

- JEFFREY, G. A., POPLE, J. A. & RADOM, L. (1974). *Carbohydr. Res.* **38**, 81–95.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- LARSON, A. C. (1970). *Crystallographic Computing*, edited by F. R. AHMED, pp. 291–294. Copenhagen: Munksgaard.
- MCCONNELL, J. F., SCHWARTZ, A. & STEVENS, J. D. (1977). Unpublished results.
- NEUTRON DIFFRACTION COMMISSION (1969). *Acta Cryst.* **A25**, 391–392.
- PANAGIOTOPOULOS, N. C., JEFFREY, G. A., LAPLACA, S. J. & HAMILTON, W. C. (1974). *Acta Cryst.* **B30**, 1421–1430.
- PARK, Y. J., JEFFREY, G. A. & HAMILTON, W. C. (1971). *Acta Cryst.* **B27**, 2393–2401.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1978). **B34**, 193–199

Crystal and Molecular Structure of 3,3'-Diethylthiatricarbocyanine Iodide, an Infrared Photographic Sensitizing Dye

BY JOSEPH A. POTENZA, LARRY ZYONTZ AND WALTER BOROWSKI

Wright and Rieman Chemistry Laboratories, Rutgers, The State University of New Jersey, New Brunswick, NJ 08903, USA

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The crystal structure of the title compound, a model infrared photographic sensitizing dye, has been determined by a single-crystal, three-dimensional X-ray diffraction study. The compound crystallizes in space group $P2_1/n$ with four $C_{25}H_{25}IN_2S_2$ units in each unit cell of dimensions $a = 17.932$ (7), $b = 18.244$ (9), $c = 7.569$ (2) Å and $\beta = 102.54$ (3)°. The structure was solved by the heavy-atom method and refined by least-squares techniques to a conventional R value of 0.084 for 2180 independent reflections with $F^2 > 2\sigma(F^2)$. The structure consists of sheets of $C_{25}H_{25}N_2S_2^+$ cations roughly parallel to $(10\bar{1})$ and separated by I⁻ ions. Between these sheets, the cations are centrosymmetrically related and stacked in columns along c . In contrast to many structures of thiacyanocyanine and imidocarbocyanine dyes, the cations in the present structure do not stack in the 'slipped deck of cards' arrangement with large intralayer areas of overlap between heterocyclic groups. The cations exist in the all-*trans* configuration and may roughly be described as S-shaped with the heterocyclic groups bent and twisted from the central chain in opposite directions. Bond distances within the seven-atom central chain are alternately long and short as indicated by a χ^2 test, suggesting incomplete electron delocalization between the cation halves.

Introduction

The response of modern photographic films to long-wavelength radiation is completely dependent on the action of sensitizing dyes (Mees & James, 1966). The limited blue and ultraviolet sensitivity resulting from direct absorption of light by silver halide microcrystals is augmented by adsorbed dyes which are thought to form close-packed aggregates on the crystal surface. In favorable cases, dye-adsorbed quanta are as effective as body-adsorbed quanta in generating the photographic latent image; this high quantum efficiency extends across the visible spectrum and into the near infrared (Bird, Zuckerman & Ames, 1968) where absorbed quanta have only approximately half the energy required for the direct production of an electron-hole pair in silver bromide.

Previous investigations of the dye sensitization process have shown that attachment of the organic

dye to the substrate is a critical step (Bird, Norland, Rosenoff & Michaud, 1968). The total crystal surface available for occupancy is limited (Bird, 1974) and the formation of different aggregate structures may shift the region of absorption and sensitization. Since the nature of the aggregate formed must, to some extent, depend on the geometry of the dye itself, to understand the phenomena associated with dye adsorption, precise structural parameters for representative sensitizing dyes are required.

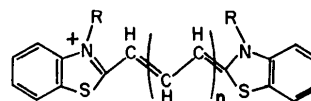


Fig. 1. Generic formula of a class of sensitizing dyes. When $n = 0, 1, 2,$ or 3 , the cations are thiacyanine, thiacyanocyanine, thiadicyanocyanine, and thiatricyanocyanine respectively.

The majority of useful photographic sensitizers are positively charged cyanine dyes (Hamer, 1964) which possess benzene-like chains of CH units terminating in nitrogen-containing heterocyclic residues. Structural data for the cyanines and related dyes have been reviewed recently by Smith (1974). One important class of sensitizing dyes has the generic formula given in Fig. 1. Of these, the thiacyanocyanine dyes are highly useful visible sensitizers; a number of structural studies of compounds in this class have been reported including those of Wheatley (1959), Potenza & Mastropaolo (1974) and Stoekli-Evans (1974). In contrast, for the longer thiadicyanocyanine and thiatribocyanine compounds, which sensitize in the near infrared, no detailed structural information is available. The cation 3,3'-diethylthiatribocyanine has long been considered as a model long-wavelength sensitizer, and so we have chosen it as the subject of a crystallographic study.

