

The C(3') methoxy group is nearly coplanar with the phenyl ring. By contrast, due to the presence of the C(2'') hydroxy group, the C(3'') methoxy group is aligned with O(3'')—C(7'') nearly perpendicular to the phenyl ring plane. The steric crowding resulting from multiple substitution of the phenyl rings has an effect on the planarity of the rings, with larger than normal deviations from coplanarity being found. Particularly affected are C(3') and C(4'), which are 0.015 and 0.012 Å out of plane, and C(3''), C(4'') and C(5''), which are 0.013, 0.025, and 0.019 Å out of plane.

Although the H atoms of the hydroxy groups could not be found, all three hydroxy groups are presumed to take part in hydrogen bonding, as shown by the intermolecular O...O distances O(1)...O(2''), 2.76 Å; O(4'')...O(3'), 2.93 Å; O(4'')...O(4'), 2.97 Å; and the angles O(1)...O(2'')—C(2''), 128°; C(4'')—O(4'')...O(3'), 136°; and C(4')—O(4')...O(4''), 122°. It is assumed that O(4'') acts as a donor toward O(4') of the same neighbor, but we cannot rule out the possibility that O(4'') may act as a donor

toward O(4') with the proton of the latter not being involved in hydrogen-bond formation.

References

- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
 HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
 HUGHES, E. W. (1941). *J. Am. Chem. Soc.* **63**, 1737–1752.
 KUPCHAN, S. M., SHIZURI, Y., BAXTER, R. L. & HAYNES, H. R. (1977). *J. Org. Chem.* **42**, 348–350.
 KUPCHAN, S. M., SHIZURI, Y., MURAE, T., SWEENEY, J. G., HAYNES, H. R., SHEN, M.-S., BARRICK, J. C., BRYAN, R. F., VAN DER HELM, D. & WU, K. K. (1976). *J. Am. Chem. Soc.* **98**, 5719–5720.
 KUPCHAN, S. M., SWEENEY, J. G., BAXTER, R. L., MURAE, T., ZIMMERLY, V. A. & SICKLES, B. R. (1975). *J. Am. Chem. Soc.* **97**, 672–673.
 KUPCHAN, S. M., SWEENEY, J. G., MURAE, T., SHEN, M.-S. & BRYAN, R. F. (1975). *Chem. Commun.* pp. 94–95.
 SHEN, M.-S., BRYAN, R. F., BAXTER, R. L., SWEENEY, J. G. & KUPCHAN, S. M. (1974). Abstracts ACA Summer Meeting, Pennsylvania State Univ., p. 207.

Acta Cryst. (1978). **B34**, 329–332

5,5'-Diethoxycarbonyl-3,3'-diethyl-4,4'-dimethyl-2,2'-pyrromethene

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(Received 15 July 1977; accepted 15 September 1977)

Abstract. C₂₁H₂₈N₂O₄, monoclinic, *P*2₁/*c*, *a* = 20.372 (4), *b* = 4.572 (1), *c* = 24.404 (4) Å, β = 113.69 (2)°, *M_r* = 372.5, *Z* = 4, *D_x* = 1.19 g cm⁻³. The molecule displays a planar *syn-Z* conformation which is stabilized by intramolecular N—H...N hydrogen bonding. The nitrogen proton is statistically disordered between the two N atoms. As, in addition, the geometries of the two rings are similar, this leads to the pyrromethene system displaying approximate C_{2v} symmetry in the crystal lattice.

Introduction. Cell dimensions were determined by a least-squares fit to settings for 15 reflexions (*±hkl*) on a Syntex *P*2₁ four-circle diffractometer (Cu *K*α radiation, λ = 1.54178 Å). Intensity measurements were carried

out in the θ–2θ mode (3.0 ≤ 2θ ≤ 135.0°) with graphite-monochromated Cu *K*α radiation, at scan speeds varying linearly between 2.93 (150 c.p.s. and below) and 29.30° min⁻¹ (4000 c.p.s. and above). Scan and background times were equal. A Lorentz-polarization correction was applied; an absorption [μ(Cu *K*α) = 5.9 cm⁻¹] correction was not applied. After application of the acceptance criterion *F* ≥ 3.0σ(*F*), 3157 unique reflexions were retained for use in the structure analysis. The structure was solved by direct methods (*SHELX* 76, G. M. Sheldrick) and refined by blocked full-matrix least squares with anisotropic temperature factors for all the non-hydrogen atoms. The H atom positional parameters were freely refined with individual isotropic temperature factors. A difference synthesis revealed a corresponding H atom for both of the N atoms. These were

