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Structure of 6-Methyl-4-phenyl-8-phenylmethylene-3,4,5,6,7,8-hexahydro-2(1H)-quinazolinethione

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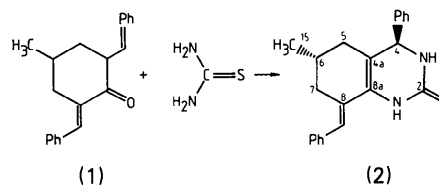
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Abstract. $C_{22}H_{22}N_2S$, $M_r = 346.50$, monoclinic, $P2_1/c$, $a = 15.919$ (1), $b = 6.320$ (1), $c = 19.039$ (2) Å, $\beta = 105.00$ (1)°, $V = 1850.2$ (4) Å³, $Z = 4$, $D_x = 1.24$ Mg m⁻³, $\lambda(\text{Cu K}\alpha) = 1.54184$ Å, $\mu = 0.154$ mm⁻¹, $F(000) = 736$, $T = 296$ (1) K, $R = 0.047$ for 3348 observed reflections. Only X-ray analysis could reveal the stereochemistry of the title compound furnished by the reaction of 2,6-dibenzylidene-4-methylcyclohexanone with thiourea. It has been shown to be the diastereomer in which the 4-phenyl moiety is bound axially while the 6-methyl group assumes an equatorial position.

Introduction. Earlier we have studied the reactions of 2,6-diarylidene-cyclohexanones with thiourea in basic media (Lóránd, Szabó & Neszmélyi, 1977). Now, these investigations have been extended over the cyclohexane-ring-substituted 2,6-diarylidene-cyclohexanones. The reaction of 2,6-dibenzylidene-4-methylcyclohexanone (1) with thiourea yielded 6-methyl-4-phenyl-8-phenylmethylene-3,4,5,6,7,8-hexahydro-2(1H)-quinazolinethione (2). According to ¹H NMR spectra of (2) only one diastereomer is formed, which is depicted in the reaction scheme. However, on the basis

of the ¹H NMR studies we could not decide on the two possible isomers. Furthermore, we were also interested in the stereochemistry of 4-phenyl-8-phenylmethylene-3,4,5,6,7,8-hexahydro-2(1H)-quinazolinethione, studied earlier (Lóránd, Szabó & Neszmélyi, 1977). Therefore, an X-ray analysis of (2) (melted at 384–387 K) has been performed.



Experimental. Colourless crystals of which a sample of dimensions $ca\ 0.17 \times 0.34 \times 0.56$ mm was mounted on a CAD-4 diffractometer equipped with graphite monochromator. Cell constants were refined by least-squares fit for 25 centred reflections collected in the range $20 \leq \theta \leq 39^\circ$. $\omega/2\theta$ scan in the range $0.017 \leq (\sin\theta)/\lambda \leq 0.626$ Å⁻¹ with scan width $0.45^\circ + 0.30^\circ \tan\theta$. 3801 unique, non-zero and not systematically absent ($h0l\ l = 2n + 1$, and $0k0\ k = 2n + 1$ for space group $P2_1/c$) reflections were recorded with $h: 0$ to 19, $k: 0$ to 7 and $l: -23$ to 23, of which – after

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Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters B_{eq} (Å²) for the non-hydrogen atoms with e.s.d.'s in parentheses

$B_{eq} = \frac{1}{3}\text{trace}(BG)$ where G is the direct metric tensor.