Experimental

Crystal data and data collection

A sample of 3,3'-diethylthiatribocyanine iodide was purchased from the Eastman Kodak Company and recrystallized by slowly evaporating a solution consisting of 20 mg of the dye and 30 ml of dichloroethane. The evaporation was carried out under nitrogen with a partial vacuum. A blue crystal of dimensions $0.23 \times 0.18 \times 0.18$ mm was glued to the end of a glass rod and placed on a Syntex $P2_1$ four-circle computer-controlled diffractometer. Subsequent examination of the data revealed a monoclinic unit cell with systematic extinctions of $h0l$ when $h + l = 2n + 1$ and of $0k0$ when $k = 2n + 1$; this fixed the space group as $P2_1/n$. Unit-cell parameters $a = 17.932$ (7), $b = 18.244$ (9), $c = 7.569$ (2) Å and $\beta = 102.54$ (3)° were determined from a least-squares analysis of 12 reflections obtained using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The calculated volume of the unit cell was 2417 Å³, leading to a calculated density of 1.496 g cm⁻³. This was in good agreement with the measured value of 1.481 (2) g cm⁻³ obtained by flotation in *trans*-1,2-dichloroethylene and carbon tetrachloride.

All data were collected at room temperature (23 ± 2 °C) with graphite-monochromated Mo $K\alpha$ radiation, a scintillation counter and a pulse-height analyzer set to admit approximately 90% of the $K\alpha$ peak. Reflections with $2 < 2\theta < 60$ ° were recorded using a θ - 2θ scan. The scan rate was constant at 3.26 ° min⁻¹ while the scan range was varied from 1.40 ° at low 2θ to 1.79 ° at $2\theta = 60$ °. Background measurements were made at the beginning and end of each scan with the counter stationary; the total time for background counting was equal to the scan time. Three standard reflections were measured at intervals of 47 reflections.

They were consistent to ± 4 % over the period of data collection and showed no significant trend.

7262 reflections were collected and corrected for Lorentz and polarization effects. Absorption corrections were not applied (μ for Mo $K\alpha = 15.2$ cm⁻¹). An estimate of the overall scale factor was obtained by Wilson's method and was subsequently refined. Each of the 2180 unique reflections for which $F^2 > 2\sigma(F^2)$ was used in the structure determination and refinement. Here, standard deviations were assigned as $\sigma(F^2) = (Lp^{-1}) [N_t + (0.03N_n)^2]^{1/2}$ where N_t is the total count (background plus scan), N_n is the net count (scan minus background) and 0.03 is a measure of instrumental instability.

Structure determination

The structure was solved by the heavy-atom method and refined by least-squares techniques. Approximate coordinates for the I⁻ ion and two S atoms were determined unambiguously from a normal-sharpened three-dimensional Patterson map; the computer programs used have been described previously (Potenza, Giordano, Mastropaolo & Efraty, 1974). The

Table 1. Fractional atomic coordinates ($\times 10^4$) for the non-hydrogen atoms in 3,3'-diethylthiatribocyanine iodide

Estimated standard deviations are given in parentheses.

	x	y	z
I	1768.1 (6)	10974.5 (5)	4750 (2)
S(1)	3237 (2)	9284 (2)	4856 (5)
S(2)	7794 (2)	12151 (2)	10759 (5)
N(1)	3200 (6)	7919 (5)	5695 (13)
N(2)	8926 (5)	11414 (6)	12563 (14)
C(1)	2422 (7)	8795 (6)	3968 (16)
C(2)	1737 (8)	9001 (8)	2912 (17)
C(3)	1138 (7)	8526 (8)	2333 (17)
C(4)	1219 (7)	7819 (8)	2905 (16)
C(5)	1902 (8)	7567 (8)	4012 (18)
C(6)	2495 (7)	8063 (7)	4527 (17)
C(7)	3663 (6)	8511 (6)	6032 (17)
C(8)	4355 (7)	8530 (7)	7246 (18)
C(9)	4815 (7)	9175 (6)	7650 (17)
C(10)	5537 (8)	9198 (7)	8854 (18)
C(11)	5975 (8)	9842 (7)	9177 (18)
C(12)	6654 (7)	9912 (8)	10350 (16)
C(13)	7068 (8)	10585 (7)	10532 (18)
C(14)	7774 (7)	10671 (7)	11594 (18)
C(15)	8192 (7)	11330 (6)	11732 (15)
C(16)	9233 (8)	12120 (7)	12357 (17)
C(17)	9996 (7)	12337 (8)	12983 (20)
C(18)	10151 (8)	13043 (8)	12577 (22)
C(19)	9612 (9)	13511 (7)	11649 (22)
C(20)	8856 (9)	13301 (7)	11053 (20)
C(21)	8679 (7)	12587 (6)	11436 (16)
C(22)	3424 (8)	7201 (7)	6510 (20)
C(23)	3909 (11)	6762 (10)	5527 (26)
C(24)	9393 (7)	10789 (7)	13440 (17)
C(25)	9699 (8)	10362 (7)	12087 (20)

remaining non-hydrogen atoms were determined by a series of three, three-dimensional difference Fourier maps, each successive map being phased by an increasing number of atoms.

