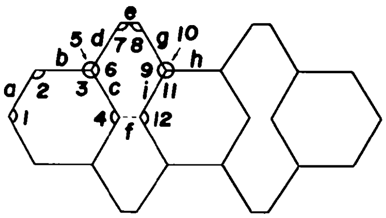
Table 2. *Mean molecular structures of* (I) *and* (III)

The mean number is the mean bond distance, $\bar{x} = \Sigma x_i/n$, where x_i is the individual bond distance observed, and n is the number of chemically equivalent bond distances. The lower number is the estimated standard deviation of the mean, $\sigma(\bar{x}) = (s^2/n)^{1/2}$, where s is the variance, $s = \Sigma (x_i - \bar{x})^2/(n-1)$.



Bond	*n*	(I)	(III)	Angle	*n*	(I)	(III)
a	4	1·3868 Å	1·3738 Å	*1*	2	120·15°	119·60°
		19	55			35	20
b	4	1·3920	1·3875	*2*	4	120·47	121·03
		21	23			6	17
c	4	1·3923	1·3955	*3*	4	118·03	118·28
		27	40			10	38
d	4	1·5060	1·5100	*4*	2	121·85	120·40
		0	26			15	120
e	4	1·5653	1·5593	*5*	4	121·50	120·73
		11	47			16	33
f	2	2·6665	2·6980	*6*	4	119·10	119·20
		49	170			12	33
g	4	1·5150	1·5175	*7*	4	110·78	110·53
		17	27			10	31
h	2	1·4005	1·4015	*8*	4	112·63	114·03
		5	15			28	20
i	4	1·3995	1·3963	*9*	4	117·35	117·40
		20	11			5	12
				10	4	124·30	124·90
						15	15
				11	4	117·70	117·43
						4	13
				12	2	123·30	123·20
						60	10

an electron-releasing methyl group on the deformation of the benzene rings to that in (IV) (Hama, Kai, Yasuoka & Kasai, 1977) is observed. (3) is due to the steric repulsion between the methyl group and the terminal benzene ring opposite it. The shortest non-bonded distance between H(8) and the methyl hydrogen atoms is 1·92 Å. Fig. 3 shows a side view of the molecule indicating the out-of-plane deformations of the benzene rings. The three benzene rings are in the boat conformation. They deviate from the mutually parallel position because of the large steric repulsion between them and the methyl group. The diehedral angles between the benzene planes, $\angle AB = 16{\cdot}3°$ and $\angle BC = 22{\cdot}5°$ (Fig. 3), are much larger than those in (I) (1·3 and 10·4°, respectively).

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Structure of Thiamine Free Base

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Abstract. $C_{12}H_{16}N_4OS$, 2,6a-dimethyl-6a,8,9,9a,10a,11-hexahydrofuro[2,3-*h*]thiachromine, monoclinic, $P2_1/c$, $a = 6{\cdot}789\ (1)$, $b = 15{\cdot}682\ (1)$, $c = 12{\cdot}857\ (1)$ Å, $\beta = 116{\cdot}84\ (1)°$, $Z = 4$, $D_x = 1{\cdot}44$, $D_m = 1{\cdot}42$ g cm^{-3}. Molecules related by a center of symmetry form a dimer through a pair of N—H···N hydrogen bonds. One of the S—C bonds is unusually long (1·895 Å).

Introduction. Thiamine free base was obtained by passing carbon dioxide gas into a dioxane solution of a thiamine sodium salt. Its molecular structure has been