	x	y	z	B_{eq} (Å ²)
S	0.61099 (2)	0.17947 (8)	-0.02549 (2)	3.618 (4)
N(1)	0.7409 (1)	-0.0682 (2)	0.0426 (1)	3.08 (1)
N(3)	0.6066 (1)	-0.1580 (3)	0.0562 (1)	3.86 (1)
C(2)	0.6540 (1)	-0.0280 (3)	0.0275 (1)	3.12 (1)
C(4)	0.6385 (1)	-0.3278 (3)	0.1083 (1)	3.24 (1)
C(4a)	0.7328 (1)	-0.3737 (3)	0.1137 (1)	2.97 (2)
C(5)	0.7706 (1)	-0.5630 (3)	0.1576 (1)	3.37 (2)
C(6)	0.8683 (1)	-0.5476 (3)	0.1871 (1)	2.93 (2)
C(7)	0.9086 (1)	-0.4850 (3)	0.1259 (1)	2.89 (2)
C(8)	0.8743 (1)	-0.2770 (3)	0.0914 (1)	2.60 (2)
C(8a)	0.7804 (1)	-0.2448 (3)	0.0831 (1)	2.71 (2)
C(9)	0.6257 (1)	-0.2755 (3)	0.1826 (1)	3.25 (1)
C(10)	0.5883 (1)	-0.4206 (4)	0.2196 (1)	4.33 (1)
C(11)	0.5821 (1)	-0.3811 (4)	0.2894 (1)	5.84 (1)
C(12)	0.6118 (1)	-0.1956 (5)	0.3227 (1)	6.73 (2)
C(13)	0.6473 (2)	-0.0474 (4)	0.2858 (1)	6.70 (5)
C(14)	0.6548 (1)	-0.0877 (4)	0.2164 (1)	4.72 (3)
C(15)	0.9066 (1)	-0.7517 (3)	0.2244 (1)	3.77 (3)
C(16)	0.9248 (1)	-0.1265 (3)	0.0738 (1)	2.86 (2)
C(17)	1.0203 (1)	-0.1287 (3)	0.0843 (1)	2.67 (2)
C(18)	1.0674 (1)	-0.3016 (3)	0.0698 (1)	3.14 (2)
C(19)	1.1568 (1)	-0.2915 (3)	0.0815 (1)	3.61 (1)
C(20)	1.2012 (1)	-0.1092 (3)	0.1088 (1)	3.77 (1)
C(21)	1.1559 (1)	0.0642 (3)	0.1228 (1)	3.74 (2)
C(22)	1.0663 (1)	0.0555 (3)	0.1094 (1)	3.18 (2)

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

S—C(2)	1.688 (2)	C(8)—C(16)	1.344 (2)
N(1)—C(2)	1.361 (1)	C(9)—C(10)	1.382 (3)
N(1)—C(8a)	1.408 (2)	C(9)—C(14)	1.372 (3)
N(3)—C(2)	1.326 (2)	C(10)—C(11)	1.380 (3)
N(3)—C(4)	1.460 (2)	C(11)—C(12)	1.358 (4)
C(4)—C(4a)	1.506 (2)	C(12)—C(13)	1.377 (4)
C(4)—C(9)	1.517 (2)	C(13)—C(14)	1.382 (3)
C(4a)—C(5)	1.494 (2)	C(16)—C(17)	1.481 (2)
C(4a)—C(8a)	1.344 (2)	C(17)—C(18)	1.392 (2)
C(5)—C(6)	1.514 (2)	C(17)—C(22)	1.393 (2)
C(6)—C(7)	1.521 (2)	C(18)—C(19)	1.383 (2)
C(6)—C(15)	1.522 (3)	C(19)—C(20)	1.381 (3)
C(7)—C(8)	1.507 (2)	C(20)—C(21)	1.375 (3)
C(8)—C(8a)	1.475 (2)	C(21)—C(22)	1.383 (2)
C(2)—N(1)—C(8a)	123.3 (2)	N(1)—C(8a)—C(4a)	119.7 (2)
C(2)—N(3)—C(4)	126.9 (2)	N(1)—C(8a)—C(8)	117.7 (2)
S—C(2)—N(1)	120.3 (2)	C(4a)—C(8a)—C(8)	122.6 (2)
S—C(2)—N(3)	122.8 (2)	C(4)—C(9)—C(10)	120.7 (3)
N(1)—C(2)—N(3)	116.9 (2)	C(4)—C(9)—C(14)	121.0 (3)
N(3)—C(4)—C(4a)	110.7 (2)	C(10)—C(9)—C(14)	118.2 (3)
N(3)—C(4)—C(9)	111.4 (2)	C(9)—C(10)—C(11)	121.2 (3)
C(4a)—C(4)—C(9)	110.5 (2)	C(10)—C(11)—C(12)	120.2 (4)
C(4)—C(4a)—C(5)	116.2 (2)	C(11)—C(12)—C(13)	119.2 (4)
C(4)—C(4a)—C(8a)	121.1 (2)	C(12)—C(13)—C(14)	120.8 (4)
C(5)—C(4a)—C(8a)	122.6 (2)	C(9)—C(14)—C(13)	120.4 (3)
C(4a)—C(5)—C(6)	112.4 (2)	C(8)—C(16)—C(17)	128.3 (2)
C(5)—C(6)—C(7)	109.3 (2)	C(16)—C(17)—C(18)	124.5 (2)
C(5)—C(6)—C(15)	111.6 (2)	C(16)—C(17)—C(22)	117.9 (2)
C(7)—C(6)—C(15)	112.3 (2)	C(18)—C(17)—C(22)	117.5 (2)
C(6)—C(7)—C(8)	112.5 (2)	C(17)—C(18)—C(19)	121.0 (3)
C(7)—C(8)—C(8a)	114.2 (2)	C(18)—C(19)—C(20)	120.3 (3)
C(7)—C(8)—C(16)	123.6 (2)	C(19)—C(20)—C(21)	119.7 (3)
C(8a)—C(8)—C(16)	122.1 (2)	C(20)—C(21)—C(22)	120.0 (3)
		C(17)—C(22)—C(21)	121.4 (3)

