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Stereochemistry of Pyrylo-2-Monomethinecyanine and its Thioanalogues

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ABSTRACT

Using X-ray diffraction, the molecular and crystal structures of 4,6,4′,6′-tetra-tert-butyl-substituted pyrylo-2-, thiopyrylo-2- and (pyrylo-2)(thiopyrylo-2)monomethinecyanine perchlorates were investigated. Their cations were found to be planar, existing in ZE-, ZZ- and ZZ-conformations, respectively. It was found that their bond lengths alternate considerably and that bond angles were distorted. The disposition of the anion was found to be different for all the compounds investigated. Based on CNDO/2 quantum-chemical calculations, stereochemical configuration of pyrylo-2-monomethinecyanine and its thioanalogues was evaluated.

1 INTRODUCTION

Pyrylo-2-cyanines and their heteroanalogues and benzo-homologues are useful compounds in the study of the colour of dyes. Several specific characteristics are observed in their electronic absorption spectra,[1–3] particularly when compared to the spectra of the isomeric dyes containing heterocyclic residues attached to the chromophore through the 4-position.

It is apparent from Fig. 1 that the visible absorption band of pyrylo-2-monomethinecyanine (**I**) has a more pronounced vibration structure than that of the 4-isomer (**II**), the former being considerably broader and less intense.

To evaluate the shape of the absorption bands of pyrylo-2-cyanines and their analogues, it is necessary to investigate the bond-length alternation in

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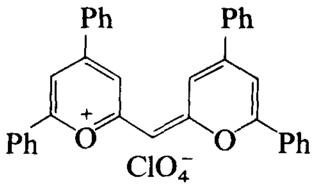
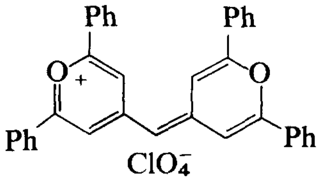


I



II

their chromophores, since this influences the vibronic interactions responsible for the band shapes. Information on bond-length alternation is also useful when studying the participation of the individual bonds in the entire conjugative system of pyrylo-2-cyanines and their analogues, a factor which seems to account for such distinct differences in the colour of these isomers[1−3] (Fig. 1).

The abnormally high, first vinylene shift (219 nm) was initially observed for thiopyrylo-2-cyanines.[1] It was suggested that this resulted from interaction of the non-bonded sulphur atoms in the monomethinecyanine molecule. For this interaction to occur, the dye must have a certain conformation, but the use of ^{1}H-NMR studies on thiopyrylo-2-monomethinecyanine proved to be unsuccessful.[4,5]

In media of low polarity, in which the salt-like dyes exist as ion pairs and ion-pair associates,[6,7] the absorption spectra of pyrylo-2-cyanines are significantly changed. In the interpretation of these spectral changes, the ion-pair structure (i.e. the disposition of cation and anion relative to each other) is relevant.

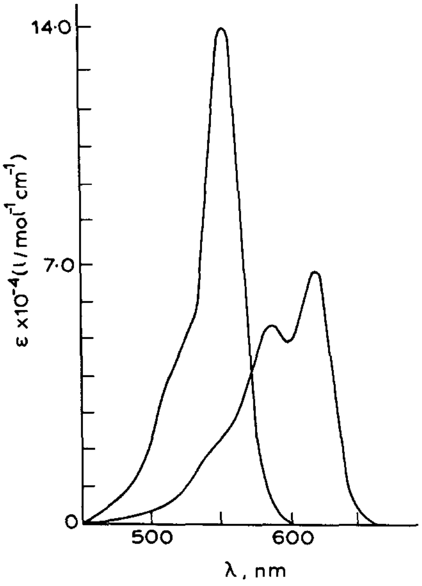
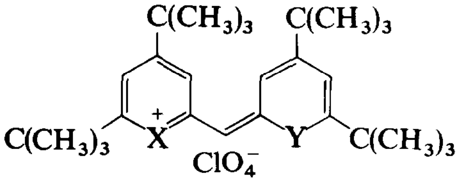


Fig. 1. Electronic absorption spectra of isomeric dyes **I** and **II** in methylene chloride.