All non-hydrogen atoms were refined anisotropically with a block-matrix refinement initially and full-matrix refinement for the last cycles. Atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1974). All atoms were treated as neutral species except I which was treated as the anion. Both real and imaginary components of the anomalous dispersion were included for I and S

Table 2. Calculated fractional atomic coordinates ($\times 10^3$) for hydrogen atoms in 3,3'-diethylthiatricarbocyanine

A value of $B = 4.36 \text{ \AA}^2$, obtained from the Wilson plot, was used for all H atoms.

	x	y	z
H(C2)	167	950	253
H(C3)	68	869	155
H(C4)	79	750	256
H(C5)	197	705	439
H(C8)	455	808	786
H(C9)	462	963	706
H(C10)	573	875	946
H(C11)	576	1029	856
H(C12)	686	949	1107
H(C13)	683	1100	984
H(C14)	800	1025	1230
H(C17)	1038	1201	1365
H(C18)	1067	1322	1298
H(C19)	977	1400	1137
H(C20)	848	1363	1041
H(C22-1)	297	693	658
H(C22-2)	368	726	774
H(C23-1)	404	629	611
H(C23-2)	437	701	550
H(C23-3)	364	666	430
H(C24-1)	909	1048	1401
H(C24-2)	981	1097	1435
H(C25-1)	1000	996	1263
H(C25-2)	1001	1067	1150
H(C25-3)	929	1017	1116

(*International Tables for X-ray Crystallography*, 1974). Refinement was based on F and the function minimized was $\sum w(|F_o| - |F_c|)^2$. Weights, set according to $w = 1/\sigma^2$, were chosen by an analysis of variance to make $|\Delta F|/\sigma$ independent of $|F_o|$. This procedure led to a graph which could best be described by the following lines:

$$\begin{aligned}\sigma(F_o) &= -0.125 + 0.250|F_o| \text{ for } |F_o| < 15.8 \\ \sigma(F_o) &= 10.06 - 0.392|F_o| \text{ for } 15.8 < |F_o| < 21.6 \\ \sigma(F_o) &= 1.52 + 0.003|F_o| \text{ for } 21.6 < |F_o| < 46.6 \\ \sigma(F_o) &= -0.988 + 0.055|F_o| \text{ for } |F_o| > 46.6.\end{aligned}$$

After several refinement cycles, H positions were calculated, confirmed with electron density maps, and treated as fixed atoms for further refinement. Final values for $R_F = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ were 0.084 and 0.081 respectively. For the final refinement cycle, all parameter changes were less than σ , the e.s.d. obtained from the inverse matrix. A final difference Fourier map showed no significant features.

Final atomic parameters are listed in Table 1 for non-hydrogen atoms and in Table 2 for H atoms.*

Description of the structure and discussion

The structure consists of $C_{25}H_{25}N_2S_2^+$ cations separated by I^- ions. A view of the cation, showing the crystallographic numbering scheme, is given in Fig. 2. Bond distances and angles are listed in Table 3. The central C chain [C(8)—C(14)] is in the all-*trans* configuration. S atoms from each half of the dye cation are *cis*, a geometry which generally results from an all-*trans* central chain because of steric effects. Both methyl groups are to one side of the cation plane. Previous

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32903 (14 pp.). Copies may be obtained from the authors or through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

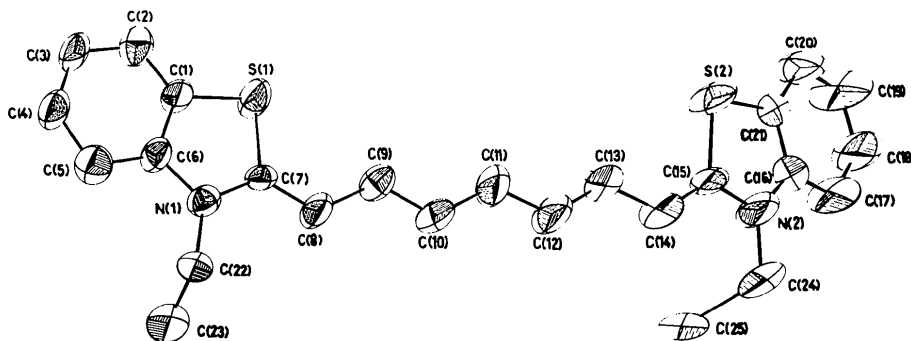


Fig. 2. View of 3,3'-diethylthiatricarbocyanine showing the crystallographic numbering scheme.

