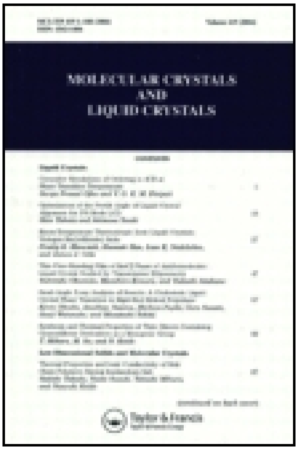

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Polymorphism and the Molecular and Crystal Structures of a Second Order Nonlinear Optical Compound Containing a 1,3-Dithiole Ring

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Polymorphism and the Molecular and Crystal Structures of a Second Order Nonlinear Optical Compound Containing a 1,3-Dithiole Ring

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[Cyano(ethoxycarbonyl)methylene]4,5-dimethyl-2-ylidene-1,3-dithiole, designed as an organic nonlinear optical material for the second harmonic generation (SHG), exhibits crystallographic polymorphism: the SHG inactive α-form crystallizes in the centric, triclinic space group $P\bar{1}$ from acetone solution, while the SHG active β-form does so in the non-centric $P1$ from ethanol solution. In the β-crystal, all the molecular dipole moments favorably align with same orientation in layers.

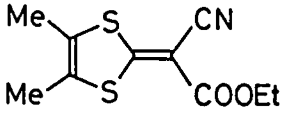
Keywords: second order nonlinear optical substance, second harmonic generation (SHG), polymorphism, molecular structure, crystal structure, dithiole

1. INTRODUCTION

Crystallographic polymorphism indicating more than one possible crystal structure for a substance has been the subject of much interest in the search for nonlinear optical materials, principally in the form of bulk single crystals showing SHG. Often polymorphism appears due to slight differences in the crystal growth environment, such as temperature and solvents. Crystal structures of three such examples have been reported so far.[1]

[Cyano(ethoxycarbonyl)methylene]2-ylidene-1,3-dithioles (formulae 1-3) have been designed, synthesized, and characterized for nonlinear optical properties. Compound 1 shows efficient SHG of magnitude 24 times that of urea.[2] Compound

2 is also active, but compound 3 is inactive. Here the X-ray molecular and crystal structures for polymorphic crystals of 1, obtained from solutions of different solvents, are reported.



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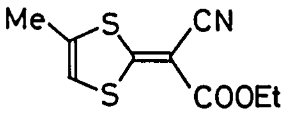

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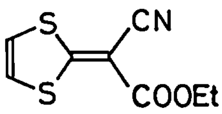

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2. EXPERIMENTAL

a. Crystallization

Slow evaporation of the acetone from a solution of compound 1 at room temperature gave almost colorless, transparent, plate-like crystals, designated the α-form. In contrast crystallization from an ethanol solution produced colorless, transparent, columnar crystals, designated the β-form. On irradiation with YAG-laser light, the β-form crystals exhibited highly efficient SHG, whereas the α-form crystals were inactive.[2] Thus novel polymorphism due to differences in the solvents of crystallization was found.

b. X-Ray diffraction

Preliminary oscillation and Weissenberg photographs of both crystals indicated the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ was assumed for the SHG inactive α-form and the noncentric space group P1 for the SHG active β-form; later these space groups were confirmed. These findings are consistent with the general principle for SHG. The crystallographic data are summarized in Table I. Accurate unit cell parameters were obtained with graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å) from the least-squares treatment of 2θ angles of high-angle reflections carefully measured on a Rigaku four-circle diffractometer.