For a meaningful treatment of the colour of pyrylo-2-cyanines and their analogues, it is necessary to have full information concerning bond-length alternation, molecular planarity and conformation, and the relative disposition of the cation and anion. In this paper, X-ray diffraction analysis (XRDA) is used as a source for this data.

2 MATERIALS AND METHODS

The dyes investigated were of general formula



III–V

III: X = Y = O
IV: X = O, Y = S
V: X = Y = S

The synthesis of these compounds has been previously described.[4] Their crystals were prepared by dissolving the dyes in ethanol, and then adding twice the volume of diethyl ether to the ethanolic solution. The solutions were kept for 24 h at 20°C and then for 48 h at −5°C. The crystals of **III** contained ether of crystallization, which evaporated in air, making the samples unsuitable for XRDA.

Crystals of **III** were orthorhombic at 25°C: a = 17·768(5), b = 18·997(7), c = 9·637(4) Å, V = 3253(5) $Å^3$, d(calc) = 1·01 g cm^{-3}, Z = 4, space group is Pna 2_1 (a molecule of diethyl ether was present). Crystals of **IV** were monoclinic at 25°C: a = 12·287(3), b = 20·616(2), c = 12·076(9) Å, β = 107·28(4)°, V = 2920(4) $Å^3$, Z = 4, d(calc) = 1·16 g cm^{-3}, space group is $P2_1/c$. Crystals of **V** were monoclinic at 25°C: a = 14·172(1), b = 10·935(1), c = 19·788(1) Å, β = 108·60(6)°, V = 2906(1) $Å^3$, d(calc) = 1·46 g cm^{-3}, Z = 8, space group is C2/c (the molecule is disposed on the two-fold axis).

Unit-cell parameters and intensities of independent reflections 2661 (**III**), 3934 (**IV**) and 2277 (**V**) were measured with an automatic four-circle CAD 4 diffractometer (λ MoK_α, graphite monochromator, ω: θ scanning with the speed ratio of 1·2:1; $2\theta \leq 120°$). The structures were solved by the direct method using a MULTAN program and refined by the full-matrix least-square technique in the anisotropic approximation. The reflections 1981 (**III**), 2381 (**IV**) and 1826 (**V**) with $F^2 \geq 3\sigma$ were used in the calculations. The calculated coordinates of all hydrogen atoms were included in the refinement in the isotropic approximation with the fixed positional and thermal parameters $B_{iso} = 5$ $Å^2$. The final R-values were 0·060 (R_w = 0·084)