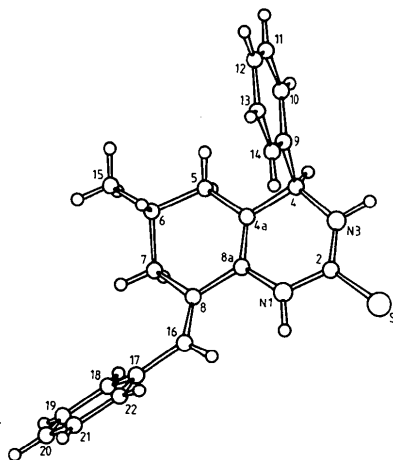


Fig. 1. Perspective view of the molecule with atomic numbering. Bare numbers are for carbon atoms unless indicated otherwise. H atoms are shown but not labelled.

data correction — 3348 with $I \geq 3\sigma(I)$ were taken as observed. Three standard reflections (008, 440, 743) were monitored every hour and showed no loss or gain in intensity during data collection. The phase problems were solved by the *MULTAN82* program (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) using $275 \geq E$ normalized structure factors. Full-matrix least-squares refinement minimized the $\sum w(\Delta F)^2$ function for 227 variables with $w = 4F_o^2/\sigma(F_o^2)^2$. At the end of the isotropic refinement an empirical absorption

correction was applied by the *DIFABS* program (Walker & Stuart, 1983); max. and min. relative transmission coefficients were 1.317 and 0.680. Final $R = 0.047$, $wR = 0.063$, $R_{tot} = 0.054$, $S = 6.25$. Max. and min. peak heights in the final $\Delta\rho$ map $0.45(4)e \text{ \AA}^{-3}$, $(\Delta/\sigma)_{max} = 0.1$. Positions of H atoms bound to C atoms were generated from assumed geometries; those belonging to N atoms were located in a difference Fourier map; they were added to the structure-factor calculations with a mean isotropic temperature factor ($B_{IH} = B_{IX} + 1 \text{ \AA}^2$ where $X = C$ or N). Scattering factors were taken from the applied program system: Enraf-Nonius (1983) *SDP-Plus* adapted to a PDP 11/34 minicomputer with local modifications.

