

Fig. 4. Pyrromethene valence tautomers.

formal bond order of 1.5, the latter 1.0. As would be expected on account of the N—H...N hydrogen bonding the bond angle of 126.1 (2)° at the methine bridge of (I) is significantly smaller than those of 132° in the hydrobromide of (I) and 128 (1) or 129 (1)° in the nickel(II) complex. The N(1)...N(6) distance in (I) is 2.75 Å, the N(1)—H(61) and N(6)—H(11) distances being 2.24 and 2.20 Å respectively. The H(11)—N(1)—C(1) and H(61)—N(6)—C(9) angles of 124 (2) and 120 (2)° are smaller than the H(11)—N(1)—C(4) and H(61)—N(6)—C(6) angles of 129 (2) and 133 (2)°.

The distribution of the bond lengths in (I) displays considerable similarities with those of the B and C rings in (II), suggesting that it is a reasonable simplification to regard the latter bile pigment as a pyrromethene with conjugating α substituents.

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4-(2-Carboxyvinyl)- α -cyanocinnamic Acid Dimethyl Ester, a Photooligomerizable Crystal

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Abstract. C₁₅H₁₃NO₄ (CVCCMe); $M_r = 271.3$; monoclinic, $P2_1/a$, $a = 11.387(3)$, $b = 29.737(8)$, $c = 3.956(1)$ Å, $\beta = 91.67(4)^\circ$; $Z = 4$, $D_x = 1.346$, $D_m = 1.350$ g cm⁻³. The molecule is nearly planar. A parallel plane-to-plane stack is found around the short c axis, in which the molecules overlap completely. This type of stacking is in contrast to that in the photo-polymerizable diolefin crystals, where interacting molecules are stacked with a displacement of about half a molecule in the direction of the long axis.

Introduction. In the serial studies on the photo-polymerizable crystals of symmetrical diolefinic com-

pounds, we have discussed the polymerization mechanism on the basis of the crystal structures of monomers and polymers (Nakanishi, Hasegawa & Sasada, 1977). Unsymmetrical diolefins in a chiral crystal have also been found to undergo the same type of polymerization to give optically active polymers (Addadi, Cohen & Lahav, 1975). The crystal structure of CVCCMe, one of the unsymmetrical diolefins which give rise to amorphous oligomers (Nakanishi, Nakanishi & Suzuki, 1976), was analysed in order to clarify the correlation between photoreactivity and molecular arrangement.

CVCCMe was synthesized from terephthalaldehyde by successive condensation with malonic acid and

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cianoacetic acid, followed by esterification with methanol. Thin, yellowish, plate-shaped crystals were grown from a methanol solution by slow evaporation. The specimen used was a fragment of a plate, $0.10 \times 0.10 \times 0.03$ mm in size. The space group was determined from photographs. The precise lattice constants and intensity data were obtained from measurements on a Rigaku computer-controlled four-circle diffractometer, with graphite-monochromatized Cu $K\alpha$ radiation. All reflexions within the range of $2\theta < 150^\circ$ were collected by use of the 2θ - ω scan mode with a scan rate of 4° min^{-1} . Stationary background counts were accumulated for 10 s before and after each scan. Out of 2467 reflexion intensities, 1195 were greater than $3\sigma(|F_o|)$ and were used for structure determination. No correction was made for absorption ($\mu = 9.54 \text{ cm}^{-1}$).

By iterative symbolic addition procedures, the signs of 260 reflexions out of 343 with $|E| \geq 1.4$ were determined in terms of one symbol. One of the corresponding E maps revealed the positions of all non-hydrogen atoms except for those of the cyano residue.

Table 1. Fractional atomic coordinates ($\times 10^4$ for C, N, O; $\times 10^3$ for H)

Estimated standard deviations are in parentheses.