TABLE 1
Basic Bond Lengths and Valence Angles in Cations of Dyes **III**–**V**

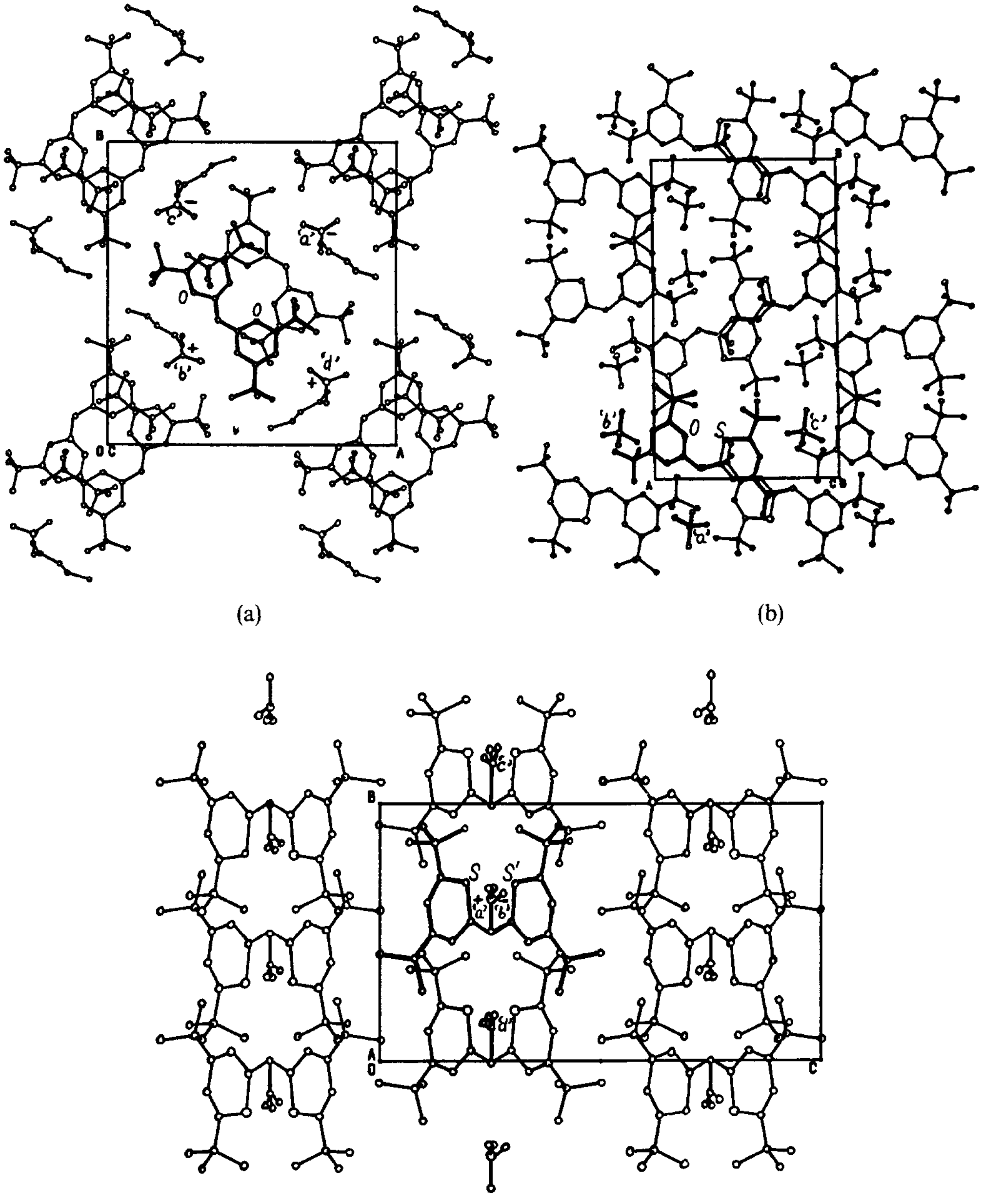
Atom	*Atom*	*Length* (*Å*)			*Atom*	*Atom*	*Atom*	*Angle* (°)		
		III	IV	V				III	IV	V
1	2	1·339(6)	1·724(6)	1·731(3)	2	1	6	122·8(5)	103·3(3)	105·0(1)
2	3	1·372(7)	1·402(6)	1·432(4)	1	2	3	117·5(5)	122·4(5)	120·0(2)
3	4	1·364(8)	1·384(7)	1·359(4)	2	3	4	123·6(5)	124·8(6)	126·0(2)
4	5	1·399(8)	1·408(8)	1·428(4)	3	4	5	117·2(5)	119·9(5)	121·1(2)
5	6	1·377(8)	1·354(7)	1·348(4)	4	5	6	120·6(6)	126·6(4)	126·4(3)
6	1	1·387(7)	1·704(4)	1·740(4)	5	6	1	118·3(5)	122·9(4)	121·5(2)
1′	2′	1·363(7)	1·412(8)	1 731(3)	2′	1′	6′	124·6(4)	115·1(4)	105·0(1)
2′	3′	1·343(6)	1·416(7)	1·432(4)	1′	2′	3′	116·5(5)	122·7(5)	120·0(2)
3′	4′	1·391(6)	1·377(8)	1·359(4)	2′	3′	4′	123·2(5)	118·7(5)	126·0(2)
4′	5′	1·388(8)	1·403(8)	1·428(4)	3′	4′	5′	117·0(5)	119·2(4)	121·1(2)
5′	6′	1·361(7)	1·337(6)	1·348(4)	4′	5′	6′	121·9(5)	121·8(5)	126·4(3)
6′	1′	1·371(6)	1·418(6)	1·740(4)	5′	6′	1′	116·9(5)	122·5(5)	121·5(2)
2	7	1·382(7)	1·402(8)	1·391(3)	1	2	7	122·6(4)	119·8(4)	122 1(2)
2′	7	1·376(7)	1·411(9)	1·391(3)	1′	2′	7	129·0(5)	118·0(5)	122·1(2)
					2	7	2′	128·2(5)	128·7(6)	133·8(2)