Discussion. Atomic coordinates of non-H atoms are in Table 1.* The molecular geometry with atomic numbering is shown in Fig. 1. Bond lengths and angles are given in Table 2.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51157 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The partly saturated pyrimidine-2-thione ring assumes a rather flattened envelope conformation [Cremer & Pople's (1975) puckering parameters if the atomic sequence is chosen from N(1) through C(2) to C(8a): $Q = 0.114$ (2) Å, $\varphi = 171.2$ (10), $\theta = 70.4$ (9)°] with C(4) on the flap to which the phenyl ring is bound pseudoaxially [C(9)–C(4)–N(3)–C(2) = 110.3 (3)°]. The planar thiourea moiety is characterized by the C–S and C–N multiple bonds similar to those found in other structures. The relevant difference between the lengths of C(2)–N(1) and C(2)–N(3) multiple bonds [$\Delta = 0.035$ (2) Å] can be attributed to the difference in the hybridization of the adjacent carbon atoms C(8a)– sp^2 vs C(4)– sp^3 . The carbo ring of the quinazoline skeleton due to the three sp^3 C atoms possesses a slightly distorted [puckering parameters if the atomic sequence is chosen from C(4a) through C(5) to C(8a): $Q = 0.471$ (2) Å, $\varphi = 316.9$ (3), $\theta = 130.3$ (2)°] half-chair shape. C(6) with the highest out-of-plane displacement [0.317 (2) Å] from the least-squares plane of the ring bears the methyl substituent in an equatorial position [C(15)–C(6)–C(7)–C(8) = –177.0 (3)°].

In the crystal lattice centre-of-symmetry-related pairs of molecules form dimer associates with the hydrogen-bond parameters

	$D \cdots A$ (Å)	$H \cdots A$ (Å)	$DH \cdots A$ (°)
N(3)–H(3)···S(1–x, –y, –z)	3.362 (3)	2.40 (2)	159 (1)

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Structures of Thiamine Hexafluorophosphate Monohydrate, Thiaminium Diperchlorate, Thiaminium Bis(hexafluorophosphate) Tetrahydrate, and Thiaminemonophosphate Hexafluorophosphate Dihydrate

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Abstract. $C_{12}H_{17}N_4OS^+.PF_6^-.H_2O$ (1), $M_r = 428.336$, monoclinic, $P2_1/n$, $a = 12.968$ (2), $b = 11.381$ (2), $c = 12.335$ (3) Å, $\beta = 92.71$ (2)°, $V = 1818.5$ (6) Å³, $Z = 4$, $D_x = 1.564$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 3.28$ cm⁻¹, $F(000) = 880$, $T = 293$ K, $R = 0.047$ for 2522 reflections; $C_{12}H_{18}N_4OS^{2+}.2ClO_4^-$ (2), $M_r = 465.265$, monoclinic, $P2_1/n$, $a = 18.728$ (5), $b = 7.683$ (1), $c = 13.968$ (3) Å, $\beta = 101.87$ (2)°, $V = 1966.9$ (7) Å³, $Z = 4$, $D_x = 1.571$ g cm⁻³, $\mu(\text{Mo } K\alpha) = 4.82$ cm⁻¹, $F(000) = 960$, $T = 293$ K, $R = 0.064$ for 2771 reflections; $C_{12}H_{18}N_4OS^{2+}.2PF_6^-.4H_2O$ (3), $M_r = 628.351$, monoclinic, $P2_1/a$, $a = 11.198$ (2), $b = 26.659$ (7), $c = 8.407$ (2) Å, $\beta = 90.03$ (2)°, $V = 2510.0$ (9) Å³, $Z = 4$, $D_x = 1.663$ g cm⁻³, $\mu(\text{Mo } K\alpha)$

$= 3.65$ cm⁻¹, $F(000) = 1280$, $T = 293$ K, $R = 0.060$ for 2190 reflections; $C_{12}H_{18}N_4O_4PS^+.PF_6^-.2H_2O$ (4), $M_r = 526.330$, triclinic, $P\bar{1}$, $a = 11.633$ (1), $b = 11.255$ (2), $c = 8.441$ (2) Å, $\alpha = 78.80$ (2), $\beta = 94.90$ (1), $\gamma = 103.63$ (1)°, $V = 1052.7$ (3) Å³, $Z = 2$, $D_x = 1.679$ g cm⁻³, $\mu(\text{Mo } K\alpha) = 3.84$ cm⁻¹, $F(000) = 540$, $T = 293$ K, $R = 0.045$ for 3092 reflections. In each compound, the thiamine moiety that adopts the F conformation holds a monovalent anion in a position in which the anion interacts with the thiazolium ring *via* a hydrogen bond with the acidic C(2)H and an electrostatic interaction with the positively charged S(1) atom, and it further contacts, possibly electrostatically, with the pyrimidine (or pyrimidinium) ring.

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