molecular separations significantly less than the sum of the respective van der Waals radii.

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The Crystal Structure of 2-Diphenylmethyl-4,4-diphenyl-6-methyl-4*H*-3,1-benzothiazine

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$C_{34}H_{27}NS$, triclinic, $P\bar{1}$ (No. 2), $a = 9.963$ (3), $b = 14.937$ (4), $c = 9.356$ (4) Å, $\alpha = 90.50$ (4), $\beta = 105.44$ (4), $\gamma = 111.02$ (4)°, $Z = 2$, $D_c = 1.29$ g cm^{-3}, μ(Cu $K\bar{\alpha}$) = 13.0 cm^{-1}. The crystal structure determination has proved that thiobenzophenone (I) and diphenyl-*N-p*-tolylketenimine (II) react to give a substituted 4*H*-3,1-benzothiazine.

$$Ph_2C=S$$

(I)

$$Ph_2C=C=N-\langle\bigcirc\rangle-CH_3$$
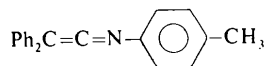
(II)

Introduction

The reaction between *N*-arylketenimines and thiobenzophenones leads to 1:1 adducts which appear from spectroscopic data (IR, NMR and MS) to have the structure of 4*H*-3,1-benzothiazine derivatives. While the most common reactivity mode of ketenimine cycloaddition is that occurring on the cumulative C=C or C=N double bond (Krow, 1971), the formation of

(III)

the 3,1-benzothiazine must involve the cumulene system *and* the C=C bond of the *N*-aryl ring. In order to provide an unequivocal structure assignment of the observed products, we have carried out the crystal structure determination of the title compound (III) derived from the reaction of thiobenzophenone (I) and diphenyl-*N-p*-tolylketenimine (II). In addition it may be stressed that this is the first structure determination of a 4*H*-3,1-benzothiazine system.

Intensities were collected on an automated Philips PW 1100 diffractometer with monochromated Cu $K\alpha$ radiation and the $\omega/2\theta$ scan technique. Of the 2012 reflexions collected ($\theta \leq 45°$), 178 having $I_o \leq 2\sigma(I_o)$ were considered unobserved. Intensities were not corrected for absorption [μ(Cu $K\bar{\alpha}$) = 13.0 cm^{-1}; crystal dimensions 0.11 × 0.19 × 0.30 mm]. Lorentz and polarization corrections were applied as usual. Scattering factors for S, C and N atoms were taken
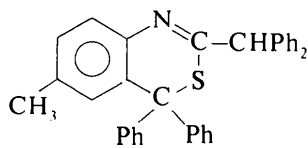
Table 1. *Positional* $(\times 10^4)$ *and thermal* $(\times 10^3)$ *parameters for non-hydrogen atoms, with e.s.d.'s in parentheses*

