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THE CRYSTAL STRUCTURE OF 3,3'-DIETHYL-THIACYANINE BROMIDE

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The crystal structure of the title compound was determined by X-ray analysis. The dye ion has approximately C_s symmetry. The short S...S distance(2.994 Å) implies a strong interaction between them. The cations are stacked on top of each other along the c-axis with the separation of about 3.5 Å.

Hitherto many spectroscopic and photographic studies on the spectral sensitizing dyes have been extensively carried out, but there have been only a few X-ray crystallographic studies[2]. The title compound, $[(C_9H_9NS)_2CH]^+Br^-$, one of the fundamental dyes, is investigated by X-ray diffraction to elucidate the molecular and crystal structure.

The crystals[3] belong to the triclinic space group $P\bar{1}$, with two formula units in a cell of dimensions: a = 11.881, b = 9.912, c = 8.089 Å, α = 102.3, β = 97.1, γ = 102.3°. The intensity data were collected on a four circle automatic diffractometer[4]. The independent reflections within the range of 2θ less than 55° were measured by the ω-2θ scan technique using Mo Kα radiation. Thus a total of 2587 reflections were obtained, which had intensities greater than three times their standard deviations.

The structure was solved by the heavy-atom method and refined by the method of least squares. Anisotropic temperature factors were applied to the bromine and sulfur atoms. All the hydrogen atoms were found from a difference map and they were included in the calculation of the structure factors. The conventional R factor was 6.2 %.

The dye cation, shown in Fig. 1, has approximate symmetry C_s through the C(m) atom. The resonance between the two extreme structures is inferred to be

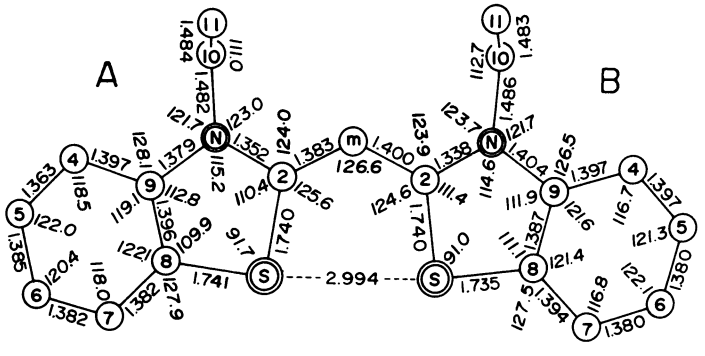

Fig. 1. The structure of the dye cation. The standard deviations of the distances and angles are: 0.007 Å for S-C, about 0.01 Å for the other bonds, 0.3° for C-S-C and about 0.5° for the other angles.

almost complete. All the atoms, except the methyl groups and the hydrogen atoms on the methylene groups, are nearly coplanar. In particular, the chain of five atoms, S-C(2)-C(m)-C(2)-S, is quite closely coplanar with the mean atomic deviation of 0.003 Å. The S...S distance, 2.994 ± 0.002 Å, is somewhat shorter than the usual van der Waals contact. This implies that a bonding interaction is present between the sulfur atoms, as expected from the result of an MO calculation by the Hückel method on this dye[5,6], and as suggested by Nyburg et al. in their studies on sulfur compounds[7].

The crystal structure is shown in Fig. 2. The planar dye ions are tilted by 14° from the ab-plane and are stacked on top of each other, forming a cationic column along the c-direction. Both interplanar spacings of the dye ions across the centers of symmetry at $(\frac{1}{2},\frac{1}{2},0)$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ are almost equal, 3.5 Å.

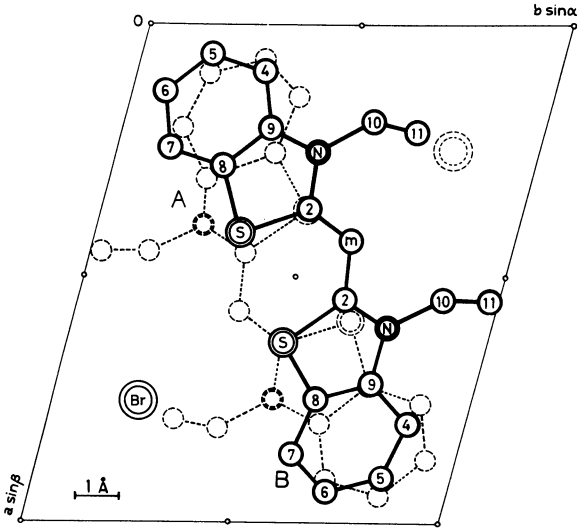

Fig. 2. The crystal structure viewed down the c-axis. The atoms drawn by solid lines are inverted to the atoms drawn by broken lines by the center of symmetry at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$.

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2) C. E. K. Mees and T. H. James, eds.,"The Theory of the Photographic Process", MacMillan, New York(1966).
3) Crystals were kindly supplied by Japanese Research Institute for Photographic Dyes Co., Ltd., and were recrystallized from ethanol as light yellow columns.
4) The authors are grateful to Dr. Y. Shiozaki for his kind arrangements for data collection by the diffractometer at Hokkaido University.
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6) A calculation based on the SCF MO method is in progress by Dr. S. Nakayama.
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