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

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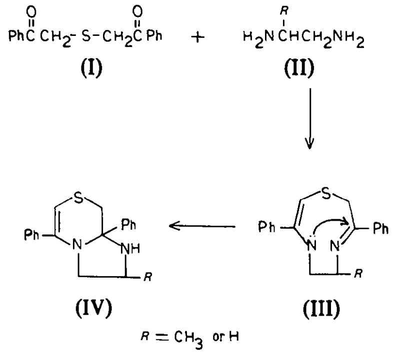
Abstract

The title compound $C_{18}H_{18}N_2S$ is monoclinic with unit-cell dimensions $a = 7{\cdot}4729\,(11)$, $b = 23{\cdot}5631\,(10)$, $c = 8{\cdot}7006\,(14)$ Å, $\beta = 104{\cdot}965\,(16)°$. The space group is $P2_1/c$ with $Z = 4$, $d_m = 1{\cdot}31$, $d_c = 1{\cdot}323$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, μ(Mo $K\alpha$) = $1{\cdot}71$ cm^{-1}. The structure was solved by direct methods. A full-matrix least-squares refinement based on 1909 reflections with $F \geq 3\sigma(F)$ converged to give $R = 0{\cdot}0669$ and $R_w = 0{\cdot}058$. All non-H atoms were refined anisotropically. H atoms were located on geometrical considerations and during refinement they were kept isotropic. S—C(sp^2) and S—C(sp^3) distances are 1·747 (4) and 1·796 (5) Å respectively. The C—S—C bond angle is 97·8 (2)° and the average C—C bond distance in the phenyl rings is 1·392 Å.

Introduction

The condensation reaction of 2,2′-thiodiacetophenone (I) with 1,2-diaminopropane (II) proceeds *via* the formation of thiadiazonine (III), which on transannular interaction of the N atom with C=N results in the formation of the imidazo[2,1-*c*][1,4]thiazine system (IV). This has been established with the help of ^{13}C NMR spectral studies on a series of products isolated from a number of similar reactions (Sandhu, Tandon & Singh, 1980). The formation of a bicyclic product has been confirmed by crystal-structure determination (Sandhu & Hundal, 1982) of the product where $R = CH_3$. However, when the same reaction is carried out with 1,2-diaminoethane, R = H, the ^{13}C spectra of the product indicated the presence of a thiadiazonine ring system. An X-ray diffraction study of this product was considered essential to provide unequivocal evidence for or against the formation of a thiadiazonine ring system.



Experimental

Colourless prismatic crystals of the compound under consideration were grown from ethyl acetate solution by slow evaporation. Preliminary space-group information was obtained from the Weissenberg photographs. The final accurate unit-cell parameters and intensity data were determined on a CAD-4 diffractometer.

Reflections were scanned in the ω–2θ mode with ω scan width $(0{\cdot}85 + 0{\cdot}35\tan\theta)°$. The maximum scan time for each reflection was 60 s. Two standard reflections (410 and 204) were measured at regular intervals to provide a check on crystal and electronic stability. The variations observed in the intensities did not necessitate any corrective measures. 3193 reflections within the range $1{\cdot}5 < \theta < 25°$ were collected.

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Intensities were corrected for Lp effects, but not for absorption (Sheldrick, 1976). Common reflections were averaged and reflections with $F_o < 3\sigma(F_o)$ were treated as unobserved. This gave a set of 1909 reflections.

The structure was solved by means of direct methods using *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1978). The largest 184 normalized structure-factor amplitudes ($E > 1{\cdot}2$) were selected as input for phase determination. An E map computed with the set of signs with the best figure of merit gave an indication of the positions of all the non-H atoms. However, analysis of bond lengths and angles revealed that the values deviated too much from the expected values. Therefore only positions of the S atom, three C atoms and two N atoms were used in the initial phasing model and other atoms were located by application of successive Fourier syntheses.

The structure was refined by full-matrix least squares using *SHELX*. In the initial stages all atoms were kept isotropic and all reflections were assigned unit weights. In the final stages of refinement an overall scale factor, positional parameters for all non-H atoms and anisotropic thermal parameters for S, N and C atoms were varied. The H atoms were located by geometrical considerations. The C—H bond distances were held constant at 1·08 Å. All the H atoms were assigned an overall $U_{\rm iso}$ value of 0·07 Å^2. Complex neutral-atom scattering factors were employed for all non-H atoms (Cromer & Mann, 1968; Cromer & Liberman, 1970). The refinement converged to a final R value of 0·0669 and $R_w = 0{\cdot}058$. Each reflection was given a weight = $1/\sigma^2(F)$, where $\sigma(F)$ is based on counting statistics.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2 ×10^3) *with e.s.d.'s in parentheses*