The integrated intensity data were collected on the diffractometer. Details of the intensity measurements are given in Table II. To check electronic and crystal stability, the intensities of five reflections were measured after every 50 reflections. No remarkable variation was observed for these monitoring intensities during the data collection. The intensities were corrected for the Lorentz and polarization factors, but not for absorption. The reflections of which observed structure amplitudes exceeded three times their estimated standard deviations (e.s.d.) were considered as observed and used for the structure determinations.

c. Preliminary X-ray studies on compounds 2 and 3

Many attempts were made to obtain suitable crystals for X-ray diffraction, but were unsuccessful. Needle crystals of compound 2 obtained from a methanol solution were monoclinic with a unit cell volume V = 510 Å^3 and Z = 2, the space group being probably $P2_1$. Plate-like crystals of compound 3 obtained from an acetone solution were also monoclinic, and from the systematic extinctions of

TABLE I

Crystal Data*

	α-form	β-form
Formula	$C_{10}H_{11}NO_2S_2$	$C_{10}H_{11}NO_2S_2$
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	P1
Unit cell dimensions		
a/Å	8.711(2)	8.043(9)
b/Å	9.748(2)	9.018(8)
c/Å	7.800(1)	4.088(7)
α/°	95.50(2)	97.81(13)
β/°	107.67(2)	93.71(12)
γ/°	109.14(2)	98.13(9)
Volume, V/Å^3	582.0(2)	289.7(6)
Z	2	1
D_X/g cm^{-3}	1.3771(5)	1.383(3)
D_m/g cm^{-3}**	1.372	1.378
μ(Mo Kα)/cm^{-1}	4.26	4.28

*E.s.d.'s are given in parentheses.
**Measured by flotation method.

reflections, the space group was determined to be centrosymmetric $P2_1/c$. X-Ray studies are continuing.

3. STRUCTURE DETERMINATION

The structure of the α-crystal was solved straightforwardly by the direct method using "MULTAN 78" program package,[3] and refined by the block-diagonal least-squares method. Anisotropic thermal vibrations were assumed for the nonhydrogen atoms. All the hydrogen atoms were found from a difference Fourier map and refined isotropically. The final residual index, $R(=\Sigma|\,|F_o| - |F_c|\,|\,/\,\Sigma|F_o|)$, was 0.044. The structure of the β-crystal was solved by the heavy-atom method: the one sulfur atom was fixed at the origin of the cell of P1, and the other sulfur was found from a Patterson map. Successive Fourier and least-squares treatment gave

TABLE II

Intensity Measurement

	α-form	*β*-form
Diffractometer	Rigaku four-circle automatic diffractometer	
Radiation	Mo Kα (λ=0.71069 Å), graphite monochromatized	
Scan mode	ω - 2θ	
Scan rate, ($d\omega/d\theta$)/° min^{-1}	8	4
Background counting	8 s × 2	10 s × 2
Scan limit, 2θ/°	55	55
Specimen size/mm^3	0.63×0.60×0.26	0.42×0.27×0.18
Number of reflections measured	2659	1679
used[$\|F_o\| > 3\sigma(F)$]	2247	1337

all the nonhydrogen atoms. The hydrogen atoms were not found, probably due to some imperfection of the crystal. The refinement converged to an R of 0.099.

Final positional and thermal parameters are given in Tables III and IV. Lists of the anisotropic thermal parameters and those of the observed and calculated structure factors may be obtained from the first author (KN) on request.

4. DESCRIPTION OF THE STRUCTURES AND DISCUSSION

a. Molecular structures

Figures 1 and 2 show the molecular structures. The bond distances and angles are given in Table V.

The molecule in the α-crystal is planar within ±0.08 Å except for the C(8) atom, which protrudes from the mean molecular plane. On the other hand, all the atoms in the β-molecule are roughly coplanar within ±0.12 Å. This conformational difference between the α- and β-molecules is probably due to the different molecular environment in each crystal, as described in the following section.

In view of the different precision for the analyses of the α- and β-crystals, corresponding bond lengths and angles are in agreement with each other within the range of about twice their e.s.d.'s except that: the C(2)=C(3) length of 1.335(5) Å in the α-molecule almost corresponds to a double-bond length, while that of 1.39(2) Å in the β-molecule is slightly elongated. The difference between the O(1) . . . C(7) distances may be caused by the different orientation of the ethyl

TABLE III

α-CRYSTAL: Final fractional atomic coordinates and equivalent isotropic temperature factors, B_{eq}, for the nonhydrogen atoms and isotropic factors, B_{iso}, for the hydrogen atoms. B_{eq} is defined using anisotropic temperature factors, B_{ij}, as,

$$B_{eq} = B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{12}ab\cos\gamma + B_{23}bc\cos a + B_{31}ca\cos\beta$$