Table 1. *Atomic fractional coordinates* (× 10^4, *for* H × 10^3) *for thiamine free base*

	x	*y*	*z*		*x*	*y*	*z*
N(1)	4992 (2)	3793 (1)	5056 (1)	H(C4)	651	174	391
C(2)	4463 (2)	3002 (1)	5225 (1)	H(C5)	891	277	332
N(3)	5020 (2)	2281 (1)	4863 (1)	H'(C5)	653	328	229
C(4)	6121 (3)	2383 (1)	4226 (1)	H(C8)	1189	599	221
C(4a)	6653 (2)	3164 (1)	3937 (1)	H'(C8)	979	617	269
C(1a)	6089 (2)	3874 (1)	4416 (1)	H(C9)	939	526	62
C(5)	7694 (3)	3289 (1)	3135 (1)	H'(C9)	768	606	71
N(6)	8938 (2)	4100 (1)	3402 (1)	H(C9a)	654	431	79
C(10a)	7707 (2)	4812 (1)	3518 (1)	H(C10a)	894	531	386
N(11)	6683 (2)	4664 (1)	4252 (1)	H(N11)	603	510	452
C(6a)	9551 (2)	4347 (1)	2485 (1)	H(Me2)	250	231	588
C(9a)	7540 (3)	4759 (1)	1432 (1)	H'(Me2)	404	320	673
S(10)	5617 (1)	5091 (1)	1977 (1)	H"(Me2)	164	324	546
O(7)	11149 (2)	5011 (1)	2960 (1)	H(Me6a)	925	312	155
C(8)	10436 (3)	5772 (1)	2270 (2)	H'(Me6a)	1192	333	286
C(9)	8631 (3)	5496 (1)	1100 (2)	H"(Me6a)	1123	388	161
C(Me2)	3093 (3)	2922 (1)	5870 (2)				
C(Me6a)	10564 (3)	3613 (1)	2107 (1)				

determined on the basis of chemical and spectroscopic evidence (Takamizawa, Hirai, Ishiba & Makino, 1971). This study was undertaken to confirm it and to provide the detailed structure.

The systematic absences are *h*0*l* when *l* is odd, and 0*k*0 when *k* is odd. 1595 independent reflexions with $\theta \leq 57°$ were collected on a Hilger & Watts Y290 diffractometer with Ni-filtered Cu *Kα* radiation and a crystal with dimensions 0·3 × 0·3 × 0·3 mm. The intensities were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by the use of the program *MULTAN* (Main, Germain & Woolfson, 1970) with local modifications on a FACOM 270-30 computer. After anisotropic refinement on the non-hydrogen atoms by the block-diagonal least-squares technique, the *R* value converged to 0·030 for 1332 reflexions with $|F_c| > \sigma(F_o)$ and $|\Delta F| < 3\sigma(F_o)$. $\sigma(F_o)$ was estimated as $[\sigma_1^2(F_o) + 0{\cdot}00111|F_o|^2]^{1/2}$, where $\sigma_1(F_o)$ is the e.s.d. depending on the counting errors. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).[*] Final positional parameters are given in Table 1.

Discussion. A perspective view of the dimer molecule is given in Fig. 1. The hydrogen bonding is between N(11) of one molecule and N(1) of another molecule related by the center of symmetry in the crystal. The interatomic distances N(11)···N(1), N(11)–H(N11) and H(N11)···N(1) are 2·977, 0·97 and 2·03 Å, respectively, and the angle N(11)–H(N11)···N(1) is 166°. The *B*/*C* and *C*/*D* ring junctions adopt the *cis* form.

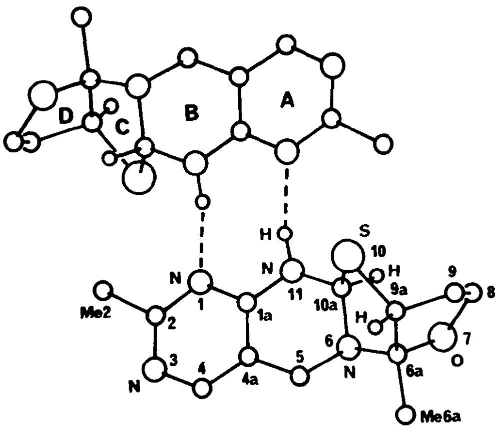

Fig. 1. Perspective view of the dimer molecule with the atom-numbering and ring-labelling systems.

N(6) in ring *B* is displaced by 0·53 Å out of the mean plane of the rest of the atoms, N(6) in ring *C* by 0·62 Å, and C(9) in ring *D* by 0·55 Å.