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

	x	y	z	$U_{\rm eq}$
N(1)	1·2282 (7)	0·2128 (2)	1·2574 (6)	41·6 (3)
C(2)	1·4187 (10)	0·2093 (4)	1·2492 (9)	58·1 (5)
C(3)	1·4180 (9)	0·1938 (3)	1·0829 (8)	41·5 (4)
N(4)	1·2475 (7)	0·1599 (2)	1·0328 (5)	29·4 (3)
C(5)	1·1824 (8)	0·1423 (2)	0·8740 (6)	27·4 (3)
C(6)	1·0048 (9)	0·1476 (3)	0·7900 (8)	33·2 (4)
S	0·8288 (2)	0·1833 (1)	0·8491 (2)	43·6 (9)
C(8)	0·9719 (9)	0·2192 (3)	1·0189 (7)	39·7 (4)
C(9)	1·1154 (8)	0·1795 (3)	1·1205 (7)	30·6 (3)
C(11)	1·3175 (8)	0·1122 (2)	0·8054 (7)	30·1 (3)
C(12)	1·3056 (9)	0·1158 (3)	0·6417 (7)	40·2 (4)
C(13)	1·4262 (10)	0·0853 (3)	0·5758 (8)	44·2 (4)
C(14)	1·5616 (9)	0·0515 (3)	0·6705 (8)	45·3 (4)
C(15)	1·5759 (10)	0·0485 (3)	0·8335 (9)	42·2 (4)
C(16)	1·4560 (9)	0·0779 (3)	0·9031 (7)	33·7 (3)
C(21)	1·0251 (8)	0·1288 (2)	1·1834 (7)	26·7 (3)
C(22)	0·9003 (8)	0·1398 (3)	1·2745 (7)	36·5 (3)
C(23)	0·8197 (10)	0·0957 (3)	1·3380 (8)	45·3 (4)
C(24)	0·8609 (10)	0·0400 (3)	1·3076 (8)	47·9 (4)
C(25)	0·9825 (10)	0·0278 (3)	1·2160 (8)	43·9 (4)
C(26)	1·0643 (9)	0·0732 (3)	1·1553 (8)	37·0 (4)

Discussion

The main aim of this structure determination was to decide whether the reaction product is a monocyclic thiadiazonine or a bicyclic imidazothiazine system. It has been found that the structure in the solid state is 2,3,8,8a-tetrahydro-5,8a-diphenyl-1*H*-imidazo[2,1-*c*]-[1,4]thiazine. The final atomic positions are listed in Table 1.* Fig. 1 shows the numbering used in the structure analysis.

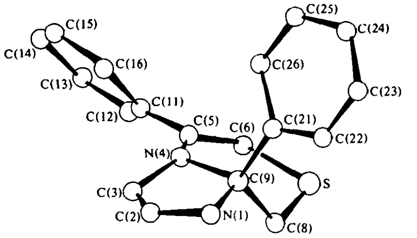

Fig. 1. View of the molecule down the *c* axis.

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

S—C(8)	1·796 (5)	S—C(6)	1·747 (4)
C(8)—C(9)	1·523 (6)	N(1)—C(9)	1·491 (5)
N(4)—C(9)	1·470 (5)	C(21)—C(9)	1·540 (5)
C(2)—N(1)	1·446 (6)	C(3)—C(2)	1·492 (6)
N(4)—C(3)	1·472 (5)	C(5)—N(4)	1·403 (5)
C(5)—C(6)	1·345 (6)	C(11)—C(5)	1·480 (5)
C(11)—C(12)	1·407 (6)	C(12)—C(13)	1·387 (6)
C(13)—C(14)	1·380 (7)	C(14)—C(15)	1·396 (6)
C(15)—C(16)	1·389 (6)	C(16)—C(11)	1·412 (6)
C(21)—C(22)	1·396 (5)	C(22)—C(23)	1·387 (6)
C(23)—C(24)	1·388 (7)	C(24)—C(25)	1·385 (7)
C(25)—C(26)	1·401 (6)	C(26)—C(21)	1·378 (6)

