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The Polymorphic Structures of a Squarylium Dye. The Monoclinic (Green) and Triclinic (Violet) Forms of 2,4 bis(2-hydroxy 4-diethylaminophenyl)-1,3-cyclobutadienediylium 1,3-diolate

Joel Bernstein [a] & Ehud Goldstein (choshen) [a]

[a] Department of Chemistry, Ben-Gurion University of the Negev, P.O. Box 653, Beer Sheva 84105, Israel

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The Polymorphic Structures of a Squarylium Dye. The Monoclinic (Green) and Triclinic (Violet) Forms of 2,4 bis(2-hydroxy 4-diethylaminophenyl)-1,3-cyclobutadienediylium 1,3-diolate

JOEL BERNSTEIN† and EHUD GOLDSTEIN (CHOSHEN)

Department of Chemistry, Ben-Gurion University of the Negev, P.O. Box 653, Beer Sheva 84105 Israel

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The title compound, a candidate for solar photovoltaic applications, crystallizes in at least two polymorphic structures. Triclinic form: a = 11.911 (4), b = 7.401 (9), c = 6.501 (7) Å, α = 92.78 (7), β = 111.9 (4), γ = 98.08 (6)°, $P\bar{1}$, Z = 1, R = .054, R_w = .046 for 955 reflections with $F_0 > 2\sigma(F_0)$. Monoclinic form: a = 15.72 (4), b = 7.283 (3), c = 9.591 (3) Å, β = 106.11 (8)°, $P2_1/a$, Z = 2, R = .084, R_w = .077 for 804 reflections $F_0 > 2\sigma(F_0)$. In both structures the geometric features of the essentially planar molecule are compatible with significant contributions from classical low energy resonance structures. Cocrystallization of the two modifications as well as two morphologies for the monoclinic form can be rationalized on the basis of competition between a small number of intermolecular interactions, which are discussed.

INTRODUCTION

The last two decades have witnessed a renewal in the potential utilization of organic solids in optical and electronic applications, and the organic dyes rank high among the materials which are prime candidates for these applications. A variety of molecules have been synthesized in the search for suitable materials. In particular, the

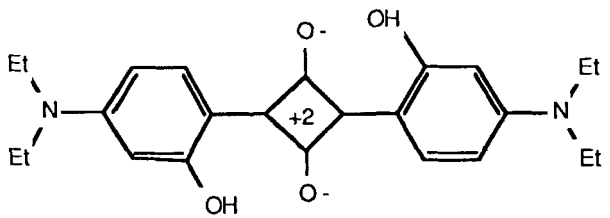
†Address correspondence to this author.

squarylium class of organic dyes has been studied for potential use in a variety of applications, including optical storage systems,[1] photovoltaic cells,[2] electrophotographic processes[3] and solar energy conversion.[4]

Clearly, the bulk properties of any candidate material depend as much on the packing motif in the crystal as on the molecular properties. The ultimate goal in studying and developing these substances is to be able to combine the knowledge of the required molecular and crystal structure in order to design the properties into the desired material. To meet this goal requires an understanding of the relationship between the structure and the properties of the solid.

One potentially very fruitful approach to investigating structure-property relationships is to study polymorphic systems. These systems have the distinct advantage that the molecular moiety is kept constant so the only variable from one material to the next is the three-dimensional structure of the various crystal forms. The combination of structural studies with physical measurements on polymorphic systems thus can yield particularly useful information towards the attainment of the goal of designing materials with specifically desired properties.

We have recently investigated the structural and spectroscopic properties of some organic dye systems with the aim of clarifying the relationship between their structure and optical properties.[5,6] Among them was the dimorphic squarylium dye **I**, which has been considered a prime candidate for electrooptical applications.[4a,b,7] An earlier preliminary report[6] on this material was followed by a detailed discussion of the spectroscopic properties.[8] We report here the details of the structural aspects of this system.[9]



I

EXPERIMENTAL

The material was provided by Exxon Research and was recrystallized from methylene chloride. The two forms were observed to cocrys-

tallize; they are easily distinguishable by their shape and their color. The significance of this cocrystallization will be discussed below.

Triclinic Form. Acicular crystals with a violet sheen are elongated along [001] and exhibit {100}, {1$\bar{1}$0} and {010} forms. The crystal morphology is shown in Figure 1a. Cell constants were determined from a least squares fit of 14 reflections $3.7° < 2\theta < 17.2°$; they are given in Table I. Data were collected on a Syntex automated diffractometer with a scan rate which varied from 3–24° min^{-1}, and were corrected for Lorentz and polarization factors prior to averaging equivalent reflections. The structure was solved via direct methods with the SHELX76[10] structure package; 11 of the thirteen non-hydrogen atoms appeared in the E-map; the remaining two appeared in subsequent difference Fourier maps. Least squares refinement with