Bond lengths and angles are shown in Fig. 2. The mean e.s.d. values are 0·003 Å for bond lengths and 0·2° for angles. Comparisons of the corresponding bond orders in the dimer and monomer, calculated by the CNDO/2 method (Pople & Beveridge, 1970), indicated the bonds of N(1)–C(1a) and N(11)–C(1a) to be significantly affected by the formation of the dimer: they are lengthened and shortened, respectively. All the bond lengths show a good correlation with the bond orders. However, the S(10)–C(10a) bond (e.s.d. = 0·002 Å) is unusually long compared with those observed in thiazolidine rings [ranging from 1·80 to 1·84 Å (Argay, Kálmán, Lazar, Ribár & Tóth, 1977)], and the N(6)–C(10a) bond is considerably shorter than N(6)–C(5) and N(6)–C(6a). The other bonds are

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[*] Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33728 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

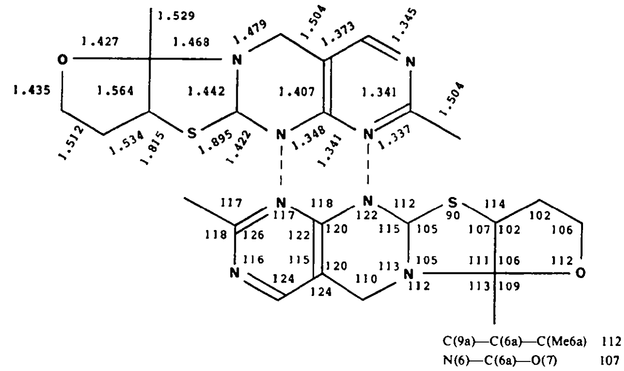

Fig. 2. Bond distances (Å) and angles (°).

as expected, though C(6a)–C(9a) seems to be slightly long.

It has been reported that, at the initial stage of the reaction between thiamine free base and an isocyanate derivative, the S(10)–C(10a) bond is cleaved in a polar solvent (*e.g.* dimethylformamide) to generate the S anion, but not in a less-polar solvent (*e.g.* chloroform) (Takamizawa, Makino & Yonezawa, 1974). Although the bond length might not directly correspond to the reactivity of the bond, it is interesting that the opening of the thiazolidine ring is probably correlated with the unusually long S–C bond.

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Ethyl 3-[4,5-Dimethoxy-2-(5-methyl-2-pyridylsulfamoyl)phenyl]propionate

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Abstract. $C_{19}H_{24}N_2O_6S$, M_r = 408·47, monoclinic, $P2_1/c$, a = 10·143 (6), b = 9·002 (5), c = 22·167 (23) Å, β = 95·48°, Z = 4, D_m = 1·341, D_c = 1·346 g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å. The methoxy groups are nearly coplanar with the phenyl ring, and pairs of molecules, across a centre of symmetry, are connected by N–H···N hydrogen bonds.

Introduction. Derivatives of benzothiazinone have been shown to have an effect on the central nervous system (Sianesi, Redaelli, Magistretti & Massarani, 1973) and are known to have anti-inflammatory activity (Lombardino & Wiseman, 1971). A number of sulphonamides, with structural similarities to benzothiazinone, have recently been synthesized (Camoutsis & Catsoulakos, 1976) and are being tested for pharmacological activity. Crystallographic studies are also being carried out in an attempt to relate structure and activity.

Intensity data were collected on an Enraf–Nonius CAD-4 diffractometer and measured by the $\omega/2\theta$ scan in the range $3 < \theta < 70°$. 12 289 measurements were made, of which 4983 were too small to measure significantly and 411 were intensity checks. Merging of equivalent reflections gave 3217 unique reflections (merging R = 0·0627) but 101 of these had $I < 3\sigma(I)$ and were not used in the analysis. The structure was solved by direct methods using the *EEES* program of the *SHELX* package (Sheldrick, 1976). Four sets of phases were produced and E maps calculated. On one E map 17 of the 28 non-hydrogen atoms were found