Erscheint 9mal jährlich – Paraît 9 fois par an

1. The Crystal Structure of 5,5',7,7'-tetramethyl-3,3',9-triethyl thiacarbocyanine perchlorate

by **Helen Stoeckli-Evans**
Institut de chimie de l'Université de Neuchâtel, Switzerland

(29. X. 73)

Summary. The crystal structure of the title compound has been determined by X-ray crystallographic analysis from diffractometer data. The compound is found to exist in the crystalline state as the mono-*cis* isomer (a). The conjugated chain is in a folded configuration and the two sulfur atoms are on opposing sides. It is the first time such a mono-*cis* isomer has been analysed by X-ray crystallography.

Introduction. – Carbocyanine and thiacarbocyanine dyes are used extensively for spectral sensitization. The sensitivity of a photographic material is extended outside its intrinsic absorption region by coating the material with a solution of the dye. Such dyes exhibit strong absorption and a tendency to form aggregates with close intermolecular spacing and strong coupling. Studies of the crystal structure of such dyes have been carried out in the hope that they may lead to an understanding of the formation of such aggregates.

The crystal structure analysis of the title compound was originally undertaken in order to obtain accurate bond lengths and angles for a model of the compound used to form monolayer aggregates. Here a solution of the dye (where the ethyl groups attached to N(3) and N(3') have been replaced by long stearyl chains II, Fig. 1) is placed on the surface of a substrate such as water and slowly overcompressed [1]. Small crystals are formed which exhibit strong J aggregate absorption bands in the visible spectrum.

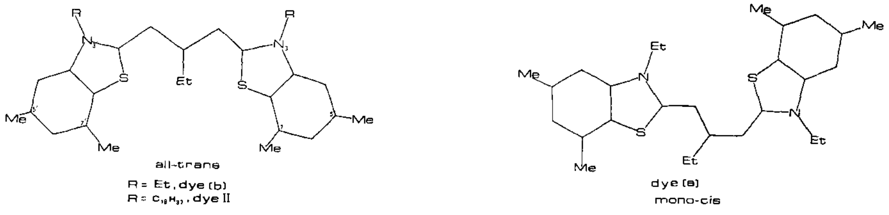

Fig. 1. Cis *and* trans *forms of thiacarbocyanines*

At the start of this work the only structural information in the literature for a similar compound was from *Wheathley*'s [2] [3] two-dimensional analyses of 5,5'-dimethyl-3,3'-diethyl-thiacarbocyanine and its 1:1 ethanol solvate. In the meantime several carbocyanine dyes where the sulfur atoms are replaced by substituted nitrogen atoms have been studied [4]–[6]. All these compounds are unsubstituted in the 9 *meso* position and were found to exist in the all-*trans* configuration (b), Figure 1. However, a recent report [11] of the structure analysis of the 1:1 acetic acid solvate of 3,3′,9-triethyl-5,5′-dichlorothiacarbocyanine bromide indicates that this molecule also exists in the crystalline state as the all-*trans* isomer.

From spectroscopic and other data *West & al.* [7] have concluded that for 9-alkyl *meso* substituted thiacarbocyanine dyes, the all-*trans* isomer is probably the more stable. They also concluded that the mono-*cis* form (a) is likely to exist in solution in equilibrium with the all-*trans* form. In form (a) there is a 180° rotation of one heterocyclic nucleus with respect to the other. It is further stated that for the all-*trans* structure, the close approach of the two sulfur atoms to the *meso* alkyl group makes it doubtful that the chromophoric chain is completely coplanar, especially when the alkyl group is ethyl (as in the compound under study). Moreover, the overcrowding in the all-*trans* structure (b) may be not much less than in the mono-*cis* structure (a). They concluded that structure (a) for the 9-alkyl dyes is of comparable stability to structure (b) and that both might exist in dynamic equilibrium.

The visible absorption spectra of an alcoholic solution of such a 9-ethyl thiacarbocyanine dye [7] was resolved at low temperature into two component bands. These were attributed to the two stereoisomers, one all-*trans*, the other mono-*cis*. X-ray analysis shows that the title compound, a 9-ethyl substituted thiacarbocyanine dye, exists in the crystalline state as the mono-*cis* isomer.