	x	y	z
C(7')	3374 (6)	-574 (2)	1236 (19)
O(2')	3735 (4)	-128 (1)	2260 (12)
O(1')	2136 (4)	157 (1)	-350 (13)
C(6')	3044 (5)	210 (2)	1250 (16)
C(5')	3535 (5)	645 (2)	2383 (16)
C(4')	3008 (5)	1019 (2)	1501 (15)
C(3')	3387 (5)	1484 (2)	2299 (14)
C(2')	4469 (5)	1585 (2)	4003 (16)
C(1')	4796 (5)	2022 (2)	4586 (16)
C(1)	2657 (5)	1842 (2)	1338 (16)
C(2)	2972 (5)	2285 (2)	1960 (16)
C(3)	4076 (5)	2379 (2)	3604 (15)
C(4)	4471 (5)	2834 (2)	4339 (15)
C(5)	4052 (4)	3240 (2)	3493 (14)
C(6)	4686 (5)	3649 (2)	4750 (16)
O(1)	5539 (4)	3635 (1)	6594 (12)
O(2)	4192 (4)	4023 (1)	3568 (10)
C(7)	4765 (6)	4438 (2)	4601 (19)
C(8)	2993 (5)	3316 (2)	1448 (15)
N(1)	2175 (4)	3378 (2)	-206 (14)
H(C7')1	392 (6)	-77 (2)	202 (18)
H(C7')2	315 (7)	-59 (3)	-87 (21)
H(C7')3	263 (5)	-64 (2)	224 (16)
H(C5')	428 (4)	62 (2)	405 (13)
H(C4')	230 (6)	98 (2)	-23 (18)
H(C2')	500 (4)	133 (2)	432 (13)
H(C1')	553 (6)	212 (3)	583 (19)
H(C1)	195 (5)	175 (2)	8 (15)
H(C2)	244 (5)	254 (2)	119 (14)
H(C4)	525 (4)	287 (2)	581 (11)
H(C7)1	433 (5)	467 (2)	384 (16)
H(C7)2	553 (5)	444 (2)	341 (17)
H(C7)3	477 (6)	446 (2)	718 (20)

The cyano residue was located in the following Fourier synthesis. The parameters were refined by the block-diagonal least-squares method with $\omega = 0.5$ for $|F_o| \leq 1.0$ and $\omega = 1.0$ for $|F_o| > 1.0$. Isotropic H atoms were first located geometrically and then refined. The final R value was 0.073.* Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Final atomic coordinates are given in Table 1.

Discussion. The molecular structure and the numbering system used are shown in Fig. 1. The molecular dimensions of the right and left halves of CVCCMe in Fig. 1 are quite similar to those of dialkyl esters of p -phenylenedi(α -cyanoacrylic acid) and p -phenylene diacrylic acid respectively (Nakanishi, Ueno & Sasada, 1976a, 1978).

The benzene ring, cyanoethylene [C(3)-C(4)-C(5)-C(6)...C(8)-N(1)], ethylene [C(3')-C(4')-C(5')-C(6')] and carbonyl groups A [C(5)-C(6)-O(1)...O(2)] and B [C(5')-C(6')-O(1')...O(2')] are planar within a deviation of 0.013 Å from their respective mean planes.* Referring to the benzene plane, the cyanoethylene rotates by 7.2° about C(3)-C(4), and the carbonyl A by 2.7° about C(5)-C(6) in the same direction. Furthermore, in the same direction, the ethylene rotates by 5.1° about C(3')-C(4') and the carbonyl B by 3.3° about C(5')-C(6'). The benzene ring makes dihedral angles of 10.4 and 4.3° with carbonyls A and B respectively. Thus, the molecular skeleton consisting of the above five groups is nearly planar within a deviation of 0.17 Å from the mean plane.* The methyl groups rotate by only 1.2 and 2.0° about C(6)-O(2) and C(6')-O(2') respectively.

The crystal structure viewed along c is shown in Fig. 2. The molecules are piled up infinitely along the shortest crystal axis (c axis) to form a parallel plane-to-plane stack which is quite different from that of photopolymerizable crystals; in the latter crystals, molecules are stacked along a ~ 7 Å axis, displaced by half a molecule in the direction of the molecular long axis, to form a characteristic plane-to-plane stack (Nakanishi, Ueno & Sasada, 1978). The length of the c axis is just the shortest intermolecular distance between reactive double bonds and is close to those found in photopolymerizable crystals (3.94 Å on average), rather than to those in photostable crystals (4.187 and 4.369 Å) (Nakanishi, Ueno & Sasada, 1976b). The second shortest distance longer than 5 Å is found between molecules in different stacks (related by the a glide) (Table 2). Therefore, it is most probable that the double

* Lists of structure factors, thermal parameters and deviations of atoms from some least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33006 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

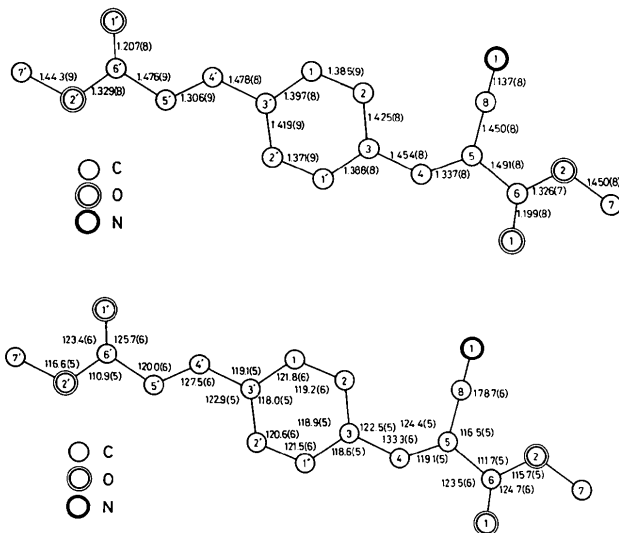


Fig. 1. Bond lengths (Å) and angles (°). The estimated standard deviations are in parentheses.