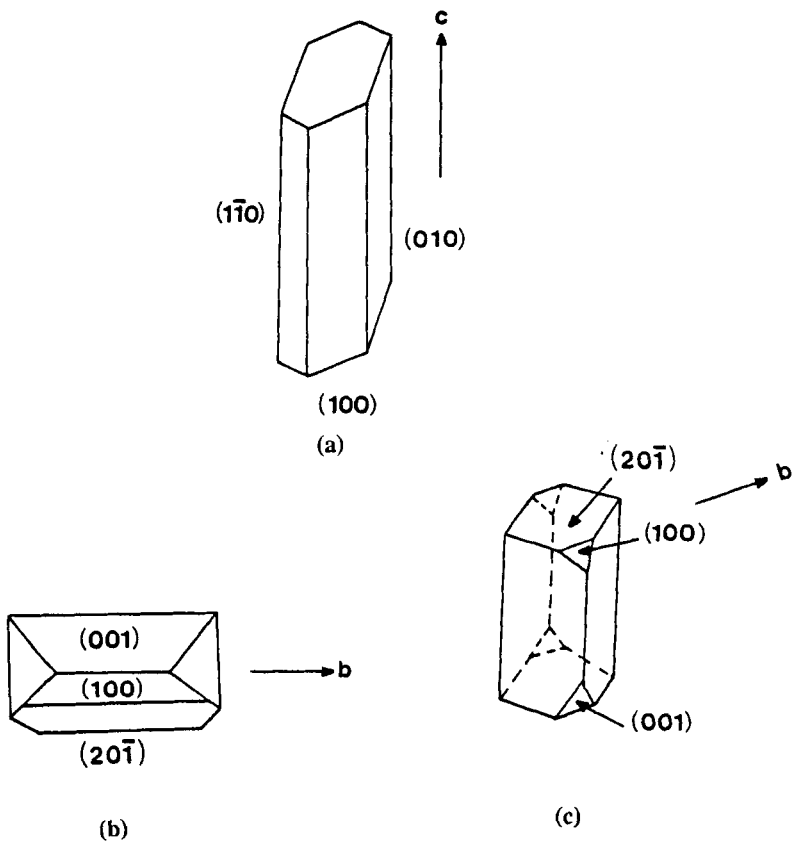


FIGURE 1 Morphologies of the two crystal forms. (a) triclinic crystal; (b,c) monoclinic crystal.

TABLE I

Crystal data for the two polymorphs of **I**
$C_{24}H_{28}N_2O_4$, M.W. 408.26
All diffraction measurements with MoKα radiation (λ = .71069 Å)

	Triclinic Form	Monoclinic Form
a(Å)	11.911(4)	15.72(4)
b	7.401(9)	7.283(3)
c	6.501(7)	9.591(3)
α,β,γ(°)	92.78(7), 111.9(4), 98.08(6)	106.11(8)
V(Å^3)	523.4	1055.6
space group	$P\bar{1}$	$P2_1/a$
ρ_c(g-cm^{-3})	1.30	1.29
ρ_m(g-cm^{-3})	1.31	1.28
Z	1	2
$2\theta_{max}$ for data collection (°)	50	55
Total intensities measured	2170	2741
Total unique intensities	1445	1791
Total number $F_o > 2\sigma(F_o)$	955	804
Final R for $F_o > 2\sigma(F_o)$	.054	.084
Final R_w for $F_o > 2\sigma(F_o)$	.046	.077

isotropic temperature factors converged at $R = 0.089$ at which point 12 of the 14 hydrogen atoms were revealed in a difference map. The remaining hydrogen atoms were found in subsequent cycles. The difference map at convergence ($R = 0.062$) strongly suggested the presence of disorder which involves the positions of the hydroxyl groups. A model for the disorder which places the hydroxyl oxygens for both rings at the second position *ortho* to the cyclobutyl portion of the molecule with an occupancy of ~10% is chemically reasonable and refined satisfactorily to $R = 0.054$ and $R_w = 0.046$.

Monoclinic Form. Well formed green prismatic crystals, typically 3 mm long and 1 mm wide exhibit {100}, {010}, {001}, {20$\bar{1}$} and {012} forms. Two morphologies are observed (Figures 1b and 1c). The more common one was elongated along {010} with yellow-green zonal faces identified as {001}, {100} and {20$\bar{1}$} forms, while the small, rose-colored tip faces were identified as belonging to the {012} and {010} forms. The second morphology appeared after the solution had been allowed to evaporate for six days. This morphology exhibited large rose-colored faces and small yellow-green ones.

Cell constants determined from a least squares fit of 15 reflections $4.3° < 2\theta < 17.8°$ are given in Table I. Data were measured and corrected as above. The structure was also solved via direct methods,

all 13 non-hydrogen atoms appearing in the best E-map. The final stages of the refinement were complicated by disorder in the region of the diethylamino groups in addition to that of the hydroxyl groups similar to that described above. The same model employed for the triclinic form for the latter was successful in this case. A model involving statistical distribution of two orientations for the diethylamino group refined successfully.