Crystallographic Data. – Dark red crystals of the title compound, $C_{27}H_{33}S_2N_2^+ClO_4^-$ (M.W. 549.2), were grown by slow cooling from a chloroform solution. They were large flat plates, elongated along (100). Unit cell parameters were initially obtained from *Weissenberg* (h0l) and precession (hk0, 0kl) photographs ($\lambda CuK_\alpha = 1.5418$ Å) and refined by least-squares analysis of 2Θ-measurements of 16 high-angle reflections:

$$a = 9.540, \quad b = 10.350, \quad c = 15.078\,\text{Å}$$

$$\alpha = 77.14°, \quad \beta = 99.02°, \quad \gamma = 105.92°, \quad V = 1388.7\,\text{Å}^3$$

$$D_m = 1.32, \quad Z = 2, \quad D_x = 1.34, \text{ Space group } P\bar{1}.$$

The centrosymmetric space group was indicated by the N(Z) test and confirmed by the structure determination and refinement.

Intensity Measurements. – The intensity of 4867 independent reflections ($\theta \leqslant 25°$) were measured using a *Hilger & Watts* Y 290 diffractometer with graphite-monochromatized MoK_α radiation. The $\omega/2\theta$ scanning technique was used with steps of 0.01° per second, 80 steps per reflection, and a background count of 40 seconds on either side of the peak. σ (F_0) values were estimated from counting statistics. The data were corrected for *Lorentz*-polarization effects but not for absorption ($\mu_{MoK_\alpha} = 3.23$ cm^{-1}) to give relative F_0 values, and some 3272 reflections had $F_0 \geqslant 2\,\sigma\,(F_0)$. The intensity fall-off of a standard reflection was less than 4% during the data collection of ≃ 240 hours.

Structure Analysis and Refinement. – The relative F_0-values were converted to E-values. The structure was then solved by direct methods using the program SAP [8] (written by *S. R. Hall & F. R. Ahmed* of *N. R. C.*, Canada, and adapted for an IBM 1130 computer by *B. L. Vickery* of *A. R. C.*, London).

Of the 634 reflections with $E \geqslant 1.5$, 614 were signed by the symbolic addition procedure. From the corresponding E-map 28 of the 36 non-hydrogen atoms were located (R = 37%). A ($F_0 - F_c$)-synthesis showed the remaining 8 atoms. Two rounds of isotropic full-matrix least-squares (FMLS) were followed by two rounds of anisotropic block-diagonal least-squares (BDLS) ($R = 0.092$). A ($F_o - F_c$)-synthesis at this stage revealed all the hydrogen atoms, except those of the 9-ethyl group. The hydrogens of C(22) were inserted at calculated positions and those of C(23) were neglected.

Refinement continued in two stages: first, the hydrogen atoms were refined by isotropic BDLS for 4 rounds, followed by 4 rounds of anisotropic BDLS refinement of the non-hydrogen atoms. Unit weights had been used initially but now w was set equal to $1/(\sigma(F_o))^2$, which gave a uniform distribution of the quantity $\langle w(F_o - F_c)^2 \rangle$ in the final stages. Refinement was concluded when the majority of parameter shifts were less than 1 e.s.d. ($R = 0.065$, $R_w = 0.068$). Final positional and thermal parameters are given in Tables 1 and 2 for non-hydrogen atoms and in Table 3 for hydrogen atoms.