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Table 1. *Positional parameters for the nonhydrogen atoms*

	x	y	z
N(1)	0.2782 (1)	0.8511 (3)	0.3725 (1)
C(1)	0.3178 (1)	0.8974 (3)	0.4310 (1)
C(2)	0.2922 (1)	0.7260 (4)	0.4667 (1)
C(3)	0.2343 (1)	0.5671 (3)	0.4275 (1)
C(4)	0.2263 (1)	0.6477 (3)	0.3684 (1)
C(5)	0.1768 (1)	0.5453 (3)	0.3132 (1)
N(6)	0.2190 (1)	0.8331 (3)	0.2497 (1)
C(6)	0.1721 (1)	0.6324 (3)	0.2569 (1)
C(7)	0.1218 (1)	0.5391 (3)	0.1993 (1)
C(8)	0.1391 (1)	0.6858 (4)	0.1575 (1)
C(9)	0.1997 (1)	0.8651 (4)	0.1907 (1)
C(11)	0.3791 (1)	1.0980 (4)	0.4508 (1)
O(11)	0.4167 (1)	1.1494 (3)	0.5028 (1)
O(12)	0.3891 (1)	1.2153 (3)	0.4046 (1)
C(13)	0.4507 (1)	1.4071 (4)	0.4197 (1)
C(14)	0.4496 (1)	1.5266 (6)	0.3628 (1)
C(21)	0.3220 (1)	0.7168 (5)	0.5338 (1)
C(31)	0.1875 (1)	0.3603 (4)	0.4432 (1)
C(32)	0.1279 (1)	0.5101 (5)	0.4541 (1)
C(71)	0.0600 (1)	0.3370 (4)	0.1878 (1)
C(72)	-0.0067 (1)	0.5004 (5)	0.1835 (1)
C(81)	0.1013 (1)	0.6645 (6)	0.0906 (1)
C(91)	0.2389 (1)	1.0616 (4)	0.1666 (1)
O(91)	0.2240 (1)	1.0971 (3)	0.1142 (1)
O(92)	0.2935 (1)	1.1957 (3)	0.2102 (1)
C(93)	0.3353 (1)	1.3999 (5)	0.1918 (1)
C(94)	0.3990 (1)	1.2502 (8)	0.1894 (1)

Table 2. *Positional parameters for the hydrogen atoms*

	x	y	z
H(11)	0.286 (1)	0.938 (6)	0.344 (1)
H(51)	0.139 (1)	0.392 (4)	0.315 (1)
H(61)	0.257 (2)	0.943 (7)	0.277 (1)
H(131)	0.447 (1)	1.575 (4)	0.449 (1)
H(132)	0.496 (1)	1.283 (5)	0.442 (1)
H(141)	0.463 (1)	1.351 (5)	0.344 (1)
H(142)	0.405 (2)	1.619 (7)	0.339 (1)
H(143)	0.492 (1)	1.671 (6)	0.372 (1)
H(211)	0.371 (1)	0.660 (6)	0.549 (1)
H(212)	0.329 (1)	0.915 (6)	0.552 (1)
H(213)	0.291 (1)	0.619 (5)	0.549 (1)
H(311)	0.216 (1)	0.243 (4)	0.479 (1)
H(312)	0.168 (1)	0.206 (4)	0.412 (1)
H(321)	0.100 (1)	0.356 (5)	0.467 (1)
H(322)	0.094 (1)	0.602 (5)	0.418 (1)
H(323)	0.144 (1)	0.653 (5)	0.485 (1)
H(711)	0.074 (1)	0.188 (4)	0.221 (1)
H(712)	0.051 (1)	0.215 (4)	0.151 (1)
H(721)	0.954 (1)	0.366 (4)	0.177 (1)
H(722)	0.002 (1)	0.620 (5)	0.224 (1)
H(723)	0.978 (1)	0.647 (5)	0.148 (1)
H(811)	0.130 (1)	0.586 (6)	0.072 (1)
H(812)	0.055 (1)	0.526 (6)	0.079 (1)
H(813)	0.087 (1)	0.857 (6)	0.071 (1)
H(931)	0.356 (1)	1.570 (5)	0.227 (1)
H(932)	0.303 (1)	1.486 (5)	0.150 (1)
H(941)	0.431 (2)	1.159 (7)	0.231 (1)
H(942)	0.380 (2)	1.071 (9)	0.157 (2)
H(943)	0.429 (2)	1.447 (8)	0.182 (1)

subsequently refined with fixed site-occupation factors of 0.5. Their isotropic temperature factors after the last refinement cycle were 0.043 (8) and 0.063 (10) Å², their N—H bond distances being 0.87 (3) and 0.94 (3) Å respectively. The terminal value of $R_G = (\sum w\Delta^2 / \sum wF_o^2)^{1/2}$ was 0.040, with $R_w = (\sum w^{1/2}\Delta / \sum w^{1/2}|F_o|) = 0.042$ and $R = 0.045$.* The weights adopted were those from the counting statistics. Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). Tables 1 and 2 give the final positional parameters.