Final coordinates for both structures are given in Table II; temperature factors and structure factors have been deposited.

TABLE IIA

Atomic coordinates × 10^4 for nonhydrogen atoms and × 10^3 for hydrogen atoms for the triclinic structure

Atom	*x*	*y*	*z*
O7	1959(2)	−1837(3)	4851(5)
O12	0785(2)	−2642(3)	0465(4)
N	2832(2)	2709(3)	10886(4)
C1	4883(4)	1757(7)	12434(9)
C2	3596(4)	1583(5)	12412(7)
C3	3670(5)	6060(6)	11538(11)
C4	2778(4)	4525(5)	11808(7)
C5	2277(3)	2142(4)	8664(5)
C6	2380(3)	0431(5)	7736(6)
C7	1788(3)	−0158(4)	5507(6)
C8	1053(3)	0943(4)	4013(5)
C9	0967(3)	2681(4)	4953(6)
C10	1550(3)	3266(5)	7168(6)
C11	0450(3)	0397(4)	1716(6)
C12	0346(3)	−1195(4)	0191(6)
H1A	528(4)	088(5)	1321(7)
H1B	486(3)	147(5)	1077(7)
H1C	536(3)	308(5)	1291(6)
H2A	319(3)	025(4)	1206(5)
H2B	360(3)	190(4)	1381(6)
H3A	360(4)	74(7)	1220(8)
H3B	463(4)	574(6)	1201(8)
H3C	354(4)	614(6)	1003(8)
H4A	295(2)	442(4)	1340(5)
H4B	192(3)	478(4)	1117(5)
H6	284(3)	−034(4)	871(5)
H9	038(3)	355(4)	390(4)
H10	148(3)	445(4)	778(5)
O'7†	0447(22)	3989(32)	3639(4)
OH(0)	158(6)	−217(8)	341(12)

†Occupancy of O7 and O'7 are .91 and .09 respectively.

TABLE IIB

Atomic coordinates $\times 10^4$ for nonhydrogen atoms and $\times 10^3$ for hydrogen atoms for the monoclinic structure (primed atoms are disordered—see text).

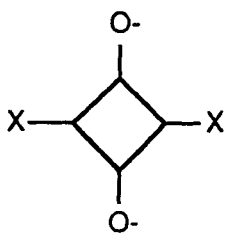
Atom No.	x	y	z
N	3366(5)	12951(6)	2138(9)
O7	5405(3)	8099(7)	2336(5)
O12	3987(2)	4975(5)	6278(4)
C1	1718(5)	13287(14)	1770(12)
C2	2647(4)	15936(11)	2500(8)
C3	3252(12)	13316(2)	−0448(10)
C4	3688(8)	13969(15)	1076(10)
C5	3642(3)	11205(5)	2516(5)
C6	4359(4)	10348(8)	2157(7)
C7	4733(3)	8775(7)	2796(5)
C8	4405(3)	7904(6)	3863(4)
C9	3704(3)	8789(7)	4204(4)
C10	3325(4)	10346(8)	3609(6)
C11	4743(3)	6248(6)	4509(5)
C12	4549(3)	5001(7)	5579(5)
H1A	174(4)	1206(11)	211(7)
H1B	130(4)	1427(7)	211(7)
H1C	162(5)	1349(10)	072(8)
H2A	275(8)	1582(17)	200(12)
H2B	262(6)	1345(12)	355(5)
H3A	371(5)	1218(10)	−033(12)
H3B	341(6)	1195(13)	−031(11)
H3C	373(5)	1427(10)	020(8)
H4A	334(6)	1526(7)	102(10)
H4B	424(3)	1438(13)	−120(11)
H6	456(3)	1083(7)	148(5)
H9	340(2)	831(5)	503(3)
H10	280(3)	1063(6)	373(5)
H(O)	546(4)	686(9)	249(6)
	Disordered atoms ($\times 10^3$)		
O7′	362(2)	783(5)	501(4)
N′	318(1)	1252(2)	161(1)
C1′	254(1)	1462(2)	302(2)
C2′	236(1)	1318(2)	184(2)
C3′	418(1)	1452(2)	064(1)
C4′	341(1)	1318(1)	032(1)
H1A′	298(4)	1410(9)	401(5)
H1B′	183(6)	1374(13)	195(10)
H1C′	279(5)	1508(11)	221(9)
H2A′	189(7)	1354(15)	140(9)
H2B′	292(6)	1242(15)	172(12)
H3A′	463(6)	1417(12)	166(10)
H3B′	382(5)	1559(8)	102(9)
H3C′	406(6)	1469(13)	−051(2)
H4A′	334(5)	1355(9)	−080(2)
H4B′	342(6)	1330(13)	144(3)

