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{12} \cos \gamma + 2U_{13} \cos \beta + 2U_{23} \cos \alpha).$$

	x	y	z	U_{eq} ($\times 10^3, \text{\AA}^2$)
N(1)	1773 (4)	4496 (6)	6995 (10)	42.9 (6)
C(2)	1630 (5)	3926 (7)	5353 (13)	42.3 (4)
C(3)	2473 (5)	3774 (7)	4914 (13)	44.4 (4)
N(4)	2987 (4)	3727 (5)	6665 (10)	35.0 (4)
C(5)	3595 (5)	2920 (6)	7067 (12)	37.7 (4)
C(6)	3760 (5)	2395 (7)	8604 (12)	41.4 (4)
S	3208 (1)	2429 (2)	10260 (4)	52.8 (1)
C(8)	2316 (5)	3045 (7)	9022 (13)	45.2 (5)
C(9)	2530 (4)	4045 (7)	8022 (11)	35.7 (4)
C(10)	1045 (6)	4512 (8)	3875 (15)	65.0 (6)
C(11)	4102 (4)	2785 (6)	5720 (12)	38.4 (4)
C(12)	4411 (5)	1770 (7)	5473 (14)	47.1 (5)
C(13)	4912 (5)	1632 (9)	4273 (14)	52.9 (6)
C(14)	5105 (5)	2510 (11)	3321 (14)	61.8 (6)
C(15)	4796 (6)	3526 (9)	3569 (15)	58.3 (6)
C(16)	4295 (5)	3663 (7)	4779 (12)	41.3 (5)
C(21)	2964 (5)	4875 (6)	9305 (12)	35.1 (4)
C(22)	3746 (5)	5230 (7)	9197 (13)	41.6 (5)
C(23)	4148 (6)	5949 (7)	10443 (14)	50.9 (5)
C(24)	3794 (6)	6327 (7)	11753 (14)	55.4 (5)
C(25)	3017 (7)	5990 (8)	11867 (14)	57.4 (6)
C(26)	2609 (5)	5274 (7)	10615 (13)	45.7 (5)

scheme used in the analysis. Table 1 contains the final positional parameters and Table 2 the bond distances and angles.

The S—C(6) bond distance of 1.740 (9) Å is comparable to the S—C(sp²) bond distances observed in other 1,4-thiazines (McDowell, 1975; Chu, Kou & van der Helm, 1978, and references therein; Argay, Kálmán, Kapor & Ribár, 1980). The C—S—C bond angle of 97.6 (4)° together with the contraction of the

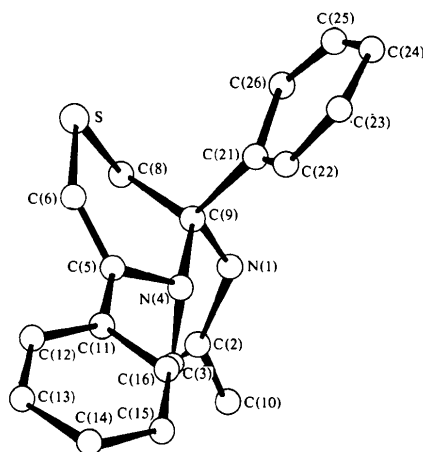


Fig. 1. View of TDIT down the *a* axis.