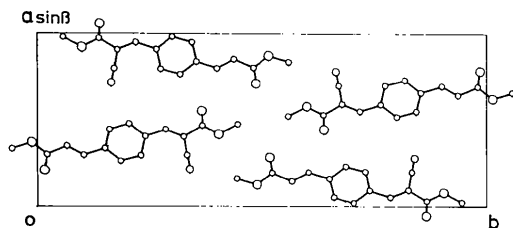


Fig. 2. The crystal structure viewed along c .

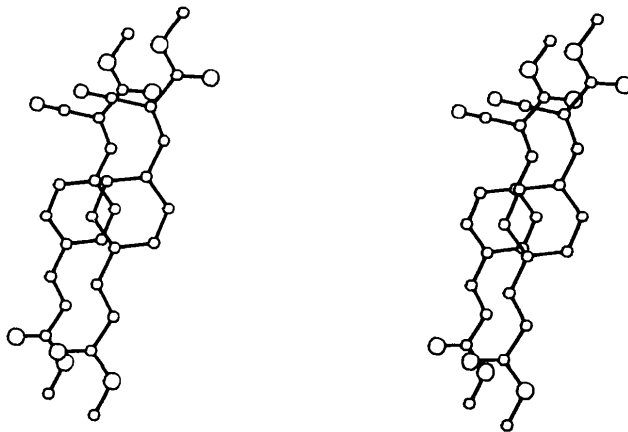


Fig. 3. A stereoview of the overlapping of interacting molecules, viewed along the normal to the mean plane of the molecule.

Table 2. Intermolecular distances (Å) between double bonds

C(4 ⁱ)...C(4 ⁱⁱ)	3.956	C(4 ⁱ)...C(5 ⁱⁱⁱ)	6.532
C(4 ⁱ)...C(5 ⁱⁱ)	3.859	C(5 ⁱ)...C(4 ⁱⁱⁱ)	6.948
C(5 ⁱ)...C(4 ⁱⁱ)	4.469	C(5 ⁱ)...C(5 ⁱⁱⁱ)	7.197
C(4 ⁱⁱ)...C(4 ⁱⁱⁱ)	3.956	C(5 ⁱ)...C(4 ⁱⁱⁱ)	5.096
C(4 ⁱⁱ)...C(5 ⁱⁱⁱ)	4.469	C(5 ⁱ)...C(5 ⁱⁱⁱ)	6.113
C(5 ⁱⁱ)...C(4 ⁱⁱⁱ)	3.838	C(4 ⁱⁱ)...C(4 ⁱⁱⁱ)	8.159
C(4 ⁱ)...C(4 ⁱⁱⁱ)	6.030	C(4 ⁱⁱ)...C(5 ⁱⁱⁱ)	7.247
C(4 ⁱ)...C(5 ⁱⁱⁱ)	6.135	C(5 ⁱⁱ)...C(4 ⁱⁱⁱ)	8.150
C(4 ⁱ)...C(4 ⁱⁱⁱ)	5.419	C(5 ⁱⁱ)...C(5 ⁱⁱⁱ)	7.105

Symmetry code

(i)	$x,$	$y,$	z
(ii)	$x,$	$y,$	$1 + z$
(iii)	$\frac{1}{2} + x,$	$\frac{1}{2} - y,$	z

surrounding monomers, the present crystal would give rise to an amorphous oligomer.

Fig. 3 shows the intermolecular contacts of interacting molecules. Some short contacts of less than 3.5 Å are found around the C(5)–C(6) bond: C(5)···C(8) 3.450, C(5)···N(1) 3.355, C(6)···C(8) 3.466, and O(1)···C(6) 3.396 Å.

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bonds in the stack react to form a cyclobutane ring with mirror symmetry, even if any one double bond in the molecule reacts preferentially. Since such cyclobutane formation breaks down the regular arrangement of

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3-Methyl-4,5-diphenyl-1,2,3-thiadiazolium Fluorosulphate

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Abstract. $C_{15}H_{13}N_2S^+ \cdot FO_3S^-$, $M_r = 352.41$, monoclinic, $C2/c$, $a = 32.233$ (8), $b = 15.058$ (8), $c = 14.546$ (4) Å, $\beta = 110.61$ (2)°, $U = 6567$ Å³, $Z = 16$, $D_x = 1.425$ g cm⁻³, $\mu(Mo K\alpha) = 3.0$ cm⁻¹. There are two molecules in the asymmetric unit; the heterocyclic rings show no significant differences. The anions exhibit different types of disorder. The structure was refined to $R = 0.083$ for 5022 unique reflexions.