DISCUSSION

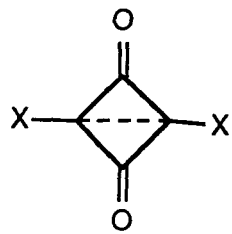
Molecular geometry

The atomic numbering is given in Figure 2. Bond lengths and bond angles for both polymorphs are presented in Table III. There is considerable agreement in these features between the molecules found in the two forms, and the geometric features of the squarylium system are all within three e.s.d.'s of those reported earlier.[5,11]

Except for the two ethyl groups the molecule, as expected, is essentially planar in both structures. The planarity of the squarylium is consistent with its crystallographic site symmetry which also requires that the phenyl rings be parallel. In addition to the three squarylium derivatives previously reported,[5,11,12] two analogous compounds, in which one[12] or two[13] of the oxygens on the cyclobutanedione system have been replaced by sulfurs have been reported. As Schleyer has noted,[12] these molecules may all be considered as derivatives of squaraines, which in turn may be represented by **IIa**, the cyclobutadiene dication, or by **IIb**, bicyclobutanedione. In all those studied to date the four-membered ring with its oxygen or sulfur substituents is planar. Schleyer *et al* also carried out ab initio and semi-empirical molecular orbital studies on these systems. They found that only those with very poor donor substituents, such as alkyl and perhaps phenyl would lead to a preference for non-planar structures, and even these would be considerably unstable. Hence this system, with relatively strong donor groups would be expected to be planar as is found.



IIa



IIb

The planar structure is compatible with the resonance structures **IIIa** and **IIIb**, which should be manifested in the following trends in the geometric features: 1) a shortening of the N—C(5) bond compared to a normal N-alkyl substituted aniline, 2) a lengthening of the

IIIa **IIIb**

C(12)—O(12) bond over a normal carbonyl value, 3) the presence of a quinoidal structure in the rings, 4) a shortening of C(8)—C(11) compared to a normal sp^2-sp^3 bond, and 5) significant double bond character in the four-membered ring. The data in Table III indicate that all of these trends are followed. The N—C(arom) bonds (1.36Å) are significantly shorter than the normal value of 1.43Å,[15] and compare favorably with that in *p*-nitroaniline (1.35Å)[16] in which there is a significant contribution from the quinoidal resonance form. The C—O bonds on the four-membered ring are slightly more than 3 e.s.d.'s longer than the 1.23 Å value generally accepted for a carbonyl bond length[17] with a value that is almost midway between that of the carbonyl and the 1.30Å observed for C—OH in carboxylic acids.[18] The latter is probably a more reasonable value for comparison than the C—OH length of 1.431Å observed in a cyclobutane-1,3-diol.[18] The quinoid structure is definitely present in the 6-membered rings with C(9)—C(10) and C(6)—C(7) being significantly shorter than the other four bonds. The values are, in fact, very similar to those representative of quinones.[19] The C—C exocyclic bonds connecting the two rings are typical of those found in benzene,[15] and for the exocyclic bonds in an earlier studied squarylium dye,[18] consistent with the proposed resonance structures. Finally, the C—C bond lengths in the 4-membered ring are about 0.08Å shorter than those in the clearly aliphatic 2,2,4,4-tetramethylcyclobutane-trans-1,3-diol,[17] also consistent with these resonance structures.

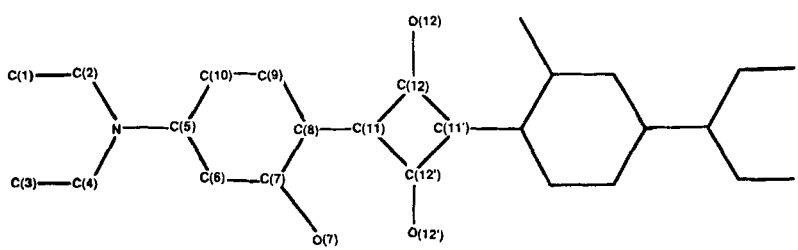


FIGURE 2 Atomic numbering for both structures.

TABLE III

Bond lengths (Å) and bond angles (°) for both polymorphs of I.