crystallographic studies of thiocarbocyanine dyes, with three C atoms in the central chain, have revealed the all-*trans* configuration in a number of cases, and the mono-*cis* configuration in one case. Structures with no alkyl substituents on the central chain (Wheatley, 1959) showed the all-*trans* configuration, while structures with a bulky 9-ethyl substituent revealed the all-*trans* configuration in one case (Potenza & Mastropaolo, 1974) and the mono-*cis* configuration in another (Stoekli-Evans, 1974). In the present structure, steric strain associated with atoms on the central chain is minimal and the all-*trans* structure is favored energetically. Reduced strain in the present structure is evidenced by the bond angles in the central chain which are equivalent ($124 \pm 1^\circ$) to within experimental error. In the all-*trans* structure of 3,3',9-triethylthiocarbocyanine, the central ethyl group caused the cation to be bowed; as a result, the central angle was reduced to 116° and the angles immediately adjacent to it were increased to 130° . The mono-*cis* cation 5,5',7,7'-tetramethyl-3,3',9-triethylthiocarbocyanine was found to be twisted as a consequence of a short S...H (chain) contact; the central angle [$123.2(2)^\circ$] is equivalent to that found here, while the adjacent angles [$130.7(2)$, $129.8(2)^\circ$] are close to those found for 3,3',9-triethylthiocarbocyanine.

Corresponding distances in heterocycle I [S(1), N(1), C(1)—C(7)] and heterocycle II [S(2), N(2), C(15)—C(21)] are equivalent within experimental error and agree well with accepted values. For example, the average C—C distance in the fused benzo rings, 1.384 Å, compares favorably with the generally accepted value of 1.39 Å, while the angles at C(2), C(5), C(17) and C(20) [av. 118.3°] are smaller than the remaining angles in the six-membered rings [C(1), C(3), etc., av.

Table 3. Bond distances (Å) and angles ($^\circ$)

I...S(1)	4.045 (4)	C(4)—C(5)	1.40 (2)
I...S(2')	3.879 (4)	C(5)—C(6)	1.39 (2)
S(1)...S(2)	9.911 (4)	C(16)—C(17)	1.41 (2)
N(1)...N(2)	12.25 (1)	C(16)—C(21)	1.38 (2)
S(1)—C(7)	1.75 (1)	C(17)—C(18)	1.37 (2)
S(1)—C(1)	1.72 (1)	C(18)—C(19)	1.37 (2)
S(2)—C(15)	1.75 (1)	C(19)—C(20)	1.39 (2)
S(2)—C(21)	1.75 (1)	C(20)—C(21)	1.39 (2)
N(1)—C(6)	1.40 (1)	C(7)—C(8)	1.37 (2)
N(1)—C(7)	1.35 (1)	C(8)—C(9)	1.43 (2)
N(1)—C(22)	1.47 (2)	C(9)—C(10)	1.41 (2)
N(2)—C(16)	1.42 (2)	C(10)—C(11)	1.41 (2)
N(2)—C(15)	1.34 (1)	C(11)—C(12)	1.35 (2)
N(2)—C(24)	1.48 (2)	C(12)—C(13)	1.43 (2)
C(1)—C(2)	1.37 (2)	C(13)—C(14)	1.35 (2)
C(1)—C(6)	1.40 (2)	C(14)—C(15)	1.41 (2)
C(2)—C(3)	1.38 (2)	C(22)—C(23)	1.49 (2)
C(3)—C(4)	1.36 (2)	C(24)—C(25)	1.48 (2)
S(1)—C(7)—N(1)	111.4 (8)	C(15)—N(2)—C(16)	115 (1)
S(2)—C(15)—N(2)	111.7 (8)	C(15)—N(2)—C(24)	122 (1)
S(1)—C(1)—C(2)	131.8 (10)	C(16)—N(2)—C(24)	123 (1)
S(1)—C(1)—C(6)	111.2 (8)	C(1)—C(2)—C(3)	124 (1)
S(1)—C(7)—C(8)	123.3 (9)	C(2)—C(3)—C(4)	118 (1)
S(2)—C(21)—C(20)	126.9 (10)	C(3)—C(4)—C(5)	121 (1)
S(2)—C(21)—C(16)	112.0 (8)	C(4)—C(5)—C(6)	118 (1)
S(2)—C(15)—C(14)	122.5 (8)	C(5)—C(6)—C(1)	122 (1)
C(1)—S(1)—C(7)	91.2 (5)	C(6)—C(1)—C(2)	117 (1)
C(21)—S(2)—C(15)	90.3 (5)	C(21)—C(20)—C(19)	116 (1)
N(1)—C(6)—C(1)	112 (1)	C(20)—C(19)—C(18)	122 (1)
N(1)—C(6)—C(5)	126 (1)	C(19)—C(18)—C(17)	123 (1)
N(1)—C(7)—C(8)	125 (1)	C(18)—C(17)—C(16)	115 (1)
N(1)—C(22)—C(23)	114 (1)	C(17)—C(16)—C(21)	123 (1)
N(2)—C(16)—C(21)	111 (1)	C(16)—C(21)—C(20)	121 (1)
N(2)—C(16)—C(17)	126 (1)	C(7)—C(8)—C(9)	124 (1)
N(2)—C(15)—C(14)	126 (1)	C(8)—C(9)—C(10)	125 (1)
N(2)—C(24)—C(25)	111 (1)	C(9)—C(10)—C(11)	123 (1)
C(7)—N(1)—C(6)	114 (1)	C(10)—C(11)—C(12)	126 (1)
C(7)—N(1)—C(22)	122 (1)	C(11)—C(12)—C(13)	122 (1)
C(6)—N(1)—C(22)	124 (1)	C(12)—C(13)—C(14)	124 (1)
		C(13)—C(14)—C(15)	124 (1)