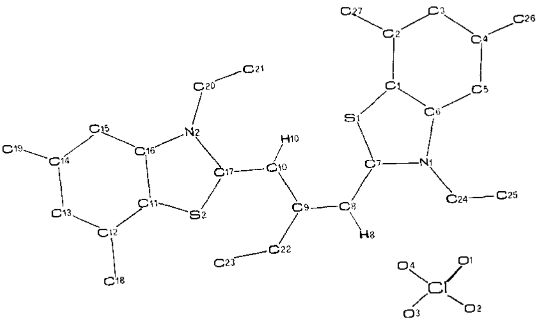

Fig. 2. *Atomic labelling system*

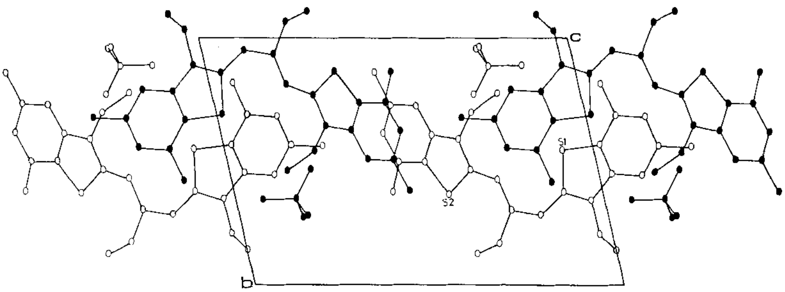

Fig. 3. *Projection of the structure onto the (100) plane*; the molecule marked ○ is above the one to its left marked ●, (see Fig. 4)

Description of the structure. – The atomic labelling system used is shown in Figure 2. The interatomic distances and angles (tabulated in Tables 4 and 5 respectively) for the cation agree well with those found in all-*trans* carboncyanines [4]–[6]. Especially noteworthy are the large angles at C(8) (129.8°) and C(10) (130.7°). The angles at C(2), C(5), C(12) and C(15) average 117.1°, the remaining angles 121.3°. Similar distortions have been noted in other compounds in which benzo rings are fused to 4- and 5-membered rings. The angles between various least-squares planes show that the cation is not planar:

25.68° between heterocycle 1 (N(1), S(1), C(1)–C(7)) and heterocycle 2 (N(2), S(2), C(11)–C(17)), 1.41° between benzo-ring (C(1)–C(6)) and hetero-ring (N(1), S(1), C(1), C(6), C(7)), and

0.86° between benzo-ring (C(11)–C(16)) and hetero-ring (N(2), S(2), C(11), C(16), C(17)).

Moreover, C(10) is considerably out of the plane through the other atoms of the methene bridge. The twist of 25.68° between the two heterocycles is clearly due to

Table 1. *Final positional parameters* (estimated standard deviation × 10^4 in parentheses)

Atom	x/a	y/b	z/c
S(2)	0.6337(2)	-0.2173(1)	-0.3728(1)
N(2)	0.5084(4)	-0.4692(4)	-0.3238(2)
C(11)	0.6827(5)	-0.3369(5)	-0.4184(3)
C(12)	0.7872(5)	-0.3120(5)	-0.4803(3)
C(13)	0.8078(5)	-0.4242(6)	-0.5064(3)
C(14)	0.7338(5)	-0.5571(5)	-0.4714(3)
C(15)	0.6311(5)	-0.5802(5)	-0.4091(3)
C(16)	0.6075(5)	-0.4680(5)	-0.3837(3)
C(17)	0.5083(5)	-0.3458(4)	-0.3085(3)
S(1)	0.3061(1)	-0.4737(1)	-0.0612(1)
N(1)	0.1984(4)	-0.2964(3)	-0.0213(2)
C(1)	0.2174(4)	-0.5175(4)	0.0377(3)
C(2)	0.1959(5)	-0.6417(4)	0.0982(3)
C(3)	0.1226(5)	-0.6518(5)	0.1733(3)
C(4)	0.0738(5)	-0.5446(5)	0.1875(3)
C(5)	0.0951(5)	-0.4204(5)	0.1255(3)
C(6)	0.1673(5)	-0.4096(4)	0.0499(3)
C(7)	0.2747(5)	-0.3109(4)	-0.0854(3)
C(8)	0.3241(6)	-0.2072(5)	-0.1580(4)
C(9)	0.4033(6)	-0.2083(5)	-0.2290(4)
C(10)	0.4244(5)	-0.3272(5)	-0.2471(3)
C(18)	0.8754(7)	-0.1678(6)	-0.5106(4)
C(19)	0.7666(6)	-0.6784(6)	-0.4965(4)
C(20)	0.4132(5)	-0.5996(5)	-0.2799(3)
C(21)	0.4871(6)	-0.6609(5)	-0.1900(4)
C(22)	0.4830(10)	-0.0540(8)	-0.2793(5)
C(23)	0.3936(11)	-0.0322(11)	-0.3497(8)
C(24)	0.1599(5)	-0.1673(5)	-0.0222(3)
C(25)	0.2827(7)	-0.0717(6)	0.0224(5)
C(26)	-0.0041(6)	-0.5601(6)	0.2716(3)
C(27)	0.2475(6)	-0.7581(5)	0.0799(4)
Cl	0.0371(2)	-0.8782(1)	-0.2262(1)
O(1)	0.1610(8)	-0.9230(7)	-0.2332(5)
O(2)	-0.0691(10)	-0.9704(9)	-0.2561(6)
O(3)	0.0486(7)	-0.7553(4)	-0.2832(4)
O(4)	0.0314(10)	-0.8807(8)	-0.1377(4)