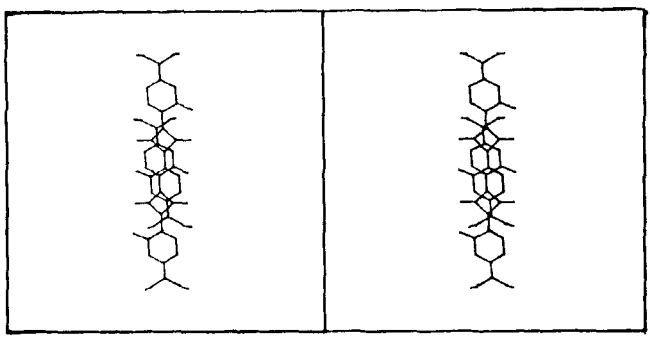
Bond Lengths	Triclinic Form	Monoclinic Form
C(1)—C(2)	1.517(7)	1.51(1)
C(2)—N	1.459(5)	1.46(1)
N—C(4)	1.462(5)	1.46(1)
C(3)—C(4)	1.502(7)	1.51(1)
N—C(5)	1.359(4)	1.360(6)
C(5)—C(6)	1.414(5)	1.412(7)
C(5)—C(10)	1.429(5)	1.425(7)
C(6)—C(7)	1.369(5)	1.354(8)
C(7)—C(8)	1.421(4)	1.418(8)
C(8)—C(9)	1.428(5)	1.392(6)
C(9)—C(10)	1.359(5)	1.334(8)
C(8)—C(11)	1.402(4)	1.392(6)
C(11)—C(12)	1.462(5)	1.465(7)
C(11)—C(12′)	1.460(5)	1.458(7)
C(7)—O(7)	1.363(6)	1.346(7)
C(12)—O(12)	1.244(6)	1.249(6)
Bond Angles		
C(1)—C(2)—C(3)	113.7(4)	116.7(7)
C(2)—N—C(4)	117.4(3)	111.0(7)
C(3)—C(4)—N	114.1(4)	111.4(10)
C(2)—N—C(5)	120.8(3)	127.4(6)
C(4)—N—C(5)	121.3(4)	121.0(7)
N—C(5)—C(6)	122.1(3)	124.4(5)
N—C(5)—C(10)	120.6(3)	117.1(5)
C(6)—C(5)—Cl(10)	117.3(3)	116.8(4)
C(5)—C(10)—C(9)	117.7(3)	118.9(5)
C(5)—C(6)—C(7)	122.0(3)	122.6(5)
C(6)—C(7)—C(8)	121.2(3)	120.4(5)
C(7)—C(8)—C(9)	116.3(3)	115.7(4)
C(8)—C(9)—C(10)	122.2(3)	125.6(4)
C(7)—C(8)—C(11)	122.7(3)	122.6(4)
C(9)—C(8)—C(11)	120.5(3)	121.7(5)
C(8)—C(11)—C(12)	135.3(3)	136.2(4)
C(8)—C(11)—C(12′)	136.1(3)	135.9(4)
C(11)—C(12)—O(12)	135.5(3)	134.6(5)
C(11′)—C(12)—O(12)	133.1(3)	133.4(5)
C(12)—C(11)—C(12′)	88.6(3)	87.9(4)
C(11)—C(12)—C(11′)	91.4(3)	92.0(4)
C(6)—C(7)—O(7)	115.5(3)	116.3(4)
C(8)—C(7)—O(7)	123.3(3)	123.3(5)

Crystal structure

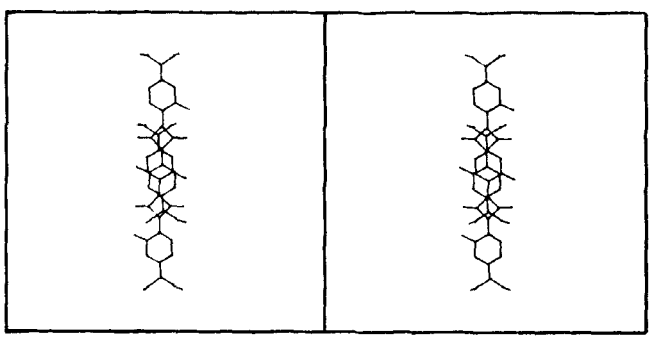
As we have pointed out earlier,[6] polymorphic materials are almost ideal systems for the study of structure-property relationships. In the case of the material reported on here the ultimate question is one of a collective property of the bulk—the photovoltaic response—as a function of the *inter*molecular relationships in the crystal. As noted

above the chemical moiety is constant for the two crystal structures so that a direct relationship may be found between the spectral properties (and associated photovoltaic response) and the structure of the solid. We concentrate here on the structural aspects.

This pair of structures provides a rather fortuitous system for probing and understanding the structural variations among polymorphs. The triclinic structure is virtually the simplest model for conceptualizing the structure of a molecular crystal, with all molecules translationally equivalent, as shown for instance in Figure 3a. The monoclinic structure, on the other hand, presents one of the simplest perturbations possible with the addition of the screw axis (and the



(a)



(b)

FIGURE 3 View of translationally related molecules in the two structures. In both cases the view is on the plane of the reference molecule. (a) triclinic structure, *c*-axis translation; (b) monoclinic structure, *b*-axis translation.

glide plane resulting from the presence of the center of symmetry to yield the $P2_1/a$ space group) as shown in any of the views of Figure 7. This difference in packing is the source of the significant difference in spectral response between the two forms[6] and provided the framework for the theoretical interpretation of the physical basis of the variation.[8]

Armed with an understanding of the structure-property relationship for a system such as this, it is natural to ask the next question: namely, how is it possible to control the crystal growth process to generate the polymorphic structure with the desired solid state properties? The conditions for growing the various polymorphs provide valuable information in this regard. We noted earlier that the two forms of **I** often appear simultaneously in the crystallization vessel. In view of the difference in structure noted above, we initially found this phenomenon somewhat surprising, since it implies a near energetic equivalence of the two forms in spite of the apparent significant difference in packing motif. A more detailed examination of the packing, however, reveals the reason for this cocrystallization.