Table 2. Interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses

N(1)—C(9)	1.483 (9)	N(4)—C(9)	1.485 (10)
C(8)—C(9)	1.549 (11)	C(21)—C(9)	1.522 (11)
C(2)—N(1)	1.442 (11)	C(2)—C(3)	1.549 (10)
C(2)—C(10)	1.546 (12)	N(4)—C(3)	1.468 (11)
C(5)—N(4)	1.428 (9)	C(6)—C(5)	1.344 (11)
C(11)—C(5)	1.495 (11)	C(12)—C(11)	1.395 (11)
C(13)—C(12)	1.395 (13)	C(14)—C(13)	1.395 (14)
C(15)—C(14)	1.395 (14)	C(16)—C(15)	1.401 (13)
C(16)—C(11)	1.390 (11)	S—C(6)	1.740 (9)
S—C(8)	1.798 (9)		
C(22)—C(21)	1.418 (10)	C(23)—C(22)	1.395 (12)
C(24)—C(23)	1.367 (14)	C(24)—C(25)	1.403 (13)
C(26)—C(25)	1.399 (13)	C(26)—C(21)	1.378 (11)
C(8)—C(9)—N(4)	110.7 (6)	C(8)—C(9)—N(1)	108.0 (6)
C(21)—C(9)—N(1)	110.6 (6)	C(21)—C(9)—N(4)	113.4 (6)
C(21)—C(9)—C(8)	110.1 (7)	C(2)—N(1)—C(9)	105.5 (6)
C(3)—C(2)—N(1)	104.9 (6)	C(10)—C(2)—N(1)	113.6 (7)
C(10)—C(2)—C(3)	112.2 (8)	N(4)—C(3)—C(2)	101.7 (7)
C(3)—N(4)—C(9)	110.7 (6)	C(5)—N(4)—C(3)	120.2 (6)
C(5)—N(4)—C(9)	119.2 (6)	C(6)—C(5)—N(4)	123.4 (8)
C(11)—C(5)—N(4)	114.6 (7)	C(11)—C(5)—C(6)	121.7 (7)
S—C(6)—C(5)	127.1 (7)	S—C(8)—C(9)	110.8 (5)
C(8)—S—C(6)	97.6 (4)	C(11)—C(12)—C(13)	120.0 (9)
C(12)—C(13)—C(14)	120.0 (9)	C(15)—C(14)—C(13)	120.0 (8)
C(16)—C(15)—C(14)	119.9 (7)	C(11)—C(16)—C(15)	119.9 (9)
C(12)—C(11)—C(5)	118.9 (8)	C(16)—C(11)—C(12)	120.2 (8)
C(16)—C(11)—C(5)	120.8 (7)	C(21)—C(22)—C(23)	119.4 (8)
C(24)—C(23)—C(22)	121.0 (9)	C(25)—C(24)—C(23)	120.2 (9)
C(26)—C(25)—C(24)	119.2 (9)	C(26)—C(21)—C(22)	119.1 (8)
C(9)—C(21)—C(22)	120.5 (7)	C(26)—C(21)—C(9)	120.4 (7)
C(25)—C(26)—C(21)	121.1 (8)	N(4)—C(9)—N(1)	103.7 (6)

Table 3. Least-squares planes and atom deviations ($\text{\AA} \times 10^3$)

Atoms marked with an asterisk have not been included in the calculation of the planes. The equations are of the form $PX + QY + RZ - S = 0$ and are defined with respect to orthogonal axes. *X*, *Y* and *Z* are expressed in Å.

Plane	Atom	Deviation	Plane	Atom	Deviation
Plane A	C(11)	2 (8)	Plane B	C(21)	-10 (9)
	C(12)	0 (10)		C(22)	5 (8)
	C(13)	0 (10)		C(23)	0 (9)
	C(14)	0 (10)		C(24)	-1 (9)
	C(15)	2 (11)		C(25)	-4 (10)
	C(16)	-2 (9)		C(26)	9 (9)
Plane C	C(9)	-121 (9)	Plane D	C(9)	-330 (8)
	N(1)	215 (7)		N(4)	35 (7)
	C(2)	-211 (9)		C(5)	131 (8)
	C(3)	121 (9)		C(6)	-45 (9)
	C(4)	-4 (6)		C(8)	392 (8)
C(10)*	459	S	-183 (3)		
Plane E	N(4)	-18 (7)	S	15 (2)	
	C(5)	40 (8)	C(8)*	601	
	C(6)	-37 (9)	C(9)*	-228	
Plane	Coefficients				
		<i>P</i>	<i>Q</i>	<i>R</i>	<i>S</i>
	<i>A</i>	-0.6681	-0.1885	-0.7198	-7.862
	<i>B</i>	-0.2756	0.7653	-0.5817	-0.4796
	<i>C</i>	0.2977	0.2977	-0.1863	-4.5945
<i>D</i>	-0.4680	-0.7094	-0.5290	-7.899	
<i>E</i>	-0.5398	-0.7150	-0.4439	-7.7367	