Table 2. *Anisotropic vibrational parameters,* expressed in the form $\exp(-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl))$ (estimated standard deviations $\times 10^4$ in parentheses)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(2)	0.0648(8)	0.0576(7)	0.0578(7)	0.0158(6)	0.0213(6)	0.0048(6)
N(2)	0.0475(27)	0.0592(26)	0.0429(22)	0.0136(18)	0.0116(17)	-0.0044(17)
C(11)	0.0503(29)	0.0656(26)	0.0409(25)	0.0159(22)	0.0101(22)	0.0018(21)
C(12)	0.0521(30)	0.0833(31)	0.0395(25)	0.0148(24)	0.0103(22)	0.0056(22)
C(13)	0.0474(31)	0.0998(37)	0.0425(25)	0.0193(27)	0.0042(23)	-0.0125(24)
C(14)	0.0563(31)	0.0886(41)	0.0408(27)	0.0205(28)	-0.0023(23)	-0.0219(26)
C(15)	0.0430(33)	0.0719(38)	0.0449(26)	0.0099(28)	0.0047(23)	-0.0184(25)
C(16)	0.0423(28)	0.0664(33)	0.0353(26)	0.0130(24)	0.0043(22)	-0.0062(23)
C(17)	0.0505(28)	0.0502(31)	0.0459(23)	0.0141(23)	0.0106(20)	0.0024(21)
S(1)	0.0579(7)	0.0456(6)	0.0471(6)	0.0234(5)	0.0121(5)	-0.0065(5)
N(1)	0.0521(24)	0.0459(21)	0.0445(20)	0.0230(17)	0.0049(17)	-0.0113(16)
C(1)	0.0421(27)	0.0437(25)	0.0388(23)	0.0141(21)	0.0020(19)	-0.0127(19)
C(2)	0.0495(29)	0.0494(27)	0.0440(25)	0.0156(22)	0.0020(21)	-0.0107(20)
C(3)	0.0515(30)	0.0530(28)	0.0452(26)	0.0125(23)	0.0042(22)	-0.0064(21)
C(4)	0.0424(28)	0.0665(31)	0.0421(24)	0.0133(23)	0.0004(21)	-0.0147(22)
C(5)	0.0448(28)	0.0570(29)	0.0433(24)	0.0192(22)	0.0017(21)	-0.0157(21)
C(6)	0.0419(27)	0.0468(26)	0.0387(23)	0.0151(21)	-0.0015(20)	-0.0121(19)
C(7)	0.0537(30)	0.0422(25)	0.0503(26)	0.0188(22)	0.0048(22)	-0.0112(20)
C(8)	0.0903(40)	0.0515(30)	0.0619(31)	0.0354(28)	0.0304(29)	0.0054(24)
C(9)	0.0957(43)	0;0640(34)	0.0641(32)	0.0432(30)	0.0302(31)	0.0139(26)
C(10)	0.0623(32)	0.0559(30)	0.0477(26)	0.0216(25)	0.0189(24)	0.0039(22)
C(18)	0.1043(50)	0.0972(46)	0.0822(41)	0.0182(38)	0.0535(39)	0.0184(35)
C(19)	0.0692(39)	0.1127(47)	0.0766(38)	0.0272(34)	0.0108(31)	-0.0446(34)
C(20)	0.0418(28)	0.0577(28)	0.0490(26)	0.0057(22)	0.0111(22)	-0.0066(22)
C(21)	0.0705(37)	0.0689(34)	0.0529(30)	0.0124(28)	0.0078(27)	-0.0024(25)
C(22)	0.2299(93)	0.1524(68)	0.0822(46)	0.1338(67)	0.0759(56)	0.0492(45)
C(23)	0.1538(85)	0.2199(112)	0.1646(89)	0.0516(77)	0.0163(70)	-0.0478(79)
C(24)	0.0677(34)	0.0522(28)	0.0593(29)	0.0329(25)	0.0075(25)	-0.0117(23)
C(25)	0.0977(49)	0.0631(37)	0.1193(51)	0.0207(33)	0.0022(40)	-0.0472(36)
C(26)	0.0686(36)	0.0970(41)	0.0450(28)	0.0267(30)	0.0161(26)	-0.0093(27)
C(27)	0.0634(34)	0.0484(28)	0.0669(31)	0.0211(24)	0.0098(26)	-0.0077(23)
Cl	0.0946(11)	0.0619(8)	0.0637(8)	0.0216(7)	0.0307(7)	0.0033(6)
O(1)	0.2314(68)	0.2222(87)	0.1515(50)	0.1536(192)	0.0653(49)	0.0001(65)
O(2)	0.2781(97)	0.2392(87)	0.2134(77)	-0.1640(79)	-0.0106(69)	-0.0014(65)
O(3)	0.2014(54)	0.0730(30)	0.1370(41)	0.0424(32)	0.0629(39)	0.0263(27)
O(4)	0.3724(106)	0.3046(87)	0.0680(32)	0.2384(82)	0.0469(47)	-0.0092(42)