The two structures viewed on the best plane of the reference molecule are shown in Figure 3. In this view the structures are virtually indistinguishable. In both cases the two molecules are related by a lattice translation; in the triclinic structure the translation is along

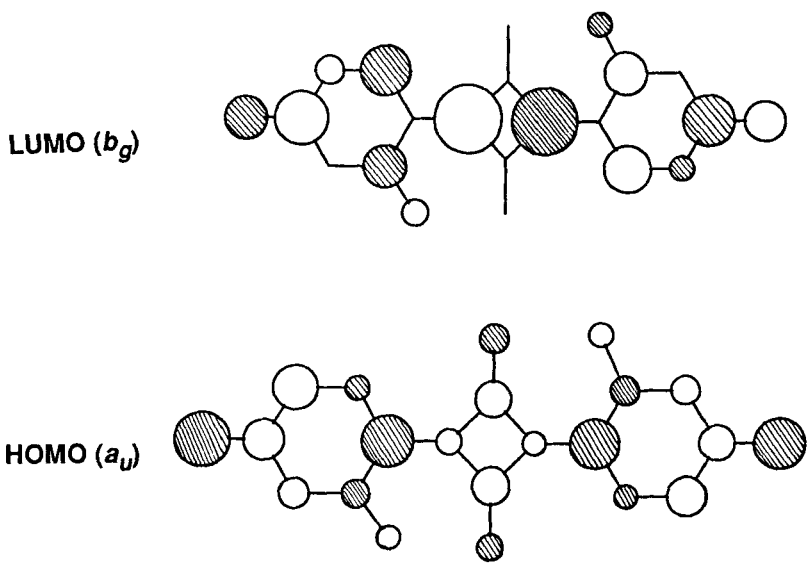


FIGURE 4 Frontier molecular orbitals for **I**.

the *c* axis, while in the monoclinic structure a *b*-axis translation relates the pair of molecules. In spite of the similarity in the overlap pattern, the plane-to-plane spacing differs significantly, being 3.40Å and 3.86Å for the triclinic and monoclinic forms respectively. This strongly suggests that the plane-to-plane stacking is the dominant interaction in this system, and that the growth of the monoclinic form is obtained by the addition of the screw axis relating the plane-to-plane stacks of molecules.

The nature of the interaction between molecules related in this fashion is of some interest. The possibility of a charge-transfer interaction based on orbital overlap arguments must be ruled out for reasons of symmetry. The HOMO and LUMO for the molecule as obtained from extended Huckel calculations[20] are shown schematically in Figure 4. For the C_{2h} point group the HOMO and LUMO belong to the a_u and b_g irreducibile representations, hence precluding orbital interaction. The partial atomic charges based on the Mulliken population analysis of the same calculation are given in Figure 5. In general the charges are consistent with the resonance structures **IIIa** and **IIIb**. The negatively charged nitrogen represents the lone pair of electrons which interacts with the formally positive squarylium ring as a result of the translation. Some other favorable "electrostatic" interactions are also present, but the one just described appears to be the dominant one. The fact that the two forms crystallize simultaneously indicates that the additional symmetry element present in the monoclinic structure is a minor, relatively low energy perturbation on the basic stacking motif.

In many cases, the crystal habit is also an important factor in the ultimate utilization of a especially substance especially when surface-

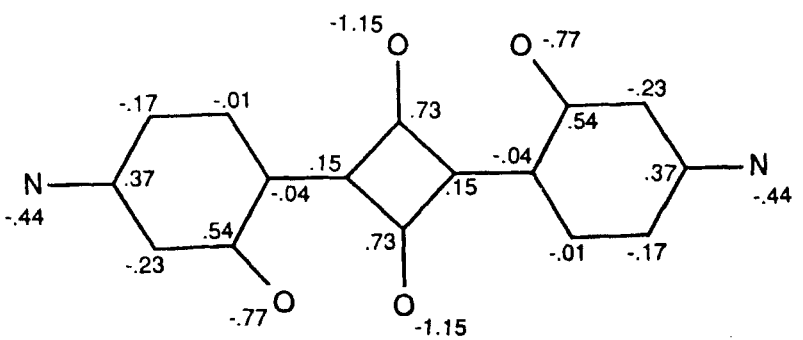


FIGURE 5 Partial atomic charges for **I** based on Mulliken population analysis of extended Huckel molecular orbitals.