(**III**), 0·073 (R_w = 0·097) (**IV**) and 0·054 (R_w = 0·084) (**V**). All calculations were carried out using a 'PDP 11/23+' computer using the SDP program (for atomic positional and thermal parameters, refer to the authors). The main bond lengths and valence angles in **III**–**V** are shown in Table 1.

Quantum-chemical calculations were carried out using a CNDO/2 program with standard parameterization,[8] bond lengths and angles from the XRDA data being used. Tert-butyl groups were not taken into consideration.

3 RESULTS AND DISCUSSION

It is apparent from the XRDA data that the cations of the symmetric pyrylo-2- and thiopyrylo-2-monomethinecyanines (**III** and **V**) are practically planar (see Fig. 2a,c). The corresponding torsional angles are C-2–C-7–C-2′–C-3′ = −1·5°, C-2′–C-7–C-2–O = +0·5° in **III** and S–C-2–C-7–C-2′ = S′–C-2′–C-7–C-2 = +1·2° in **V**. The cation of the monomethinecyanine, **IV**, is less planar, its torsional angles being S–C-2–C-7–C-2′ = −6·1° and C-2–C-7–C-2′–O = +5·4°. It should be noted that dyes of this type, containing *N*-heterocyclic end groups (e.g. 1,1′-diethyl-2,2′-quinomonomethinecyanine), exists in the EE-configuration, the dihedral angle between heterocyclic residues of the cation being estimated as 40–60°.[9]



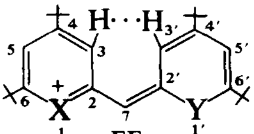
(a)

(b)

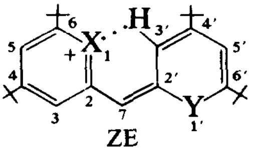
(c)

Fig. 2. Projections of crystal packings of structures **III–V**: (a) on the plane ab (**III**); (b) on the plane ab (**IV**); (c) on the plane ac (**V**). Signs '+' or '−' near anions indicate that they are disposed over or under cation plane, respectively.

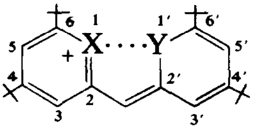
Dyes **III**–**V** can exist in the basic conformations EE, ZE and ZZ:



EE



ZE



ZZ

According to the XRDA data, pyrylo-2-monomethinecyanine (**III**) in the crystal state exists preferentially in the ZE-conformation (Fig. 2a), as it does in solution.[4,5] The ZZ-conformation is characteristic for both the unsymmetrical dye (**IV**) and the symmetrical thiopyrylo-2-monomethinecyanine, (**V**) in the crystal state (see Fig. 2b,c). Compound **IV** also exists in this form in solution,[4,5] but the conformation of solutions of dye **V**, was not identified, as indicated before.