The form of the anisotropic temperature factor is:
$$\exp|-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})|.$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	2454 (1)	1860 (1)	6933 (1)	42 (1)	35 (1)	46 (1)	17 (1)	21 (1)	7 (1)
N	4559 (4)	3405 (2)	6310 (3)	42 (2)	31 (2)	43 (2)	14 (2)	14 (2)	7 (1)
C(1)	8963 (4)	1736 (3)	8238 (4)	43 (2)	57 (3)	61 (3)	27 (2)	10 (2)	14 (2)
C(2)	7783 (4)	2151 (3)	7660 (4)	35 (3)	41 (3)	31 (2)	13 (2)	6 (2)	1 (2)
C(3)	8166 (4)	3129 (3)	7533 (4)	32 (2)	41 (3)	41 (2)	9 (2)	10 (2)	2 (2)
C(4)	7080 (4)	3509 (2)	7040 (4)	39 (3)	33 (2)	43 (2)	10 (2)	12 (2)	3 (2)
C(5)	5566 (4)	2921 (2)	6677 (3)	36 (3)	30 (2)	30 (2)	14 (2)	9 (2)	4 (2)
C(6)	5154 (4)	1930 (2)	6742 (3)	35 (2)	25 (2)	23 (2)	10 (2)	7 (2)	2 (2)
C(7)	6264 (4)	1559 (2)	7227 (3)	39 (3)	34 (2)	31 (2)	18 (2)	10 (2)	6 (2)
C(8)	3487 (3)	1278 (2)	6153 (3)	34 (2)	27 (2)	35 (2)	13 (2)	11 (2)	1 (2)
C(9)	2954 (4)	1187 (2)	4450 (4)	39 (2)	26 (2)	29 (2)	12 (2)	5 (2)	0 (2)
C(10)	1472 (4)	991 (3)	3674 (4)	41 (3)	66 (3)	42 (3)	21 (2)	1 (2)	−4 (2)
C(11)	1016 (5)	896 (3)	2133 (5)	56 (3)	72 (3)	52 (3)	34 (2)	−11 (3)	−9 (2)
C(12)	2024 (5)	988 (3)	1339 (4)	73 (3)	59 (3)	35 (2)	27 (2)	3 (3)	- 1 (2)
C(13)	3483 (5)	1156 (3)	2101 (4)	58 (3)	56 (3)	40 (3)	14 (2)	14 (2)	0 (2)
C(14)	3950 (4)	1258 (2)	3639 (4)	46 (2)	49 (2)	32 (3)	15 (2)	11 (2)	1 (2)
C(15)	3133 (3)	299 (2)	6751 (4)	29 (2)	27 (2)	44 (3)	10 (2)	13 (2)	3 (2)
C(16)	3418 (4)	248 (2)	8269 (4)	48 (2)	40 (3)	42 (3)	15 (2)	16 (2)	13 (2)
C(17)	3118 (4)	−628 (3)	8833 (4)	56 (3)	54 (3)	58 (3)	23 (2)	23 (2)	23 (3)
C(18)	2515 (5)	−1472 (3)	7884 (6)	59 (3)	41 (3)	87 (4)	19 (2)	31 (3)	27 (3)
C(19)	2236 (4)	−1434 (3)	6380 (5)	61 (3)	33 (3)	79 (4)	11 (2)	22 (2)	4 (2)
C(20)	2539 (4)	−556 (3)	5808 (4)	47 (2)	36 (3)	53 (2)	13 (2)	15 (2)	7 (2)
C(21)	3245 (4)	3026 (2)	6462 (3)	45 (3)	31 (2)	30 (2)	18 (2)	9 (2)	4 (2)
C(22)	2226 (4)	3589 (2)	6277 (3)	43 (2)	34 (2)	38 (2)	21 (2)	15 (2)	8 (2)
C(23)	1540 (4)	3692 (2)	4664 (4)	42 (2)	28 (2)	39 (2)	14 (2)	7 (2)	3 (2)
C(24)	312 (4)	3967 (2)	4332 (4)	45 (2)	41 (2)	48 (3)	21 (2)	4 (2)	2 (2)
C(25)	−352 (4)	4087 (3)	2900 (5)	54 (3)	49 (3)	56 (3)	21 (2)	−8 (3)	2 (2)
C(26)	194 (5)	3932 (3)	1756 (5)	74 (3)	46 (3)	47 (3)	17 (2)	−5 (2)	5 (2)
C(27)	1397 (5)	3654 (3)	2069 (5)	81 (3)	69 (3)	44 (3)	30 (3)	18 (2)	10 (2)
C(28)	2079 (4)	3538 (3)	3514 (4)	62 (3)	61 (3)	40 (3)	29 (2)	16 (2)	10 (2)
C(29)	3019 (4)	4559 (2)	7257 (4)	41 (2)	42 (2)	37 (3)	26 (2)	6 (2)	4 (2)
C(30)	3871 (4)	5384 (3)	6779 (4)	60 (3)	42 (3)	57 (3)	16 (2)	23 (2)	6 (2)
C(31)	4555 (5)	6244 (3)	7710 (6)	63 (3)	43 (3)	84 (4)	13 (2)	16 (3)	−7 (3)
C(32)	4394 (5)	6283 (3)	9120 (6)	61 (3)	66 (3)	65 (3)	30 (3)	−1 (2)	−22 (3)
C(33)	3562 (5)	5463 (4)	9607 (4)	75 (3)	84 (4)	41 (3)	42 (3)	4 (2)	−6 (3)
C(34)	2878 (4)	4606 (3)	8680 (4)	57 (3)	59 (3)	38 (3)	31 (2)	11 (2)	5 (2)

from Cromer & Waber (1965) and for H from Stewart, Davidson & Simpson (1965); f' and f'' values for S were taken from Cromer (1965).