C(6)—S—C(8)	97·8 (2)	C(9)—C(8)—S	111·6 (3)
N(1)—C(9)—C(8)	108·0 (4)	N(4)—C(9)—C(8)	111·0 (3)
N(4)—C(9)—N(1)	105·3 (3)	C(21)—C(9)—C(8)	112·1 (3)
C(21)—C(9)—N(1)	109·5 (3)	C(21)—C(9)—N(4)	110·8 (3)
C(2)—N(1)—C(9)	107·0 (3)	C(3)—C(2)—N(1)	107·8 (4)
N(4)—C(3)—C(2)	101·9 (4)	C(3)—N(4)—C(9)	108·8 (3)
C(5)—N(4)—C(9)	119·7 (3)	C(5)—N(4)—C(3)	120·4 (3)
C(6)—C(5)—N(4)	123·4 (4)	C(11)—C(5)—N(4)	116·0 (3)
C(11)—C(5)—C(6)	120·3 (4)	C(5)—C(6)—S	126·6 (4)
C(12)—C(11)—C(5)	120·6 (4)	C(16)—C(11)—C(5)	120·1 (4)
C(16)—C(11)—C(12)	119·2 (4)	C(13)—C(12)—C(11)	120·6 (5)
C(14)—C(13)—C(12)	120·5 (5)	C(15)—C(14)—C(13)	119·1 (5)
C(16)—C(15)—C(14)	121·9 (5)	C(15)—C(16)—C(11)	118·6 (4)
C(22)—C(21)—C(9)	118·4 (4)	C(26)—C(21)—C(9)	122·8 (4)
C(26)—C(21)—C(22)	118·8 (4)	C(23)—C(22)—C(21)	120·6 (5)
C(24)—C(23)—C(22)	119·5 (5)	C(25)—C(24)—C(23)	121·1 (5)
C(26)—C(25)—C(24)	118·3 (5)	C(25)—C(26)—C(21)	121·7 (4)

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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 36398 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The bond lengths listed in Table 2 are normal with an average non-phenyl C—C distance of 1·518 Å. The S—C(8) distance of 1·796 (5) Å lies within the range of S—C(sp^3) distances observed in the case of various 1,3-thiazine systems (Amirthalingam & Jakkal, 1972; Talberg, 1974; Sacerdoti, Bertolasi, Gilli, Dondoni & Battaglia, 1977; Menczel, Kiss, Simon, Hornyák & Lempart, 1974; Argay, Kálmán, Kapor & Ribár, 1980).

The value found in the present case for the S—C(6) bond length, 1·747 (4) Å, matches well with the value found for the S—C(sp^2) distance (Andreetti, Bocelli & Sgarabotto, 1980, and references therein).

Comparing the results of the present work with those of the study on 2,3,8,8a-tetrahydro-2-methyl-5,8a-diphenyl-1*H*-imidazo[2,1-c][1,4]thiazine (TDIT), it is found that N(4)—C(5), C(2)—C(3), N(4)—C(9), C(9)—C(21) and C(8)—C(9) distances are shorter by 0·025, 0·057, 0·015, 0·018 and 0·026 Å respectively. The C—S—C bond angle of 97·6 (4)° agrees well with 97·8 (2)° observed in the present case.

Intensity data were measured for us at Queen Mary College, London, by Dr M. B. Hursthouse. One of us (MSH) is grateful to CSIR (India) for financial assistance.

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X-ray Structure Analysis of 3-[3-Benzoyl-4-(diethylamino)-5-methyl-1-pyrazolyl]-3-(diethylamino)-2-methyl-1-phenyl-2-propen-1-one, the 1:2 Reaction Product of Dibenzoyldiazomethane and 1-(Diethylamino)propyne

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Abstract

X-ray structure analysis of the title compound ($C_{29}H_{36}N_4O_2$) has established its chemical constitution and the pathway of its formation. The crystals are monoclinic, space group $P2_1$, $a = 8{\cdot}978\,(2)$, $b = 16{\cdot}522\,(4)$, $c = 19{\cdot}307\,(6)$ Å, $\gamma = 106{\cdot}07\,(2)^\circ$, $V = 2752{\cdot}0$ Å^3, $D_x = 1{\cdot}141$, $D_m = 1{\cdot}135$ Mg m^{-3}, $Z = 4$. The structure was solved by direct methods and refined to $R = 0{\cdot}043$ for 5114 reflexions with $I > 2\sigma(I)$. The π-resonance system of the vinylogous acid amide system of the 2-methyl-1-phenyl-2-propen-1-one residue on N(1) of the pyrazole ring is not planar and shows only a small π interaction with the aromatic pyrazolyl residue. The diethylamino groups have different conformations. The nitrogen of the diethylamino group bound to the pyrazole ring is on the apex of a pyramid. The nitrogen within the vinylogous acid amide system is sp^2-hybridized and almost coplanar with its bonding neighbours. The two molecules of the asymmetric unit, which show some significant differences in conformation, are related in the crystal by an approximate *n* glide plane.

Introduction

From the reaction of dibenzoyldiazomethane (1) with 1-(diethylamino)propyne (2) two products (4) and (5)

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