Table 4. Equations of weighted least-squares planes and atomic deviations

Equations are expressed in the form $AX_o + BY_o + CZ_o = D$ where X_o , Y_o and Z_o are Cartesian axes lying along $\mathbf{b} \times \mathbf{c}^*$. \mathbf{b} and \mathbf{c}^* respectively.

Plane	A	B	C	D	Atoms defining the plane				
1	-0.6350	0.2968	0.7132	4.278	C(7) through C(15)				
2	-0.5910	0.2230	0.7752	3.696	S(1), N(1), C(1) through C(11)				
3	-0.4918	0.2431	0.8361	5.873	S(2), N(2), C(11) through C(21)				
Deviations of atoms from the planes (Å)									
Plane	S(1)	N(1)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	
1	0.130	-0.037	0.233	0.458	0.517	0.403	0.188	0.106	
2	-0.097	-0.051	-0.027	0.076	0.129	0.139	0.054	-0.027	
3	-1.217	-1.204	-1.336	-1.378	-1.465	-1.450	-1.391	-1.334	
Plane	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)	C(13)	C(14)	
1	-0.031	-0.043	0.038	-0.012	0.042	0.047	0.055	-0.032	
2	-0.075	0.013	0.058	0.109	0.123	0.218	0.175	0.173	
3	-1.114	-0.868	-0.706	-0.491	-0.366	-0.115	-0.054	0.103	
Plane	C(15)	S(2)	N(2)	C(16)	C(17)	C(18)	C(19)	C(20)	C(21)
1	-0.064	0.220	-0.330	-0.427	-0.783	-0.834	-0.552	-0.181	-0.125
2	0.091	0.195	-0.096	-0.273	-0.574	-0.723	-0.583	-0.266	-0.112
3	0.123	0.159	0.094	-0.008	-0.147	-0.254	-0.220	-0.062	0.045

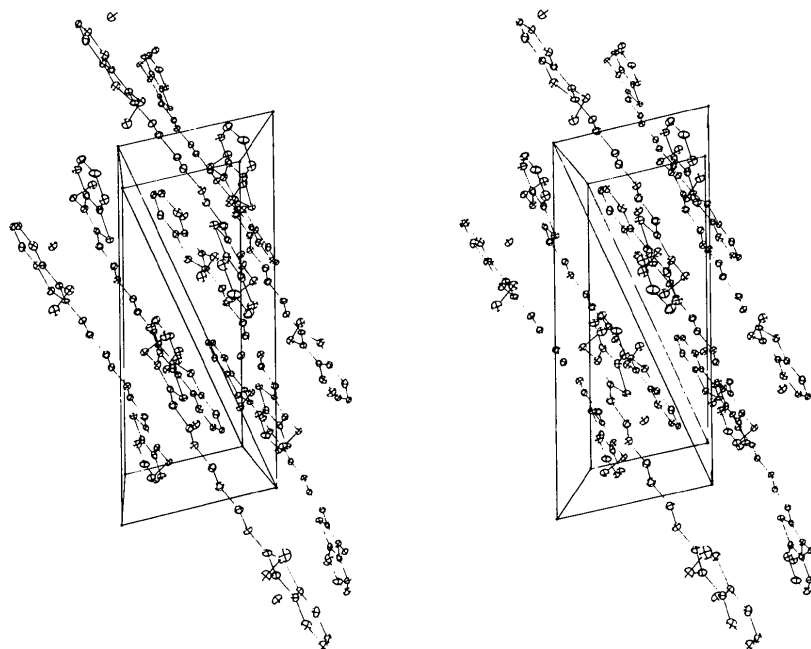


Fig. 3. Stereoscopic view of the unit-cell contents along **b**. The cell shown extends from $-b/2$ to $b/2$.