steric hindrance between S(1) and H(10). The distance between these atoms (2.47 Å) is still smaller than the sum (3.05 Å) of the standard *van der Waals* radii [9].

The perchlorate anion appears to be slightly disordered, the average Cl-O distance being short (1.348 Å) compared to the expected distance of 1.4 Å [10] and the thermal

Table 3. *Final positional and vibrational parameters for the hydrogen atoms*

	x/a	y/b	z/c	$\overline{U}^2$
H(3)	0.1136	-0.7366	0.2235	0.0361
H(5)	0.0498	-0.3487	0.1286	0.0292
H(8)	0.2991	-0.1240	-0.1635	0.0442
H(10)	0.3634	-0.4096	-0.2219	0.0120
H(14)	0.8879	-0.4077	-0.5413	0.0586
H(16)	0.5665	-0.6699	-0.3901	0.0248
H(181)	0.9285	-0.1644	-0.5470	0.0911
H(182)	0.9238	-0.1197	-0.4522	0.1994
H(183)	0.8309	-0.1307	-0.5379	0.0764
H(191)	0.8277	-0.7244	-0.4470	0.0839
H(192)	0.8213	-0.6530	-0.5441	0.1035
H(193)	0.6631	-0.7578	-0.5139	0.0871
H(201)	0.3862	-0.6630	-0.3278	0.0163
H(202)	0.3173	-0.5844	-0.2768	0.0104
H(211)	0.5816	-0.6806	-0.1926	0.0603
H(212)	0.4180	-0.7453	-0.1677	0.0572
H(213)	0.5308	-0.5944	-0.1480	0.0341
H(221)	0.6002	-0.0048	-0.2725	0.0536
H(222)	0.5190	0.0384	-0.2700	0.0194
H(241)	0.1271	-0.1304	-0.0820	0.0290
H(242	0.0593	-0.1954	0.0046	0.0273
H(251)	0.3075	-0.1088	0.0946	0.0586
H(252)	0.3921	-0.0537	0.0026	0.0920
H(253)	0.2659	0.0033	0.0189	0.0725
H(261)	0.0783	-0.5113	0.3236	0.1024
H(262)	-0.0325	-0.6388	0.2952	0.1220
H(263)	-0.0939	-0.5307	0.2553	0.0813
H(271)	0.2289	-0.8319	0.1235	0.0867
H(272)	0.1909	-0.7876	0.0186	0.1707
H(273)	0.3451	-0.7346	0.0887	0.0388

parameters higher than expected. The 9-ethyl group also has larger thermal parameters than the other two, and consequently, the apparent bond lengths are affected (Table 4).