Atom	x	y	z	B_{eq} or B_{iso}/Å^2
S(1)	0.30360(9)	0.41064(7)	0.14570(8)	4.24(2)
C(1)	0.2848(3)	0.3832(3)	0.3543(3)	3.42(6)
S(2)	0.22328(8)	0.51044(7)	0.45570(9)	4.05(2)
C(2)	0.2162(3)	0.6152(3)	0.2854(4)	4.27(8)
C(3)	0.2520(3)	0.5688(3)	0.1407(4)	4.05(8)
C(4)	0.3167(3)	0.2678(3)	0.4275(3)	3.56(7)
C(5)	0.3706(3)	0.1731(3)	0.3294(3)	4.16(8)
N	0.4134(4)	0.0996(3)	0.2467(3)	6.04(11)
C(6)	0.2932(3)	0.2399(3)	0.5995(3)	3.75(7)
O(1)	0.2517(3)	0.3182(2)	0.6918(3)	4.83(7)
O(2)	0.3210(3)	0.1174(2)	0.6389(2)	4.50(7)
C(7)	0.2989(4)	0.0752(3)	0.8062(4)	4.84(9)
C(8)	0.1163(5)	−0.0232(4)	0.7688(5)	6.41(13)
C(9)	0.1687(5)	0.7472(3)	0.3176(5)	5.54(11)
C(10)	0.2530(4)	0.6357(3)	−0.0245(4)	6.22(13)
H(7A)	0.334(4)	0.165(3)	0.889(4)	5.5(6)
H(7B)	0.382(4)	0.015(3)	0.838(4)	5.2(6)
H(8A)	0.043(4)	0.030(4)	0.712(5)	6.9(7)
H(8B)	0.106(4)	−0.074(4)	0.879(5)	7.8(8)
H(8C)	0.111(4)	−0.107(3)	0.697(4)	6.0(7)
H(9A)	0.211(4)	0.816(4)	0.287(5)	8.4(9)
H(9B)	0.192(5)	0.781(4)	0.444(5)	8.9(9)
H(9C)	0.046(5)	0.726(4)	0.257(5)	9.7(9)
H(10A)	0.272(4)	0.720(3)	0.007(4)	6.2(7)
H(10B)	0.148(4)	0.595(4)	−0.117(5)	7.0(8)
H(10C)	0.346(4)	0.632(3)	−0.063(4)	7.1(8)

groups. In both molecules the lengths of the S(1)—C(3) and S(2)—C(2) bonds are slightly longer than those of the S(1)—C(4) and S(2)—C(4) bonds; the former values agree well with those found in benzothiazoles.[5]

b. Crystal structures

α-Form. Figure 3 shows the centrosymmetric structure of the α-crystal. The two molecules shown are related to each other by the center of symmetry at (1/2, 1/2, 1/2), the molecular ovelap being shown in Figure 4. The donor part of the molecule

TABLE IV

β-CRYSTAL: Final fractional atomic coordinates and equivalent isotropic temperature factors, B_{eq}, for the nonhydrogen atoms. See TABLE III for the definition of B_{eq}.

Atom	*x*	*y*	*z*	$B_{eq}/Å^2$
S(1)	0.0 (3)	0.0 (3)	0.0 (7)	4.97(8)
C(1)	-0.2131(11)	0.0058(9)	-0.0542(19)	3.7(2)
S(2)	-0.3374(3)	-0.1490(3)	0.0427(7)	4.82(8)
C(2)	-0.1763(15)	-0.2453(11)	0.1548(23)	4.9(3)
C(3)	-0.0135(14)	-0.1760(10)	0.1297(24)	5.0(4)
C(4)	-0.2716(11)	0.1288(10)	-0.1732(23)	4.3(3)
C(5)	-0.1526(11)	0.2508(10)	-0.2383(22)	4.5(3)
N	-0.0523(13)	0.3477(11)	-0.2919(32)	7.0(4)
C(6)	-0.4483(11)	0.1349(11)	-0.2153(24)	4.6(3)
O(1)	-0.5589(9)	0.0344(9)	-0.1705(21)	5.9(3)
O(2)	-0.4811(9)	0.2600(8)	-0.3407(20)	5.4(3)
C(7)	-0.6551(11)	0.2656(15)	-0.4299(30)	6.3(5)
C(8)	-0.6620(19)	0.4153(19)	-0.5306(43)	7.4(6)
C(9)	-0.2241(19)	-0.3950(12)	0.2631(35)	6.7(5)
C(10)	0.1512(17)	-0.2307(15)	0.2157(35)	7.1(5)