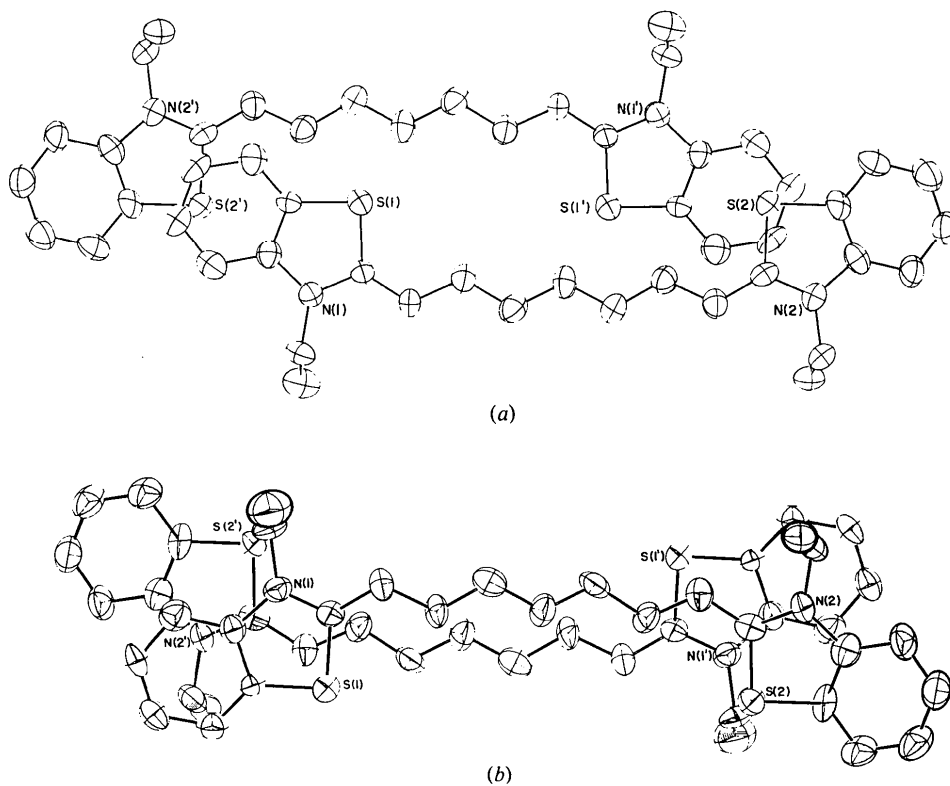


Fig. 4. The relative orientation of centrosymmetrically related cations. (a) The cation with coordinates x, y, z shown above that with coordinates $1 - x, 2 - y, 1 - z$. (b) The cation with coordinates x, y, z shown above that with coordinates $1 - x, 2 - y, 2 - z$.

120.9°], a pattern which is characteristic of benzo groups fused to four- and five-membered rings (Stoeckli-Evans, 1974). Within the central alkyl chain, bond distances are alternately short and long. This alternation, although not large, is significant as indicated by a χ^2 test and may indicate incomplete electron delocalization between the two halves of the cation. It contrasts with structural results reported for thiocarbocyanine dyes where bond lengths within the central chain were found to be equivalent. A larger alternation in central-chain bond lengths has been reported for 1,1'-diethyl-2,2'-thiazolinecarbocyanine iodide (Borowiak, Bokii & Struchkov, 1972); but, as pointed out by Smith (1974), the differences in bond lengths are not significant. To determine more precisely the nature of charge delocalization in thiatricarbocyanines, structural results for a dye with a lighter counterion, such as tosylate or chloride, would be helpful.

Deviations of the cation from planarity are large as indicated by the data in Table 4, which gives least-squares planes and atomic deviations for each half of the cation (excluding ethyl groups) and for the central alkyl chain. Atoms on the central chain show an average deviation of 0.04 Å from plane 1 with a maximum deviation of 0.06 Å. Atoms towards the center of the chain [C(11)–C(13)] show positive deviations while those towards the ends, such as C(7) and C(15), show negative deviations. This indicates that the central chain is bowed slightly. The atoms of both heterocycle I and heterocycle II show deviations from plane 1 which increase in magnitude in going towards the ends of the molecule. These deviations are primarily positive for heterocycle I and negative for heterocycle II. Therefore, the cation is best described as S-shaped, with the heterocyclic groups bent from

the central chain in opposite directions. Lastly, both heterocycle planes are also twisted slightly from the central chain, and to different degrees.

