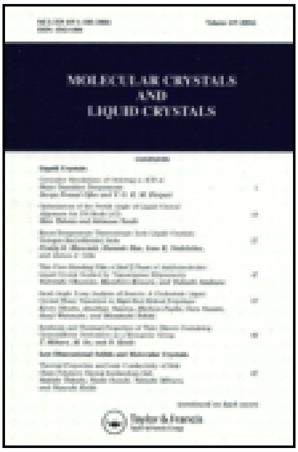

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

TOLMACHEV: Effect of the Solid Phase Structure upon Photochromic Properties of 4,4′-Bipyridine Derivatives

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To cite this article: Irina Grineva , Igor Krainov , Arkadi Polishchuk & Alexander Tolmachev (1992): TOLMACHEV: Effect of the Solid Phase Structure upon Photochromic Properties of 4,4′-Bipyridine Derivatives, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 211:1, 397-402

To link to this article: http://dx.doi.org/10.1080/10587259208025839

Mol. Cryst. Liq. Cryst. 1992, Vol. 211, pp. 397–402
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Printed in the United States of America

EFFECT OF THE SOLID PHASE STRUCTURE UPON PHOTOCHROMIC PROPERTIES OF 4,4'-BIPYRIDINE DERIVATIVES.

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(*Received July 12, 1991*)

Abstract In order to study the solid phase structure effects upon mechanism of photochromic transformations in 4,4'-bipyridine quaternary salt series new photochromic substances have been synthesized and their photochromic properties studied in single crystals. X-ray studies have been carried out, and effects of molecular and crystal structure of the substances in the ground state upon their photochromic properties were considered. Differences in molecular stacking have been found out for molecules with different photochemical properties.

Keywords: viologens, photochromism, x-ray studies, single crystal, charge transfer, packing analysis

The ability of 4,4'-bipyridine quaternary salts (viologens) to undergo high-speed reduction[1] (10^{-8}–10^{-9} s) under UV radiation is used in time-lag-free photochromic devices, information storage processes not involving silver, photocatalytic solar energy converters.[2]

In order to obtain new photochromic compounds of the bipyridine series and to study their photochemical properties we have synthesized, using the Menschutkin reaction between 4,4'-bipyridine and corresponding halides, the compounds I-V (Table I).

Alkylation of 4-4'-bipyridine is a two-stage process. Formation of mono-N-alkyl-4-4'-bipyridine is relatively easy; N-alkylation of the second nitrogen is hindered by a substantial electron density redistribution due to quaternization of the first nitrogen.

All the compounds I-V display photochromic properties in solutions and in polymeric matrices.

TABLE I Structural formulae of the compounds.

No	R_1	R_2	X
I	C_7H_{15}	C_7H_{15}	J
II	$C_{15}H_{31}$	$(CH_2)_2$-COOH	Br
III	$(CH_2)_2$-OH	$(CH_2)_2$-OH	Cl
IV	CH_2-$COOC_2H_5$	CH_2-$COOC_2H_5$	Cl
V	CH_2-COOH	CH_2-COOH	Cl

To study photochromic properties in the crystalline state, we have recorded reflection spectra of the irradiated viologen crystals using a Hitachi-330 spectrophotometer (Table II).

TABLE II Spectral characteristics of the compounds.

N	Ground state		Photoinduced form
	λ,nm	$E\times10^{-3}$, $\times mol^{-1}\times cm^{-1}$	λ,nm
I*	265; 375(475)	21.7; 1.4	—
II	265(300)	19.4	675
III	268(296)	19.8	610
IV	265(300)	16.5	630
V	264(290)	6.9	650

* no evidence of photochromic effects.

Crystalline samples were irradiated by unfiltered light of a low pressure 400 W mercury lamp for 60 s from a distance of 15 cm. Also presented in Table 2 are spectral characteristics in alcohol solutions of the compounds I-V in the ground state and, in parentheses, data on the reflection spectra of the non-irradiated crystals. It is evident from Table 2 that in the crystalline state photochromism is observed only for the compounds II-V.To explain this fact, we studied the effects of molecular and crystalline structure of the compounds I and V in the ground state upon their photochromic properties. For this purpose we have grown single crystals of the compounds I and V. X-ray studies were carried out using an automatic CAD-4 Enraf-Nonius diffractometer (MoK$_\alpha$-radiation, graphite monochromator, scan speed ratio $\omega:\theta$ =1.2:1, θ_{max}=26°).

Single crystals of the compounds I were grown from the alcohol-acetone solution (1:1). Triclinic single crystals of the compound I obtained in the form of thin plates, were red in colour and at 25°C were characterized by the following elementary ell parameters: a=6.368(3), b=7.580(2), c=14.965(4) Å, α=101.44(2), β=100.79(4), γ=91.91(3)°, V=693.7(9) Å^3, sp.gr. P $\bar{1}$, Z=1, d_{calcd}=1.456 g/cm^3. The values of the divergence factors were R=0.047 and R_w=0.062.

In the structure I the molecule is in the center of symmetry, determining an absolutely planar configuration of its bipyridine moiety. Carbon atoms of the alkyls characterized by the all-trans configuration are rotated by 86° in relation to the plane of the pyridine rings. With that, the molecule as a whole is in the trans-conformation (Fig.1).