Figures 3 and 4 show the structure projected on (100) and (010) respectively. The least-squares plane through the molecule (the two heterocycles plus the methene bridge atoms) is at an angle of 29.90° to (100). The molecules pack like a slipped deck of cards with each card related to the ones before and after centers of inversion. There is a strong inter-layer overlap involving heterocycles 2 and 2′, with a plane to plane distance of 3.54 Å, and an equally strong inter-layer overlap involving heterocycles 1 and 1″ with plane to plane distance 3.47 Å, Figure 4.

Methyl groups 5 and 5′ (C(19) and C(26) in Figure 2) are separated by a distance of 15.09 Å. If one adds the *van der Waals* radii of 2.0 Å for the methyl groups [9] the molecule has an overall length of 19.09 Å. Adjacent molecules are sedarated by 3.66 Å, hence the molecules occupy an area of 69.9 Å^2, compared with an area of 75 Å^2 for the all-*trans* molecules.

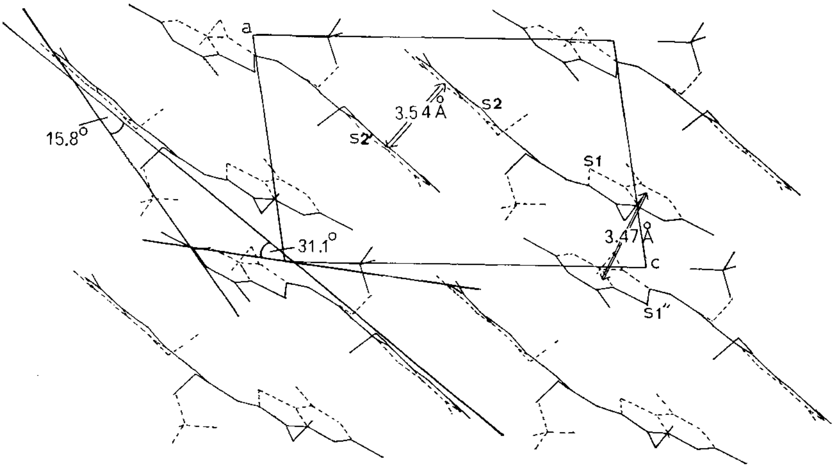

Fig. 4. *Projection of the structure onto the (010) plane.*
Also shown are some inter-planar distances and stacking angles
– – – – behind the plane of the paper
———— in front of the plane of the paper

Table 4. *Bond lengths* (Å) *with estimated standard deviations* $\times$ *10*^{3} *in parentheses*

S(1) - C(1)	1.741 (5)	S(2) - C(11)	1.737 (6)
S(1) - C(7)	1.741 (5)	S(2) - C(17)	1.749 (4)
N(1) - C(6)	1.401 (5)	N(2) - C(16)	1.402 (7)
N(1) - C(7)	1.352 (7)	N(2) - C(17)	1.348 (7)
N(1) - C(24)	1.476 (7)	N(2) - C(20)	1.483 (5)
C(24)- C(25)	1.488 (8)	C(20)- C(21)	1.516 (7)
C(1) - C(2)	1.384 (6)	C(11)- C(12)	1.405 (7)
C(1) - C(6)	1.386 (7)	C(11)- C(16)	1.376 (6)
C(2) - C(3)	1.392 (7)	C(12)- C(13)	1.376 (9)
C(3) - C(4)	1.383 (8)	C(13)- C(14)	1.388 (7)
C(4) - C(5)	1.396 (6)	C(14)- C(15)	1.399 (7)
C(5) - C(6)	1.390 (7)	C(15)- C(16)	1.384 (8)
C(2) - C(27	1.510 (8)	C(12)- C(18)	1.507 (7)
C(4) - C(26)	1.524 (8)	C(14)- C(19)	1.510 (10)
C(7) - C(8)	1.390 (6)	Cl - O(1)	1.409 (9)
C(8) - C(9)	1.407 (9)	Cl - O(2)	1.288 (9)
C(9) - C(10)	1.389 (8)	Cl - O(3)	1.355 (5)
C(10)- C(17)	1.390 (8)	Cl - O(4)	1.338 (6)
C(9) - C(22)	1.636 (9)		
C(22)- C(23)	1.273 (13)		