The ZE-conformation of the pyrylo-2-monomethinecyanine (**III**) cation suggests slightly shortened contacts C-3′...O and H-3′...O (2·94 and 2·29 Å, the sums of Van-der-Waals radii being equal 3·00 and 2·46 Å,[10] respectively), though valence angles at atoms C-2 and C-7 are greatly increased (129·0 and 128·2°, respectively; see Table 1) if compared with the ideal bond angle at sp^2-hybridized carbon atom (120°). The distortion of the valence angles indicates substantial steric hindrance. It should be also taken into account that the angle at C-7 has to be less than 120° according to theoretical estimation: the electron density is concentrated on this C-atom (see Fig. 3), and hence the p-orbital contribution in its hybridized atomic orbitals is expected to increase.[11] Steric tension will decrease in the ZZ-conformation, thus enabling a single intramolecular contact O... O′, with a possible distance of 2·58 Å, and hence the valence angles are less distorted. However, strong Coulomb repulsion of the negatively charged oxygen atoms should occur in this case (see Fig. 3). Thus, this conformation is not advantageous. As far as the EE-conformation is concerned, this should result in considerable twisting of the conjugated chain, because of the marked shortening of H-3... H-3′ contacts, as in the case of 1,1-diethyl-2,2′-quinomonomethinecyanine.[9] Thus, steric tension of the cation should be noticeably greater in comparison with the ZE-conformation.

Dyes **IV** and **V** exist in an unusual ZZ-conformation (Fig.2b,c), which is less advantageous sterically than the ZE-conformation. The ZZ-form results in rather short intramolecular contacts of the heteroatoms X... Y, whilst the steric hindrance of ZE-form is mainly due to contacts X... H and X... C (if X = O, these contacts are almost free of tension, like **III**). Since the Van-der-Waals radii of carbon (1·71 Å), oxygen (1·29 Å) and especially hydrogen (1·17 Å) atoms are lower than that of the sulphur atom (1·84 Å),[10] shorter contacts X... H, X... C are less strained than S... S and S... O.

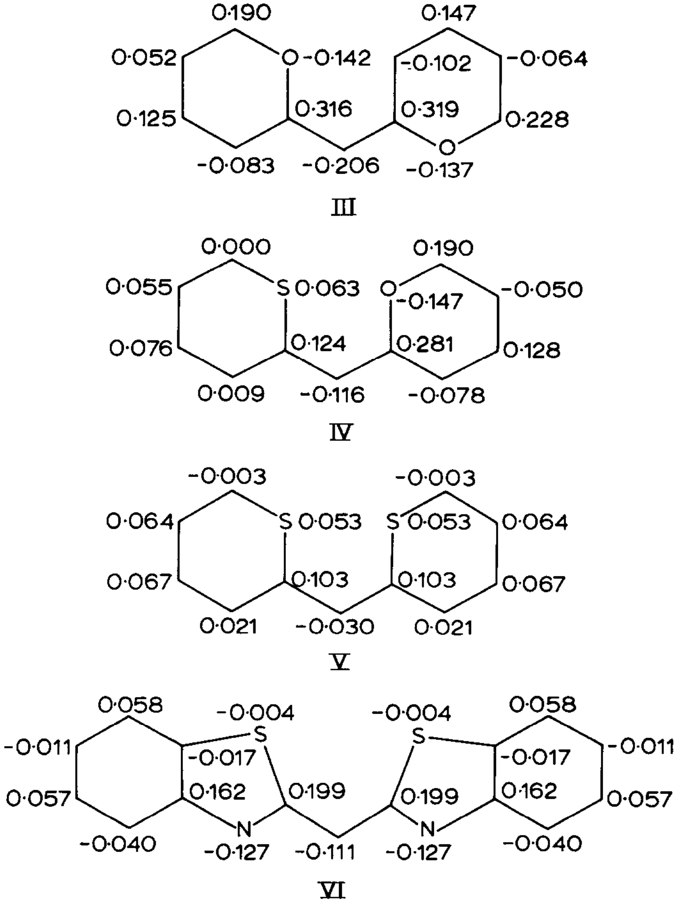
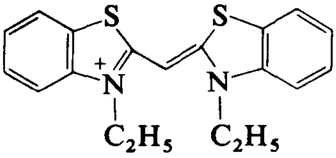


Fig. 3. Quantum-chemical calculations of electron charge distribution in the cations of dyes **III**–**VI** (via CNDO/2).