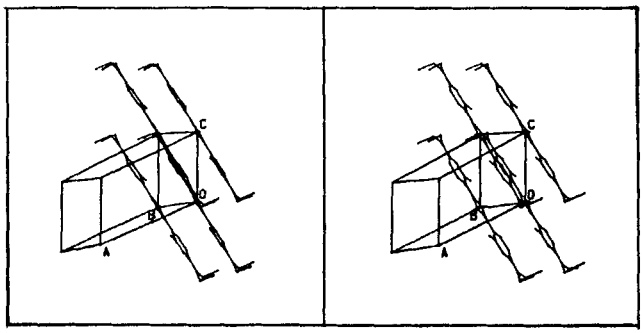
related phenomena are involved. The triclinic crystals are prisms elongated along the crystallographic *c* axis. The views of the structure given in Figure 6 contain molecules which are related only by a *c*-axis translation, the plane-to-plane interaction which dominates the packing motif. The elongation along [001] indicating the fastest rate of growth in this direction is consistent with this being the dominant intermolecular interaction, and the views on the three zonal faces give very clear evidence of how this leads to the observed crystal morphology.

The appearance of different habits for the monoclinic form is also circumstantial evidence for the delicate balance of forces involved in the crystal growth process. As noted in the experimental section, two habits appear for the monoclinic system (Figure 1b,c). For the apparently more rapidly growing (*i.e.* kinetically controlled) prismatic green habit, the crystals are elongated along the *b*-axis with prominent yellow-green {001}, {100} and {20$\bar{1}$} forms (Figure 7), and much less prominent rose-colored {012} and {010} forms (Figure 8). This indicates that a preference for growth along the *b* axis, or nearly so under these initial crystallization conditions.

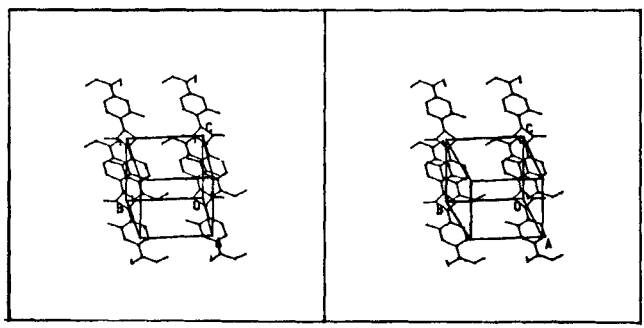
On the assumption that the molecular overlap due to the *b*-axis translation is the dominant intermolecular interaction, it is readily seen from the projections on these three faces how new molecules will easily add to the existing stack leading to the observed elongation. On the other hand the two [100] zonal faces represent competition in the stacking direction. For one side of the 'branch' of the herring bone we are looking very much on the plane of the *b*-related (and favorably overlapped) molecules. This arrangement does not favor the formation of the (012) face. The other 'branch' of the herring-bone indicates a direction which does not lead to elongation along a direction perpendicular to this face. In a rapid crystallization the first interaction appears to dominate and the face does not appear. Under more nearly equilibrium conditions the second interaction is also permitted, leading to the development of this face.

The projection on the (010) face clearly indicates how the stacks based on *b*-axis translation form normal to the face, a situation which is not favorable for the development of the face, especially under conditions varying from equilibrium. When the latter are more nearly obtained, the stacking does not dominate as strongly, molecules can attach to the crystal in other directions, and this face may be formed.

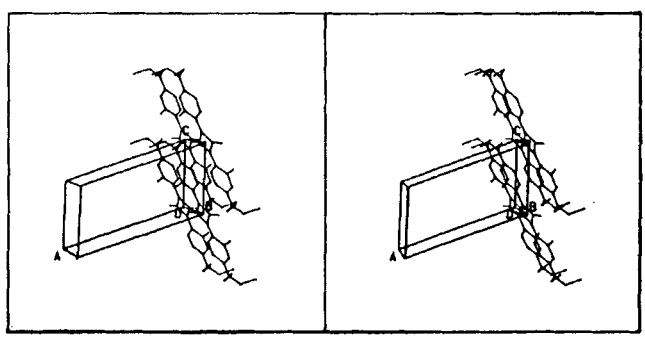
In addition to providing details on the molecular geometric properties of a relatively little studied, but potentially commercially important class of compounds, the present investigation has also dem-



(a)



(b)



(c)

FIGURE 6 Stereoviews of the triclinic structure projected onto the three [001] zonal prismatic faces shown in Figure 1a. In all three views the *c* axis is vertical, corresponding to the orientation in Figure 1a. (a) projection on $(1\bar{1}0)$ face; (b) projection on (100) face; (c) projection on (010) face.