A packing diagram is shown in Fig. 3, which is a view of the structure along **b**. The packing may be described as sheets of cations roughly parallel to (10 $\bar{1}$) and separated by I⁻ ions. Between sheets, the cations are stacked in columns along **c**. Adjacent cations in each column are related by a center of symmetry while every other cation is related by a cell translation along **c**. Columns are related to each other by the glide plane operation and by unit-cell translations in the **a** and **b** directions. The arrangement of cations within each column most closely resembles that found for the unsolvated 3,3'-diethylthiocarbocyanine bromide structure (Wheatley, 1959); it is not the simple 'slipped deck of cards' arrangement found previously for a number of thiocarbocyanine and imidocarbocyanine dyes (Smith, 1974).

Laterally displaced dye cations within a given column are stacked in two non-equivalent ways (Fig. 4) and the closest interionic contacts (Table 5) occur between these cations. For the pair related by $\bar{1}$ at $\frac{1}{2}, 1, \frac{1}{2}$ (Fig. 4a), the shortest contacts are between the benzo groups of one cation and the heterocyclic rings of the other while for the pair related by $\bar{1}$ at $\frac{1}{2}, 1, 1$ (Fig. 4b), the closest contacts are between heterocycle and central-chain atoms. The shortest distances are 3.52 Å for S...C, and 3.41 Å for C...C linkages.

The I⁻ ions are almost symmetrically placed between nonequivalent S atoms on different cations, as shown in Fig. 5. The distances I...S(1) [4.045 (4)] and I...S(2'') [3.879 (4) Å] are both within 0.15 Å of the sum of the van der Waals radii for I and S (4.00 Å). Thus, on the basis of these distances, it is not clear whether the I⁻ ions, in addition to maintaining charge neutrality, are essentially filling holes in the structure or whether the bend and twist of the heterocyclic groups are related to this interaction.

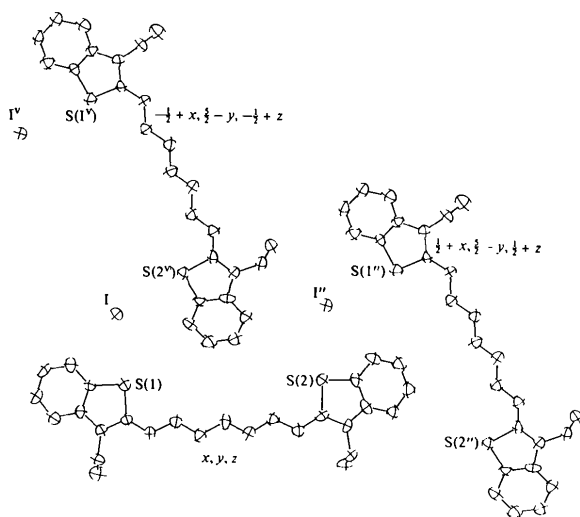


Fig. 5. Partial view of the structure along $[10\bar{1}]$ showing the location of the I⁻ ions. The symbols '' and ' refer to coordinates $\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$ and $-\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$ respectively.

Table 5. Selected interionic contacts <3.75 Å

Unprimed atoms correspond to the coordinates x, y, z given in Table 1. The symbols ', '', '' and '' correspond, respectively, to the following coordinates: $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$; $1 - x$, $2 - y$, $2 - z$; $1 - x$, $2 - y$, $1 - z$; $\frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$.

I...C(22')	3.68 (2) Å	C(2)...C(15''')	3.60 (2) Å
S(1)...C(13'')	3.66 (1)	C(3)...C(24'')	3.74 (2)
S(1)...C(14''')	3.55 (2)	C(3)...C(15''')	3.55 (2)
S(2)...N(1''')	3.53 (1)	C(3)...C(16''')	3.67 (2)
S(2)...C(6'')	3.74 (1)	C(3)...C(21''')	3.58 (2)
S(2)...C(22'')	3.52 (2)	C(4)...C(21''')	3.41 (2)
S(2)...C(2''')	3.72 (2)	C(4)...C(20''')	3.60 (2)
S(2)...C(3''')	3.56 (2)	C(6)...C(15''')	3.51 (2)
S(2)...C(4''')	3.60 (2)	C(7)...C(13''')	3.56 (2)
N(1)...C(15''')	3.74 (2)	C(8)...C(13''')	3.72 (2)
N(2)...C(3''')	3.69 (2)	C(9)...C(11''')	3.53 (2)
C(1)...C(14''')	3.59 (2)	C(9)...C(12''')	3.71 (2)
C(1)...C(15''')	3.66 (2)	C(10)...C(19''')	3.69 (2)