In **IV**, the distance S...O is 2·74 Å,[10] whilst the sum of the corresponding Van-der-Waals radii is 3·13 Å.[10] Thus, the contact is shortened by 0·39 Å. For structure **V**, the shortening of contact S...S′ is 0·58 Å (distance S...S′ and the sum of the Van-der-Waals radii is 3·1 and 3·68 Å, respectively). A considerable increase of the valence angle at the C-7 atom (128·7° for **IV** and 133·6° for **V**—see Table 1) compared with the ideal angle of 120° demonstrates the greater strain of these contacts. The increase of the relevant valence angle (by 7°), although lower than for **V** (by 13·6°), also occurs for **VI**.[11]

According to quantum-chemical calculations, the negative charge on the *meso*carbon atom of cation **VI** significantly exceeds that of cation **V** (see Fig. 3). On the basis of earlier results,[11] this should lead to a smaller angle at C-7 for **VI** compared with **V**.



VI

The distance between the sulphur atoms is 2·99 Å for the cation **VI**,[11] i.e. a value lower than the sum of two Van-der-Waals sulphur atom radii, as it is in the case of cation **V**. However, in contrast to the latter compound, **VI** exists in the conformation with minimum steric hindrances and its sulphur atoms are also almost uncharged. Repulsive forces are, therefore, relatively weak, thus enabling the sulphur atoms to be disposed opposite to each other.

The sulphur atoms in **V** carry considerable positive charges (see Fig. 3). Therefore this structure is disadvantageous, not only sterically, but also in respect of Coulomb interactions. The ZZ-conformation for cation **V** can be explained only by the electronic interaction of the non-bonded sulphur atoms. These interactions have been noted in a number of previous investigations of sulphur compounds (see, for instance, Ref. 12) and are pertinent to investigations to the abnormal colour characteristics of polymethine dyes containing sulphur heterocycles.[1,2,13,14] They should be also observed between the oxygen and sulphur atoms in **IV**, since the S... O distance in this case lies within the range of non-valency interactions of (2·00–3·25 Å),[15] as does the S... S′ distance in **V**. It should be noted that the ZZ-conformation of **IV** is additionally stabilized due to Coulomb attraction of opposite charges on the oxygen and sulphur atoms (see Fig. 3).

It is evident from the XRDA data that bond lengths alternate in heterocyclic residues of the cations **III**–**V** (see Table 1). It is significant that this alternation is quite pronounced even in **V**, which has a high packing symmetry, and it is responsible for the notable changes of bond lengths which occur on electronic excitation.[16] These changes result in the vibronic interactions becoming more intense, and hence the absorption bands broaden and the vibrational structure becomes more distinct. It is these effects which are characteristic of the electronic spectra of pyrylo-2-cyanines and their analogues.

The XRDA results also confirm the earlier suggestion about the orders of the bonds C-3–C-4, C-3′–C-4′ and C-5–C-6, C-5′–C-6′ in dye heterocyclic residues, which are almost double bonds (1·33 Å).[17] For instance, the lengths are 1·359 and 1·348 Å, respectively, for thiopyrylo-2-monomethinecyanine (**V**). Only these bonds, being the shortest, undergo the maximum change of their order on excitation and they thus contribute significantly to the vibronic interactions of the whole molecule.[16]