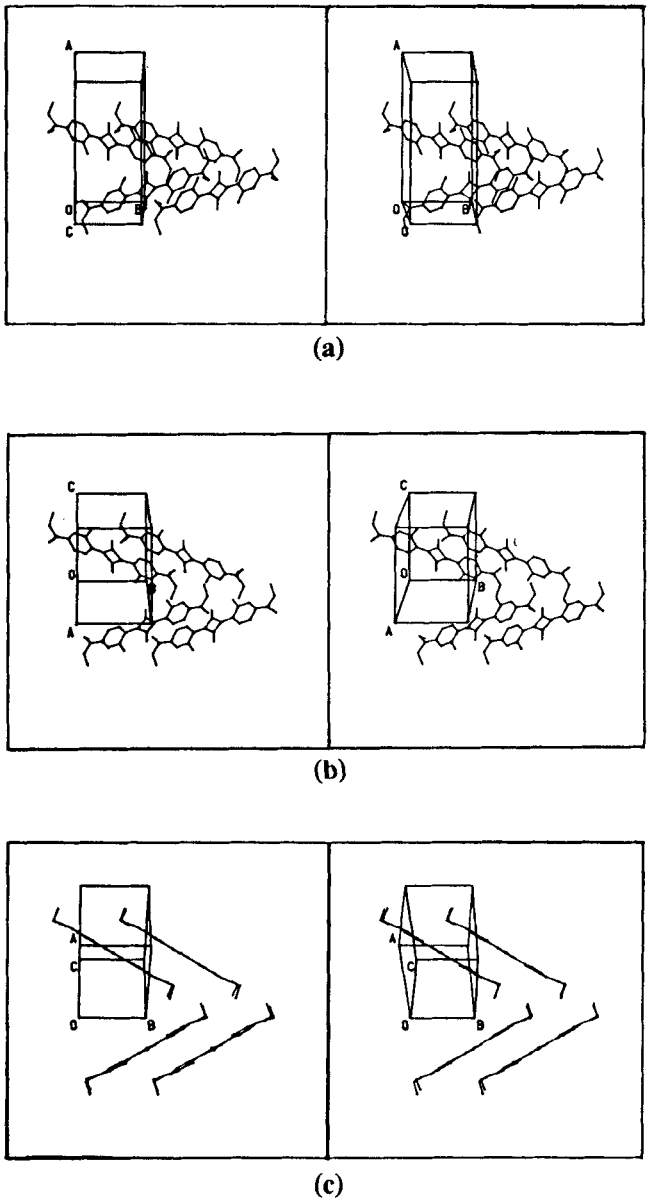


FIGURE 7 Stereoviews of the monoclinic structure projected onto the three [010] zonal prismatic (green) faces shown in Figure 1b. In all three views the *b* axis is horizontal, corresponding to the orientation in Figure 1b. (a) projection on the (001) face; (b) projection on the (100) face; (c) projection on the (20$\bar{1}$) face.

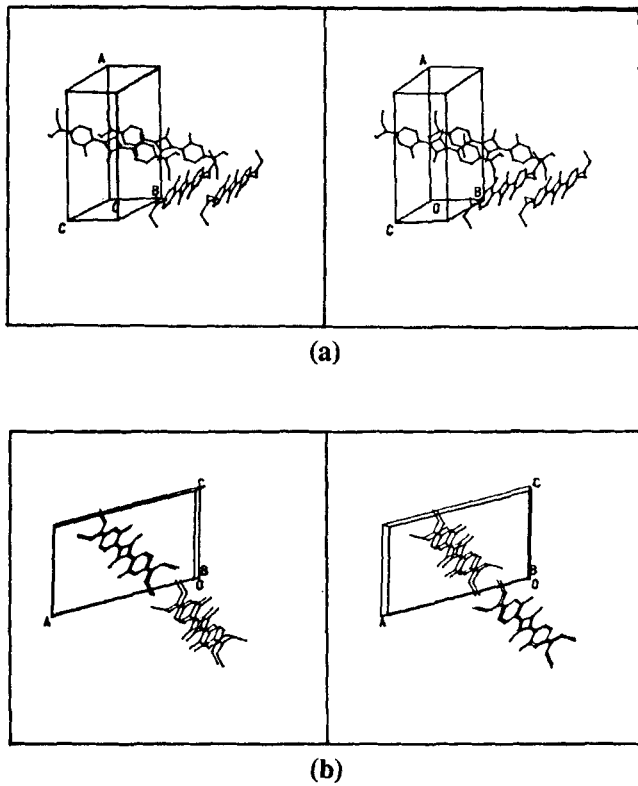


FIGURE 8 Stereoviews of the monoclinic structure projected onto the two [100] zonal (rose) faces. (a) Projection on the (012) face; (b) projection on the (010) face.

onstrated the kind of useful structural information which can be extracted from a careful examination of the packing in polymorphic structures. This can be especially meaningful in the interpretation of physical properties which are based on the extensive structural properties of the solid, and then in the preparation of additional materials with predesigned solid state properties.

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