The structure was solved by straightforward application of direct methods using the *MULTAN* program (Germain, Main & Woolfson, 1971). The following computations were mainly carried out by the XRAY 72 system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Although all the H atoms were located from the difference map made at the end of the isotropic refinement, calculated H positions (C—H bond length = 1·08 Å) were used in the subsequent refinement. A few cycles of anisotropic block-diagonal-matrix least-squares refinement of C, N and S atoms reduced R $(= \Sigma|\Delta|/\Sigma|F_o|)$ to 0·038 and R_w $|=(\Sigma w|\Delta^2|/\Sigma w|F_o|^2)^{1/2}|$ to 0·043. In the last cycle, weights were calculated as $w = 1/(1·14 + 0·0035|F_o| + 0·0003|F_o|^2)$ and the largest shift/error was 0·28. The

final values of the positional and vibrational parameters are listed in Table 1.*

Discussion

The structure consists of discrete molecular units with no significantly short intermolecular distances. A drawing of the molecule is shown in Fig. 1 and the bond distances and angles are reported in Tables 2 and 3.

The geometry of the benzothiazine system can be described with reference to the least-squares plane through the C(2)—C(7) phenyl ring (Table 4). The phenyl ring is only slightly distorted from planarity and

C(8) and N lie approximately on this plane, while C(21) and S are out of plane by −0·62 and −1·05 Å respectively. Consequently the conformation of the thiazine ring can be referred to as a deformed boat with C(8) and N pointing up and the pairs of atoms S—C(21) and C(5)—C(6) pointing down.

A direct comparison of bond lengths and angles with those of other 3,1-benzothiazines cannot be made, since this appears to be the first crystal structure determination of this class of compounds. A comparison of the C—S—C group geometry with that observed in other thiazine derivatives is reported in Table 5, which shows that the S—C bond length is completely determined by the hybridization of the bonded carbon. The value found in the present case for the S—C(21) bond

length (1·750 Å) matches well the mean value of 1·76 Å for the S—C(sp^2) bond, and that found for the S—C(8) bond length (1·838 Å) is not far from the mean value of 1·82 Å for the S—C(sp^3) bond. Moreover, the C(8)—S—C(21) bond angle (98·9°) is close to the mean value of the C—S—C angle (100·8 ∓ 2·0°) for the compounds listed in Table 5.

The N—C(5) bond length of 1·411 Å can be compared with the corresponding value (1·411 Å)