In the cations of **III–V**, bonds C–O and C–S are closer to single bonds (1·37 and 1·71 Å),[17] rather than to double bonds (1·21 and 1·66 Å).[17] This agrees with the previous supposition that the oxygen and sulphur atoms in pyrylo-2- and thiopyrylo-2-cyanines are slightly conjugated with the carbon chromophore.[1-3] Therefore, in contrast to the corresponding pyrido-2-cyanines, their main chromophore is constituted by the fragment XC-6C-5C-4C-3C-2C-7C-2′C-3′C-4′C-5′C-6′X′, rather than XC-2C-7C-2′X′. The former chromophore is much longer, and hence pyrylo-2- and thiopyrylo-2-cyanines are more deeply coloured compared with their nitrogen analogues or to the 4-isomers.

The disposition of anions differs notably in **III–V** (see Fig. 2a–c). The maximum symmetry of anion location relative to cation is realized in **V**: each cation is surrounded by four anions (ClO_4^-) that are symmetrically disposed with respect to atoms S, S′, C-2 and C-2′, which bear the greatest positive charges (see Fig. 3). There are two anions, ‘c’ and ‘d’, in the plane of cation on the two-fold symmetry axis, ‘c’ lying on the side of atoms S and S′ and ‘d’ near atoms C-2 and C-2′. Two more anions, ‘a’ and ‘b’, are disposed strictly over and under the plane of the cation near the positively charged atoms S, S′, C-2 and C-2′. Coulomb interactions between the counter ions bearing the maximum charges in this case are thus principally responsible for this type of packing, which is also promoted by the bulky tert-butyl groups. These groups hinder the approach of cations to each other, resulting in the intercation cavities being filled by the anions. Thus, multilayer translational ion-pair ‘sandwiches’ are formed in the crystal packing of thiopyrylo-2-monomethinecyanine. The whole structure is established due to Coulomb attraction between cations and anions. This interaction should also promote the stability of the ZZ-conformation of the cations of thiopyrylo-2-monomethinecyanine, with their ‘sandwich’ arrangement in the crystal packing.

The position of the anion in **IV**, which lies between the heterocyclic residues, is rather disadvantageous, because of the negatively charged oxygen atom. Therefore, in contrast to structure **V**, only one anion ‘a’ is disposed symmetrically relative to the cation on the side of the carbon atom. Two further anions, ‘b’ and ‘c’, lie on the external side of the tert-butyl groups, these being the substituents in the 6,6′ positions of heterocyclic residues.

As far as **III** is concerned, its crystals have no anions coplanar to the cation. This is evidently caused by the large negative charges on the oxygen and C-3′, atoms which are disposed opposite to each other. At the same time, the large positive charges on 6-6 and C-6′ atoms, as well as on C-2 and C-2′ atoms, enable the anions ‘a’ and ‘b’ to be located between the 6- and 6′-tert-butyl groups, and near to the central methine group. The anions ‘c’ and ‘d’ lie on both sides of the cation along its longitudinal axis.

In contrast to **V**, the cations of **III** and **IV** do not form translational 'sandwiches', since there is no anion between the heterocyclic residues that is able to 'link' cations together into 'sandwiches' due to Coulomb attraction forces. The formation of 'sandwiches' needs the presence of an anion, otherwise it is disadvantageous, since it results in cations with the same charge signs lying over each other. It is for this reason that, in **III**, the cations are mutually displaced to a notable degree. In **IV** they form pseudo-symmetric dimers in which the oxygen atoms of a cation are directed towards the sulphur atoms of another. The Coulomb attraction of these oppositely charged atoms stabilizes the packing.

Such considerable differences in the molecular packing of **III–V**, despite their similar chemical constitution, results in the facile formation of various ion pairs in the case of pyrylo-2-cyanines and their analogues. For this reason the absorption spectra of such dyes changes significantly in media of low polarity.

The information concerning the stereochemical configuration of **III–V** presented above offers an explanation for the features of the electronic spectra of pyrylo-2-cyanines and their analogues.

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