is stacked on top of the acceptor part of the adjacent molecule; the molecular dipole moments are parallel, with opposite directions, and cancel each other. The full overlap with interplanar spacing of 3.52 Å, which is slightly less than that found in the β-crystal, implies strong dipole-dipole interaction between the molecules. The other molecular overlap about the center of symmetry at (0, 1/2, 0) is only partial and the interplanar spacing of 3.80 Å is larger than the above value. Thus the α-crystal structure is regarded as consisting of molecular packing of centrosymmetric dimers.

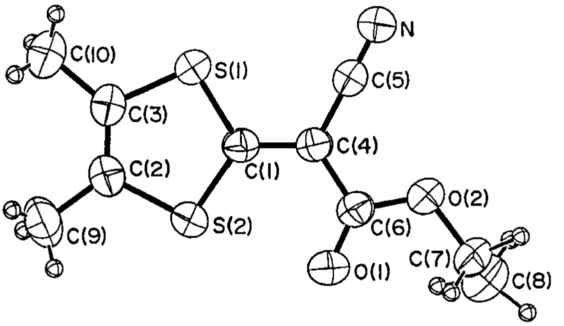

FIGURE 1 Molecular structure of the α-form viewed perpendicular to the molecular plane containing the nonhydrogen atoms except C(8). Thermal ellipsoids are scaled to include 50% probability except for the hydrogen atoms, which are represented by spheres of a fixed arbitrary radius.[4]

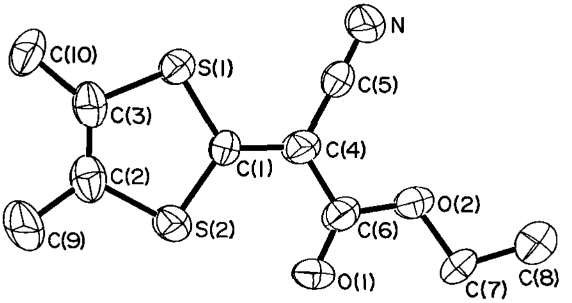

FIGURE 2 Molecular structure of the β-form viewed perpendicular to the molecular plane. Thermal ellipsoids are scaled to include 50% probability.[4]

β-Form. Figure 5 illustrates the β-structure of space group P1. The structure consists of layers and the molecules nearly lie on the (011) plane, the arrangement on which is shown in Figure 6; this arrangement is typical for the structure having the space group P1. The molecular overlap is given in Figure 7; the interplanar spacing of 3.62 Å is larger than that found in the α-crystal. All the molecules, or the molecular dipole moments, assume the same orientation, and therefore the resultant of the moments do not cancel each other out. This dipole orientation is thought to contribute to the observed SHG. The structure is stabilized electrostatically by packing in such a way that on a (011) layer, the acceptor moiety of a

TABLE V

Bond distances (in ångström units), angles (in degrees) and intramolecular nonbonding distances. E.s.d.'s are given in parentheses.