C(6)–S bond length may be interpreted in terms of π bonding between a $p\pi$ orbital of the C atom and $3d$ orbitals of the S atom (McDowell, 1975; Hosoya, 1966). Empirical calculations (Pauling, 1960) show that the bond order of this bond is about 1.25. The S–C(8) bond distance of 1.798 (9) Å agrees well with the normal S–C(sp^3) distance (Talberg, 1974).

The mean-plane calculations (Ahmed, Hall, Pippy & Huber, 1973) indicate that the S–C(6)–C(5)–N(4) segment of the thiazine moiety is planar (Table 3) within the limits of experimental error. The C(5)–N(4) bond distance of 1.428 (9) Å is significantly shorter than C(9)–N(4) and C(9)–N(1) because of the smaller radius of the sp^2 -hybridized C(5) atom.

In the imidazole ring system N(1)–C(2)–C(3), 104.9 (6)°, and C(2)–C(3)–N(4), 101.7 (7)°, are comparable to the 102.5° observed in ethylenethiourea (Wheatley, 1956).

The structure analysis has confirmed that this ring system is imidazo[2,1-c][1,4]thiazine with the methyl group attached at carbon atom 2.

Intensity measurements were carried out for us at Twente University of Technology by Ing G. J. Van Hummel and Dr Sybolt Harkema with the permission of Dr D. Feil. One of us (MSH) is grateful to CSIR, India, for a Junior Research Fellowship.

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Format for Papers to be Published in *Acta Crystallographica*, Section C

Publication of Section C of *Acta Cryst.* will commence 15 January 1983. Details of the division into three new sections are given on page 1 of Volumes A38 and B38. Section C will include all papers concerned with the straightforward determination and refinement of crystal structures such as are now published in Section B and in *Crystal Structure Communications (CSC)*. The overall format of papers in Section C will resemble that used for Short Structural Papers (SSP) but without the present restriction on length. The *Introduction* section, which in SSP's contains the experimental details, will be replaced by a new *Introduction* (analogous to the *Preliminary Information* in *CSC*) and an *Experimental* section, the latter giving the essential experimental information in an abbreviated telegraphic form similar to that used for the crystal data in the *Abstract*.

Analysis of the types of information presented in SSP's, dealing with a single material at one temperature, in the first half of 1981 shows that a typical paper includes (1) a table of atomic coordinates and isotropic or equivalent isotropic thermal parameters, (2) a table of intramolecular bond distances and angles, (3) one figure showing a projection of the molecule with thermal ellipsoids and atomic numbering

and (4) one figure showing the packing, either as a stereoview or as a projection. Most papers will be expected to conform to this 'typical' pattern, with additional tables and figures deposited as a Supplementary Publication. Papers on more than one material, or on materials at more than one temperature or pressure, may be appropriately scaled in content. All duplicated information within the paper will be deleted. A significant reduction in the resulting length of papers is expected from the new format without loss of vital information but with easier access to the information presented.

Papers submitted for consideration in *Acta Cryst.*, Section C must hence conform with the following arrangement:

The *Title* will consist of the name of the substance and the chemical formula; a qualification such as 'Structure of ...', 'New Form of ...', 'from Minas Gerais' etc. may be added.

The *Abstract* will consist (preferably in the order given here) of the formula weight, space group, unit-cell dimensions with an indication of accuracy (normally the estimated standard deviation in units of the last quoted decimal place enclosed in parentheses),* volume (Å³), *Z*, measured and calculated density, radiation and wavelength, linear absorption coefficient, measurement temperature, the final value of *R* (see below for definition) and number of unique

* All primary measured and derived quantities given in the paper must be accompanied by their e.s.d.'s.