Table 2. Bond lengths (Å) with e.s.d.'s in parentheses

|			
S—C(8)	1·838 (4)	C(15)—C(20)	1·385 (5)
S—C(21)	1·750 (4)	C(16)—C(17)	1·376 (6)
N—C(5)	1·411 (6)	C(17)—C(18)	1·376 (6)
N—C(21)	1·274 (5)	C(18)—C(19)	1·366 (7)
C(1)—C(2)	1·499 (6)	C(19)—C(20)	1·384 (6)
C(2)—C(3)	1·386 (6)	C(21)—C(22)	1·513 (6)
C(2)—C(7)	1·394 (5)	C(22)—C(23)	1·517 (5)
C(3)—C(4)	1·373 (6)	C(22)—C(29)	1·527 (5)
C(4)—C(5)	1·390 (5)	C(23)—C(24)	1·386 (6)
C(5)—C(6)	1·394 (5)	C(23)—C(28)	1·375 (7)
C(6)—C(7)	1·383 (6)	C(24)—C(25)	1·372 (6)
C(6)—C(8)	1·534 (4)	C(25)—C(26)	1·375 (8)
C(8)—C(9)	1·527 (5)	C(26)—C(27)	1·367 (8)
C(8)—C(15)	1·526 (5)	C(27)—C(28)	1·385 (6)
C(9)—C(10)	1·382 (5)	C(29)—C(30)	1·379 (5)
C(9)—C(14)	1·378 (6)	C(29)—C(34)	1·379 (6)
C(10)—C(11)	1·381 (6)	C(30)—C(31)	1·382 (6)
C(11)—C(12)	1·371 (8)	C(31)—C(32)	1·374 (8)
C(12)—C(13)	1·366 (7)	C(32)—C(33)	1·371 (7)
C(13)—C(14)	1·378 (5)	C(33)—C(34)	1·377 (6)
C(15)—C(16)	1·381 (5)		
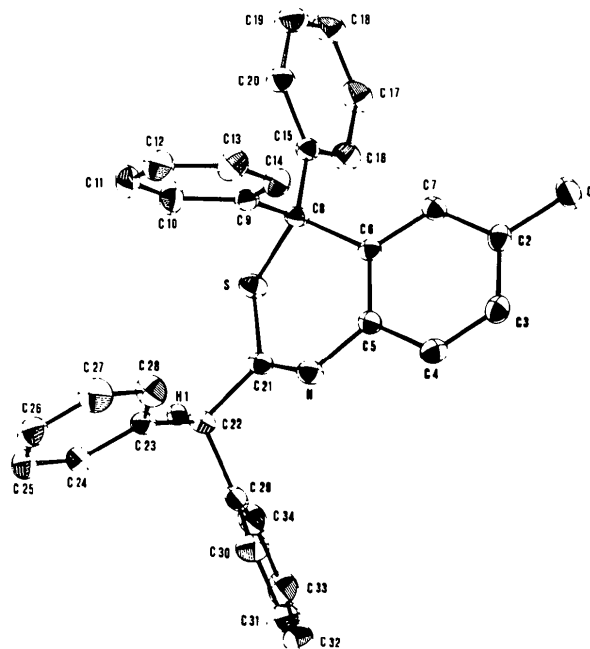
Fig. 1. An *ORTEP* view of the molecule, showing the thermal ellipsoids at 40% probability.

Table 3. Bond angles (°) with e.s.d.'s in parentheses

C(8)—S—C(21)	98·9 (2)	C(8)—C(9)—C(10)	122·0 (4)	C(21)—C(22)—C(29)	110·9 (3)
C(5)—N—C(21)	120·3 (3)	C(8)—C(9)—C(14)	119·9 (3)	C(23)—C(22)—C(29)	112·5 (3)
C(1)—C(2)—C(3)	121·3 (3)	C(10)—C(9)—C(14)	118·0 (3)	C(22)—C(23)—C(24)	118·2 (4)
C(1)—C(2)—C(7)	120·7 (3)	C(9)—C(10)—C(11)	120·8 (4)	C(22)—C(23)—C(28)	123·6 (4)
C(3)—C(2)—C(7)	118·1 (4)	C(10)—C(11)—C(12)	120·6 (4)	C(24)—C(23)—C(28)	118·2 (4)
C(2)—C(3)—C(4)	121·0 (3)	C(11)—C(12)—C(13)	118·7 (4)	C(23)—C(24)—C(25)	121·4 (4)
C(3)—C(4)—C(5)	120·6 (3)	C(12)—C(13)—C(14)	121·0 (5)	C(24)—C(25)—C(26)	120·1 (5)
N—C(5)—C(4)	115·4 (3)	C(9)—C(14)—C(13)	120·8 (4)	C(25)—C(26)—C(27)	119·0 (4)
N—C(5)—C(6)	125·2 (3)	C(8)—C(15)—C(16)	120·0 (3)	C(26)—C(27)—C(28)	121·1 (5)
C(4)—C(5)—C(6)	119·4 (4)	C(8)—C(15)—C(20)	121·7 (3)	C(23)—C(28)—C(27)	120·2 (5)
C(5)—C(6)—C(7)	119·1 (3)	C(16)—C(15)—C(20)	118·3 (3)	C(22)—C(29)—C(30)	122·7 (4)
C(5)—C(6)—C(8)	118·6 (3)	C(15)—C(16)—C(17)	121·0 (4)	C(22)—C(29)—C(34)	118·4 (3)
C(7)—C(6)—C(8)	122·1 (3)	C(16)—C(17)—C(18)	120·3 (4)	C(30)—C(29)—C(34)	118·9 (3)
C(2)—C(7)—C(6)	121·7 (3)	C(17)—C(18)—C(19)	119·5 (4)	C(29)—C(30)—C(31)	120·2 (4)
S—C(8)—C(6)	106·5 (2)	C(18)—C(19)—C(20)	120·5 (4)	C(30)—C(31)—C(32)	120·3 (4)
S—C(8)—C(9)	109·5 (3)	C(15)—C(20)—C(19)	120·5 (4)	C(31)—C(32)—C(33)	119·7 (4)
S—C(8)—C(15)	104·5 (3)	S—C(21)—N	125·3 (4)	C(32)—C(33)—C(34)	120·0 (4)
C(6)—C(8)—C(9)	110·8 (3)	S—C(21)—C(22)	113·7 (3)	C(29)—C(34)—C(33)	120·8 (4)
C(6)—C(8)—C(15)	112·6 (3)	N—C(21)—C(22)	121·0 (3)		
C(9)—C(8)—C(15)	112·5 (3)	C(21)—C(22)—C(23)	113·6 (3)		