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Table 1. *Atom coordinates* ($\times 10^4$)

The overall isotropic temperature factor for H atoms is 0.108 (6) Å².

	x	y	z
S(2)	3208 (1)	2527 (1)	2703 (1)
O(1)	3171 (2)	2318 (3)	3616 (3)
O(2)	3609 (1)	2264 (4)	2609 (3)
O(3)	2843 (1)	2119 (4)	1917 (4)
O(4)	3139 (2)	3474 (3)	2530 (3)
S(3)	0	950 (1)	2500
O(5)	-440 (3)	1139 (9)	2416 (9)
O(6)	222 (5)	1691 (9)	2365 (10)
F(7)	201 (3)	740 (9)	3629 (7)
O(8)	45 (7)	179 (8)	2086 (11)
S(4)	0	4637 (1)	2500
O(9)	203 (4)	3940 (8)	2186 (9)
O(10)	265 (5)	5413 (9)	2561 (11)
F(11)	96 (4)	4488 (10)	3596 (7)
O(12)	-427 (3)	4766 (11)	2072 (11)
S(1A)	4511 (1)	3500 (1)	3201 (1)
N(2A)	4232 (1)	4211 (4)	3555 (3)
N(3A)	3934 (1)	4594 (3)	2786 (2)
C(4A)	3922 (1)	4300 (3)	1888 (3)
C(5A)	4239 (1)	3666 (3)	1985 (3)
C(6A)	3638 (2)	5263 (4)	2966 (4)
C(11A)	3584 (1)	4621 (3)	981 (3)
C(12A)	3556 (2)	5492 (3)	710 (3)
C(13A)	3228 (2)	5775 (4)	-120 (4)
C(14A)	2930 (2)	5184 (5)	-692 (4)
C(15A)	2955 (2)	4287 (4)	-451 (3)
C(16A)	3287 (1)	4003 (3)	396 (3)

Table 1 (cont.)

	x	y	z
C(21A)	4359 (1)	3206 (3)	1228 (3)
C(22A)	4461 (2)	2312 (4)	1319 (4)
C(23A)	4589 (2)	1916 (5)	617 (5)
C(24A)	4624 (2)	2370 (5)	-163 (5)
C(25A)	4529 (1)	3257 (5)	-248 (3)
C(26A)	4394 (1)	3690 (4)	452 (3)
S(1B)	4260 (1)	2300 (1)	5568 (1)
N(2B)	4357 (1)	1706 (3)	4749 (3)
N(3B)	4089 (1)	1028 (3)	4533 (3)
C(4B)	3797 (1)	953 (3)	5010 (3)
C(5B)	3848 (1)	1653 (3)	5649 (3)
C(6B)	4132 (2)	389 (5)	3798 (5)
C(11B)	3491 (1)	196 (3)	4842 (3)
C(12B)	3116 (2)	137 (3)	4009 (4)
C(13B)	2839 (2)	-595 (4)	3901 (5)
C(14B)	2928 (2)	-1229 (4)	4593 (5)
C(15B)	3297 (3)	-1183 (4)	5400 (5)
C(16B)	3580 (2)	-454 (3)	5545 (4)
C(21B)	3594 (1)	1858 (3)	6280 (3)
C(22B)	3804 (2)	2050 (4)	7266 (3)
C(23B)	3556 (2)	2264 (5)	7836 (4)
C(24B)	3104 (2)	2310 (4)	7425 (4)
C(25B)	2894 (2)	2133 (4)	6450 (4)
C(26B)	3134 (1)	1895 (3)	5875 (3)
H(12A)	3796	5961	1159
H(13A)	3205	6468	-325
H(14A)	2669	5414	-1347
H(15A)	2718	3820	-918
H(16A)	3316	3310	601
H(22A)	4439	1935	1937
H(23A)	4664	1215	682
H(24A)	4727	2035	-707
H(25A)	4559	3627	-862
H(26A)	4317	4391	385
H(12B)	3039	648	3450
H(13B)	2545	-651	3247
H(14B)	2703	-1780	4502
H(15B)	3375	-1712	5938
H(16B)	3869	-404	6211
H(22B)	4161	2033	7589
H(23B)	3719	2398	8615
H(24B)	2913	2487	7878
H(25B)	2538	2181	6128
H(26B)	2966	1736	5105