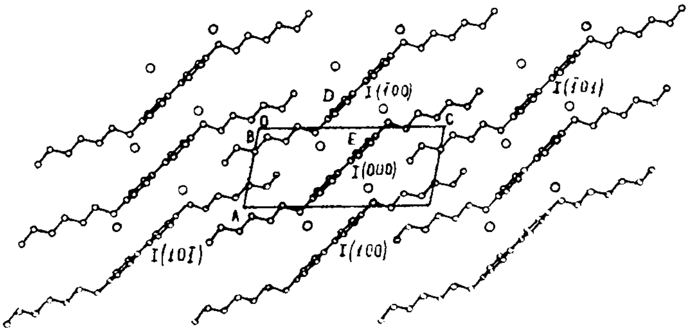

Figure 1 Stacked molecular packing of the cations I (projection along b axis).

In the crystals of the compound I molecules are stacked, which is confirmed by intermolecular interaction energy calculations.

According to energy calculations, the strongest interaction is between the molecules J(000)-J(100) and J(000)-J($\bar{1}$00) (Fig.1), which allows to distinguish stacks of molecules along the short crystallographic axis a.

The calculated data[3] on magnitudes of charges and bond orders in the bipyridinium dication (Fig.2) show that the given structure is a system of weakly bonded fragments with the bond orders averaged and electron density alternated over the pyridine cycle with the positive charge predominantly localized on the nitrogen atom.

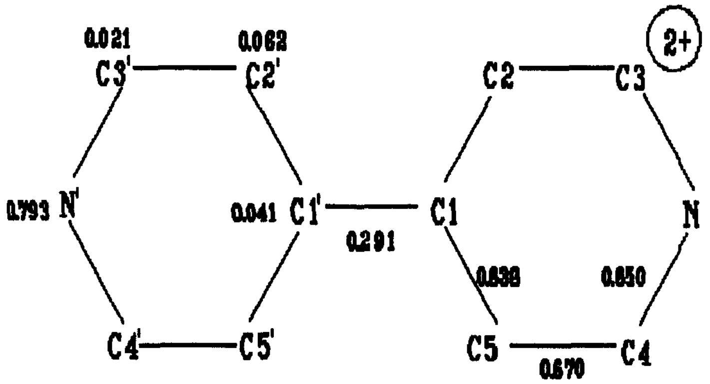

FIGURE 2 Molecular diagram of the 4,4'-bipyridinium dication.

The principal molecular packing feature in I (Fig.1) is anti-parallel stacking of the neighboring pyridine rings D,E. The distance between their centers is 3.766 Å, with regions of different electron density overlapping, which ensures charge transfer inside the stacks. The anions J^- in the crystals of the compound I (Fig.1) play the role of "linking" atoms between the molecules in stacks and between the stacks in the b axis direction.

The existence of a long-wave charge transfer band in solutions in the 375 nm region (Table 2) allows us to assume that the stack associates are partially conserved in solutions. The limiting case of such associates are dimers.

Let us consider now peculiar features of the crystal structure of the compound V, displaying photochromic properties in solutions, polymer matrices and as crystals. Colourless single crystals of the compound V grown from water solution, are prismatic in form and have the following parameters at 25°: a=8.415(3), b=9.442(6), c=10.370(3) Å, β=113.35(3)°, V=757(1) Å^3, sp.gr. $P2_1/C$, Z=2, d_{calcd}=1.524 g/cm^3. Divergence factors were R=0.036 and R_w=0.056.

In the crystal of the compound V the molecule is also in the center of symmetry and has planar configuration; end-chain C and O atoms lie in plane rotated by 74.7° in relation to the pyridine moiety plane (Fig.3).

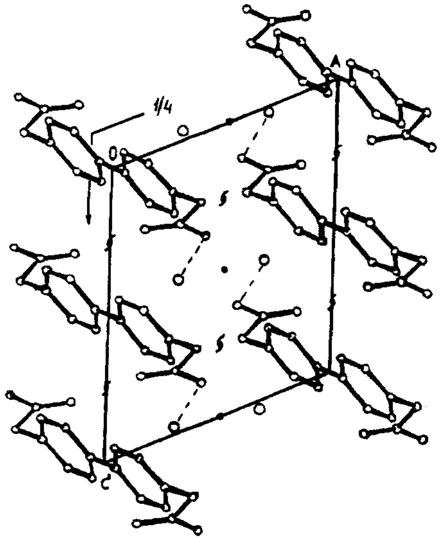

FIGURE 3 Molecular packing in the crystal V (projection along baxis). Hydrogen bonds are indicated by dashed lines.

The structure V is characterized by the presence in the crystal of hydrogen bonds O(1)-H...Cl with the following geometrical parameters: O(1)...Cl is 2.910 Å, the angle O(1)-H...Cl is 163.6°, O(1)-H - 0.89 Å (Fig.3).

As distinct from single crystals of the compound I with the stacked molecular packing, in the crystal V packing of the cation molecules is characterized by the absence of any energetically distinct associates, which is supported by intermolecular interaction energy calculations.

Thus, the nature of the substituent and the counter-ion, features of crystalline packing of the viologens do significantly affect photochromic properties in the crystalline state.

Charge transfer, determined by asymmetric distribution of electronic density in the bipyridine cycle and by the stacked molecular packing in the crystals of the compound I, causes photochromic properties to disappear in the solid state. As for hydrogen bonds (structure V), they favour electron transfer even under atmospheric oxygen.

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