Table 5. *Bond angles (degrees) with estimated standard deviations × 10 in parentheses*

C(7) - S(1) - C(1)	91.5 (1)	C(17) - S(2) - C(11)	91.5 (1)
C(7) - N(1) - C(6)	115.2 (2)	C(17) - N(2) - C(16)	115.5 (1)
C(7) - N(1) - C(24)	122.7 (1)	C(17) - N(2) - C(20)	123.4 (0)
C(6) - N(1) - C(24)	121.9 (1)	C(16) - N(2) - C(20)	121.1 (2)
S(1) - C(1) - C(6)	110.9 (1)	S(2) - C(11)- C(16)	111.2 (0)
S(1) - C(1) - C(2)	126.8 (1)	S(2) - C(11)- C(12)	127.5 (2)
C(6) - C(1) - C(2)	122.3 (1)	C(16) - C(11)- C(12)	121.3 (2)
C(1) - C(2) - C(3)	116.2 (3)	C(11) - C(12)- C(13)	116.9 (2)
C(1) - C(2) - C(27)	120.4 (1)	C(11) - C(12)- C(18)	119.4 (2)
C(3) - C(2) - C(27)	123.5 (3)	C(13) - C(12)- C(18)	123.6 (2)
C(2) - C(3) - C(4)	122.4 (2)	C(12) - C(13)- C(14)	122.4 (1)
C(3) - C(4) - C(5)	120.8 (1)	C(13) - C(14)- C(15)	119.9 (3)
C(3) - C(4) - C(26)	120.4 (2)	C(13) - C(14)- C(19)	121.0 (1)
C(5) - C(4) - C(25)	118.8 (3)	C(15) - C(14)- C(19)	119.0 (3)
C(4) - C(5) - C(6)	117.2 (2)	C(14) - C(15)- C(16)	118.2 (3)
C(5) - C(6) - C(1)	121.1 (2)	C(15) - C(16)- C(11)	121.2 (1)
C(5) - C(6) - N(1)	127.1 (2)	C(15) - C(16)- N(2)	126.9 (2)
C(1) - C(6) - N(1)	111.9 (1)	C(11) - C(16)- N(2)	111.9 (2)
S(1) - C(7) - N(1)	110.5 (1)	S(2) - C(17)- N(2)	109.9 (1)
S(1) - C(7) - C(8)	125.7 (1)	S(2) - C(17)- C(10)	126.2 (2)
N(1) - C(7) - C(8)	123.8 (2)	N(2) - C(17)- C(10)	123.8 (1)
C(7) - C(8) - C(9)	129.8 (2)	N(2) - C(20)- C(21)	111.8 (1)
C(7) - C(8) - H(8)	117.2	C(9) - C(22)- C(23)	102.5 (3)
C(9) - C(8) - H(8)	112.9	N(1) - C(24)- C(25)	111.2 (1)
C(8) - C(9) - C(10)	123.2 (2)	O(1) - Cl - O(2)	102.5 (4)
C(8) - C(9) - C(22)	112.4 (2)	O(1) - Cl - O(3)	106.7 (2)
C(10)- C(9) - C(22)	123.9 (2)	O(1) - Cl - O(4)	107.8 (2)
C(9) - C(10)- C(17)	130.7 (2)	O(2) - Cl - O(3)	111.1 (3)
C(9) - C(10)- H(10)	117.3	O(2) - Cl - O(4)	110.9 (3)
C(17)-C(10) - H(10)	111.3	O(3) - Cl - O(4)	116.7 (4)

Discussion. – From spectroscopic investigations (re-emission and fluorescence spectra) and conductivity measurements [1], the title compound has been shown to exhibit in the crystalline state a J aggregate absorption band between 610 and 620 nm. However, the compound does not form aggregates when adsorbed on various faces of AgCl and AgBr crystals, for example. It is noteworthy that the *meso*-unsubstituted dye does not form aggregates either. This can be attributed to the presence of the methyl groups at C(7) and C(7′) (Fig. 1) which presumably [12] prevent the sulfur atoms from approaching the face of the crystal and bonding to the silver atoms.