Table 4. *Displacements* (Å) *from the least-squares plane through the* C(2)–C(7) *phenyl ring*

C(2)	−0·018	C(1)	−0·067
C(3)	0·005	N	−0·125
C(4)	0·014	C(21)	−0·616
C(5)	−0·020	S	−1·049
C(6)	0·007	C(8)	0·146
C(7)	0·012		

$\chi^2 = 67\cdot5$ (five degrees of freedom).

determined as the average of ten different structures of phenothiazine and its derivatives (McDowell, 1976). The N—C(21) bond length of 1·274 Å corresponds fairly well to a pure double-bond distance.

The pattern of distances and angles of the remaining part of the molecule does not show unusual features. Torsion angles (T) defining the positions of the phenyl and diphenylmethyl groups are as follows: C(6)—C(8)—C(15)—C(16) = $T1$ = 59·7, C(6)—C(8)—C(9)—C(10) = $T2$ = −153·6, N—C(21)—C(22)—H(22) = $T3$ = −159·6, C(21)—C(22)—C(23)—C(24) = $T4$ = 163·6, C(21)—C(22)—C(29)—C(30) = $T5$ = 88·8°. To check if these angles correspond to the conformational energy minimum of the free molecule, simple calculations of non-bonded intramolecular potential energy (U) have been carried out using semi-empirical atom-pair potential curves as given by Giglio (1969). The energy minimum is achieved for the following values of torsion angles: $T1$ = 59·6, $T2$ = −155·6, $T3$ = −139·8, $T4$ = 155·5, $T5$ = 112·1°. The difference between experimental and calculated values is small for $T1$ and $T2$ but remarkable for $T3$, $T4$ and $T5$, this being in agreement with the fact that the $U(T1,T2)$ map shows a sharp minimum at (59·6, −155·6°), whereas the $U(T1,T2,T3)$ map shows an elongated three-dimensional minimum connecting the experimental and calculated points. This is consistent with current views on molecular conformations, which

are in fact affected by the crystal field only when potential-energy minima are not sharp enough (Kitaigorodsky, 1970).

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Table 5. *Comparison of* S—C *bond lengths* (Å) *and* C—S—C *bond angles* (°) *in thiazine derivatives*

Compound	S·C(sp^2)	S—C(sp^3)	C—S·C	Reference
3-Methyl-4-oxo-1,3-thiazine-2-thione	1·744	1·830	102·3	1
7,8-Dihydro-8-hydroxy-2-methyl-3H,6H-[1,3]thiazino[3,2-b][1,2,4]triazin-3-one	1·77	1·82	102·6	2
Dimethyl 4-formyl-2H,3H-1,4-benzothiazine-2,3-dicarboxylate	1·76	1·82	102	3
N-Methylphenothiazine	1·764	—	97·4	4
Phenothiazine (monoclinic)	1·770	—	99·6	5
Phenothiazine (orthorhombic)	1·762	—	100·9	6
Mean values	1·76 (1)	1·82 (1)	100·8 (20)	
Present work	1·750	1·838	98·9	

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