	α-form	β-form
Bond Distances		
C(1) - S(1)	1.721(3)	1.723(9)
S(1) - C(3)	1.743(3)	1.732(10)
C(3) - C(2)	1.335(5)	1.385(16)
C(2) - S(2)	1.750(3)	1.729(12)
S(2) - C(1)	1.719(3)	1.707(9)
C(1) - C(4)	1.379(4)	1.398(14)
C(4) - C(5)	1.423(4)	1.418(13)
C(5) - N	1.140(5)	1.157(14)
C(4) - C(6)	1.455(4)	1.430(16)
C(6) - O(1)	1.210(4)	1.218(12)
C(6) - O(2)	1.339(4)	1.352(13)
O(2) - C(7)	1.454(4)	1.433(12)
C(7) - C(8)	1.483(5)	1.471(23)
C(2) - C(9)	1.498(5)	1.485(16)
C(3) - C(10)	1.500(5)	1.514(18)

TABLE V

(*continued*)

	α-form	β-form
Bond Angles		
S(1)-C(1)-S(2)	113.8(2)	114.2(5)
S(1)-C(1)-C(4)	121.2(2)	120.5(6)
S(2)-C(1)-C(4)	125.0(2)	125.3(7)
C(1)-S(1)-C(3)	97.3(1)	97.6(5)
S(1)-C(3)-C(2)	115.5(2)	114.6(9)
S(1)-C(3)-C(10)	116.3(2)	116.8(8)
C(2)-C(3)-C(10)	128.2(3)	128.5(10)
C(3)-C(2)-S(2)	117.1(2)	116.6(8)
C(3)-C(2)-C(9)	127.0(3)	125.9(11)
S(2)-C(2)-C(9)	115.9(3)	117.5(9)
C(2)-S(2)-C(1)	96.3(1)	97.0(5)
C(1)-C(4)-C(5)	118.6(2)	118.8(8)
C(1)-C(4)-C(6)	121.4(3)	120.7(8)
C(5)-C(4)-C(6)	119.9(2)	120.4(9)
C(4)-C(5)-N	177.9(3)	178.2(11)
C(4)-C(6)-O(1)	123.2(3)	124.7(10)
C(4)-C(6)-O(2)	111.4(2)	112.3(8)
O(1)-C(6)-O(2)	125.4(3)	122.7(9)
C(6)-O(2)-C(7)	117.1(2)	115.9(8)
O(2)-C(7)-C(8)	110.8(2)	106.4(9)
Intramolecular Nonbonding Distances		
S(1) ... C(5)	2.962(3)	2.966(11)
S(2) ... O(1)	2.766(2)	2.774(9)
O(1) ... C(7)	2.720(4)	2.649(16)
O(2) ... C(5)	2.653(2)	2.663(12)

molecule is surrounded by the donor moieties of the neighboring molecules and vice versa. This is in contrast to the molecular arrangement in the α-crystal, in which only the dipole-dipole interaction across the center of symmetry at (1/2, 1/2, 1/2) is striking. No unusual intermolecular contacts are found, some of them being given in Figure 6.

An indole derivative, 3[(2-cyano-2-ethoxycarbonyl)ethenyl]-indole, crystallizes also in space group P1, and the structure is similar to the present β-structure, except that for the indole derivative no polymorphism is found. The structure is reported briefly in another article of this volume.[6]

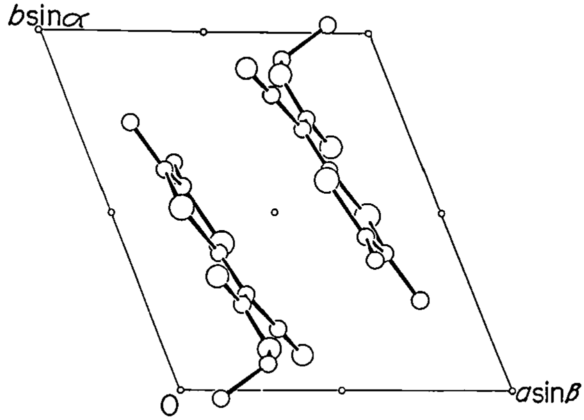

FIGURE 3 Crystal structure of the α-form viewed along the c axis. Small circles represent centers of symmetry.