As previously stated, the present analysis was undertaken to obtain accurate dimensions for a model of dye II used to form monolayer aggregates. It is almost certain [1] that dye II exists as the all-*trans* isomer with the long stearyl chains pointing away from the surface of the substrate (water). In this situation the presence of the two methyl groups in positions 7 and 7′ has no effect on the formation of aggregates.

The stacking angles within the crystal, as defined by *Norland & al.* [13] and interpreted by *Smith* [14], are 15.8° and 31.1°. These angles are of interest in connection with the quantum mechanical calculations of *Norland & al.* [13], which predict a blue-shifted spectra (H) for angles greater than 32° and a red-shifted spectra (J) for angles less than 32°, in agreement with the observed absorption band at about 615 nm.

This is the first crystal structure analysis of a stable mono-*cis* 9-*meso*-substituted thiacarbocyanine dye, that shows an aggregate absorption band. An analysis of an all-*trans* thiacarbocyanine dye that also exhibits an aggregate absorption band in the crystalline state is under way.

We would like to thank Prof. *J. D. Dunitz* and Dr. *M. Dobler*, Laboratorium für Organische Chemie, E.T.H., (Zurich) for use of the four-circle *Hilger & Watts* diffractometer and for assistance during data collection; Prof. *M. Truter*, Agricultural Research Council (London) for supplying the set of crystallographic programs XRAC for use on the IBM 1130 computer; Mr. *K. Sager*, *Ciba-Geigy Photochemie* (Marly) for initializing some of these programs on the IBM 360 computer at Basle; Dr. *R. Steiger* and Dr. *R. Kitzing*, *Ciba-Geigy Photochemie* (Marly), for suggesting the problem and supplying the material used, and for many interesting discussions, and finally to the *Centre de calcul de l'Université de Neuchâtel* for computing facilities and *Fonds national suisse de la recherche scientifique* for financial support.

BIBLIOGRAPHY

[1] *R. Steiger, R. Kitzing, R. Hagen & H. Stoeckli-Evans*, to be published J. Photogr. Sci.
[2] *P. J. Wheatley*, J. chem. Soc., 3245 (1959).
[3] *P. J. Wheatley*, J. chem. Soc., 4096 (1959).
[4] *D. L. Smith & H. R. Luss*, Acta Cryst., *B28*, 2793 (1972).
[5] *H. Yoshioka & K. Nakatsu*, Chem. Phys. Letters, *11*, 255 (1971).
[6] *D. L. Smith & E. K. Barrett*, Acta Cryst., *B27*, 969 (1971).
[7] *W. West, S. Pearce & F. Grum*, J. Phys. Chem., *71*, 1316 (1967).
[8] Crystallographic Computing, Ottawa (1969), Editor F. R. Ahmed, Copenhagen, Munksgaard.
[9] *L. Pauling*, The Nature of the Chemical Bond. 3rd. Ed. (1960), Ithaca, Cornell Univ. Press.
[10] International Tables for X-ray Crystallography (1968), Vol. III, Birmingham, Kynoch Press.
[11] *D. Mastropaolo, J. Potenza & G. Bird*, Vogel Centennial Sensitization Past and Future Conference (Aug. 1973), Vermont, U.S.A.
[12] *C. Reich, W. D. Pandolfe & G. R. Bird*, Photogr. Sci. Eng., *17*, 334 (1973).
[13] *K. Norland, A. Ames & T. Taylor*, Photogr. Sci. Eng., *14*, 295 (1970).
[14] *D. L. Smith*, Photogr. Sci. Eng., *16*, 329 (1972).