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References

- BIRD, G. R. (1974). *Photogr. Sci. Eng.* **18**, 562–568.
 BIRD, G. R., NORLAND, K. S., ROSENOFF, A. E. & MICHAUD, H. B. (1968). *Photogr. Sci. Eng.* **12**, 196–206.
 BIRD, G. R., ZUCKERMAN, B. & AMES, A. E. (1968). *Photochem. Photobiol.* **8**, 393–410.
 BOROWIAK, T. E., BOKII, N. G. & STRUCHKOV, YU. T. (1972). *Zh. Strukt. Khim.* **13**, 480–485; *Chem. Abstr.* **77**, 106391h.
 HAMER, F. M. (1964). *The Chemistry of Heterocyclic Compounds*. Vol. 18. *The Cyanine Dyes and Related Compounds*. New York: Interscience.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–98, 149–150. Birmingham: Kynoch Press.
 MEES, C. E. K. & JAMES, T. H. (1966). *The Theory of the Photographic Process*, Chaps. 11, 12, pp. 198–277. New York: Macmillan.
 POTENZA, J., GIORDANO, P., MASTROPAOLO, D. & EFRATY, A. (1974). *Inorg. Chem.* **13**, 2540–2544.
 POTENZA, J. & MASTROPAOLO, D. (1974). *Acta Cryst.* **B30**, 2353–2359.
 SMITH, D. L. (1974). *Photogr. Sci. Eng.* **18**, 309–322.
 STOECKLI-EVANS, H. (1974). *Helv. Chim. Acta*, **57**, 1–9.
 WHEATLEY, P. J. (1959). *J. Chem. Soc.* pp. 3245–3250, 4096–4100.

Acta Cryst. (1978). **B34**, 199–204

The Crystal and Molecular Structures of Six- and Seven-Membered-Ring Organophosphorus Compounds. 1,3,2-Dioxaphosphorinanes and 1,5-Dihydro-1,4,3-benzodioxaphosphins

BY A. GRAND* AND J. B. ROBERT*

Laboratoire de Chimie Organique Physique, Département de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble, 85 X, F38041, Grenoble CEDEX, France

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The structures of four six- and seven-membered-ring organophosphorus molecules have been determined by direct methods. In these molecules, the P atom is four-coordinate $\begin{array}{c} \text{O} \\ \diagup \\ \text{P}=\text{S} \\ \diagdown \\ \text{O} \end{array}$, with $R = \text{CH}_3$ or $\text{N}(\text{CH}_3)_2$.

The four molecules adopt a chair conformation with the P=S bond in the axial orientation. The flattening of the ring is smaller in the seven- than in the six-membered rings. The O–P–O and C–O–P ring angles show an increase of *ca* 2 and 3°, respectively, in going from the six- to the seven-membered ring.

Introduction

In contrast to several structure determinations of 2-*R*-2-oxo- or 2-thiono-1,3,2-dioxaphosphorinanes (Corbridge, 1974; Silver & Rudman, 1972; Drew & Rodgers, 1972; Saenger & Mikolajczyk, 1973; Cook & White, 1976; Bukowska-Strzyżewska, Michalski, Młotkowska & Skoweranda, 1976; Grand & Robert, 1975) little attention has been paid to the structure determination of the corresponding seven-membered rings. To our knowledge, only one determination has been made of a 1,3,2-dioxaphospha seven-membered ring, tetramethylenephosphoric acid (Coulter, 1975).

Solutions of 2-oxo- and 2-thiono-1,3,2-dioxaphos-

phorinanes have also been investigated by NMR spectroscopy (Bentrude & Hargis, 1970; Katritzky, Nesbit, Michalsky, Tulinowski & Zwierzak, 1970; Bartle, Edmundson & Jones, 1967; Bentrude, Tan & Yee, 1972; Bentrude & Tan, 1973; Finocchiaro, Recca, Bentrude, Tan & Yee, 1976; Dutasta, Grand, Robert & Taieb, 1974) but only a few deal with the NMR spectral analysis of the corresponding seven-membered rings (Sato & Goto, 1973; Guimaraes, Robert & Taieb, 1977). We present the solid-state structure determination of four 2-thiono-1,3-dioxaphosphorus molecules: two six- (I, II) and two seven-membered-ring (III, IV) molecules in which the same *R* groups are attached to the P atoms. The conformation of (I) has been reported (Dutasta, Grand & Robert, 1974).

The present analysis was undertaken for three main

* Faculty members of the Université Scientifique et Médicale de Grenoble; Equipe de Recherche Associée n° 674 au CNRS.