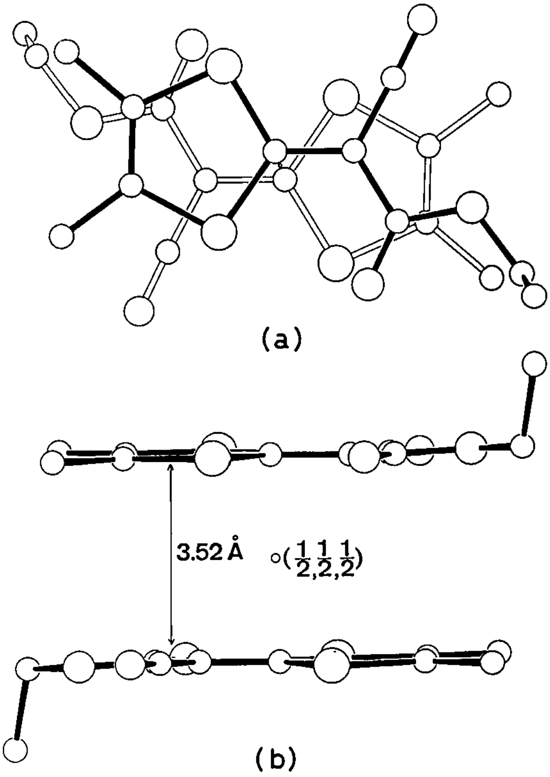

FIGURE 4 Molecular overlap related to the center of symmetry at (1/2, 1/2, 1/2), viewed (a) perpendicular to and (b) parallel to the molecular planes in the α-crystal.

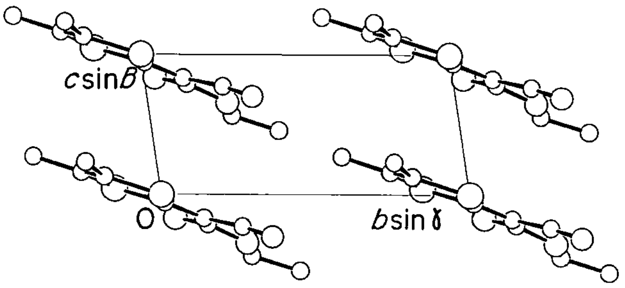

FIGURE 5 Crystal structure of the β-form viewed along the *a* axis.

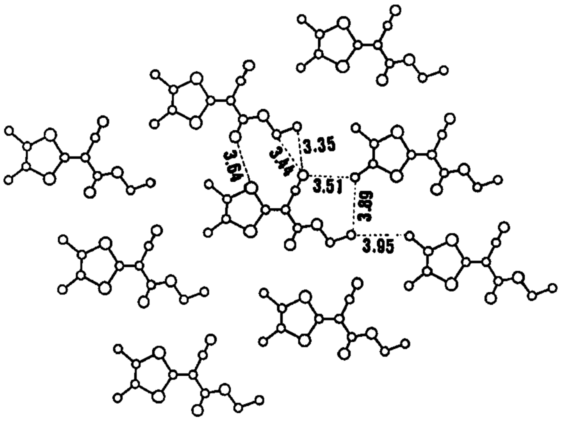

FIGURE 6 Molecular arrangement on the (0 1 1) plane in the β-crystal.

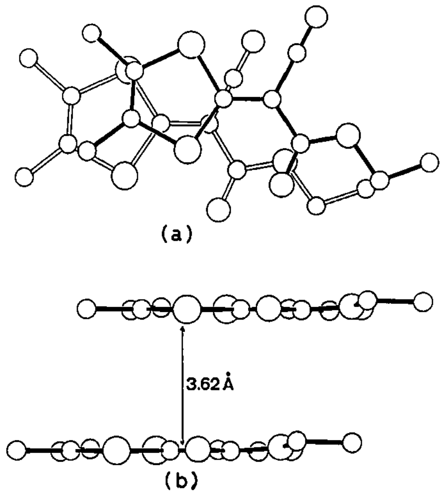

FIGURE 7 Molecular overlap in the β-crystal, viewed (a) perpendicular to (b) parallel to the molecular planes.

Remark on the crystal stability. The appearance of both crystals and the results of the structure analyses indicate that the quality of α-crystals is much better than that of the β-crystals, and therefore it can be concluded that the α-form is stable, whereas the β-form is metastable from the crystallographic point of view.

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