Discussion. Pyrromethenes are important model compounds for the study of conformational preference and bonding characteristics in the natural series of bile pigments. Their chromophore is formally equivalent to that of the *B* and *C* rings of biliverdin dimethyl ester (II), the X-ray structure of which has recently been determined (Sheldrick, 1976). X-ray structural analyses have been carried out on several metal complexes of substituted pyrromethenes, namely bis(4,4'-diethoxycarbonyl-3,3',5,5'-tetramethylpyrromethenato)copper(II) (Elder & Penfold, 1969), bis(3,3',5,5'-tetramethylpyrromethenato)nickel(II) (Cotton, De Boer & Pipal, 1970) and bis(4,4'-diethoxycarbonyl-3,3',5,5'-tetramethylpyrromethenato)palladium(II) (March, Couch, Emerson, Fergusson & Robinson, 1971), and on the hydrobromide of (I) (Struckmeier & Engel, 1977). We present here the results of the first X-ray structural characterization of a pyrromethene free base. Fig. 1 is a perspective view of (I) showing the numbering system.

* Lists of structure factors, thermal parameters and bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33005 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

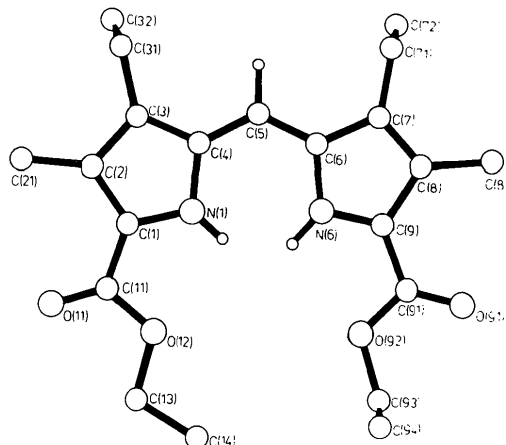
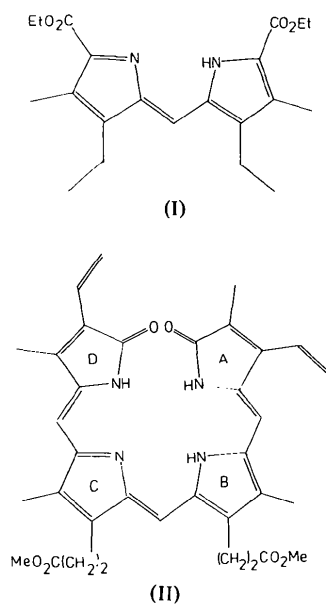


Fig. 1. The molecule of (I) in perspective with numbering system.



On the basis of semi-empirical CNDO/2 calculations Falk has predicted that a planar *syn-Z* conformation stabilized by intramolecular N—H...N hydrogen bonding will represent the energetically most favourable geometry for the pyrromethene moiety (Falk & Hofer, 1974). However, these studies also demonstrated that a degree of twist may be introduced between the two ring systems without producing a significant energetic destabilization. Indeed, conformational analysis in solution by means of a lanthanide-induced-shift technique suggested that the free-base pyrromethene system in simple derivatives is twisted about the formally single methine bridging bond by about 30° (Falk, Gergely &

Hofer, 1974b). In the present study a planar *syn-Z* conformation is observed for (I) (interplanar angle 0.6°). The stability of the planar pyrromethene skeleton is further enhanced in the crystal lattice by dispersion forces between sheets of molecules stacked parallel to one another at the van der Waals distance of 3.4–4.0 Å (Fig. 2). This phenomenon is routinely observed for other aromatic systems (e.g. nucleobases, porphyrins) as well as in related pyrromethenones (Sheldrick, Borkenstein, Blacha-Puller & Gossauer, 1977). Weak dimeric intermolecular interactions would also be expected to enhance the stability of the planar *syn-Z* conformation for pyrromethenes in solution, but it is, of course, possible that interaction with solvent molecules may lead to the observed twisting of the molecular skeleton. As a result of the statistical disorder of the nitrogen H atoms observed in the crystal lattice, it is not possible to directly compare the bond lengths and angles of (I) with those predicted by Falk for the unsymmetric pyrromethene moiety. However, the distribution of bond lengths (Fig. 3) is very similar to that observed in the bis(pyrromethenato)nickel(II) complex. In view of the satisfactory refinement ($R = 0.045$) and the low anisotropic temperature factor components for the ring atoms coupled with information from spectroscopic studies on pyrromethenes, it seems most reasonable to explain the N—H disorder on the basis of resonance between the two possible valence tautomers (Fig. 4) rather than in terms of a disordered placement of the molecule as a whole in the crystal lattice. For instance, although the presence of two non-equivalent N atoms, and *ipso facto* unsymmetrical N—H...N bonding, may be observed on the X-ray photoelectron spectroscopic time scale (Falk, Hofer & Lehner, 1974), tautomeric exchange in simple pyrromethenes is too fast, even at -100°C , to be measured by NMR (Falk, Gergely & Hofer, 1974a). The shortness of N(1)—C(1) [N(6)—C(9)] in comparison with N(1)—C(4) [N(6)—C(6)] is explicable in terms of the valence tautomers. The former bond possesses a

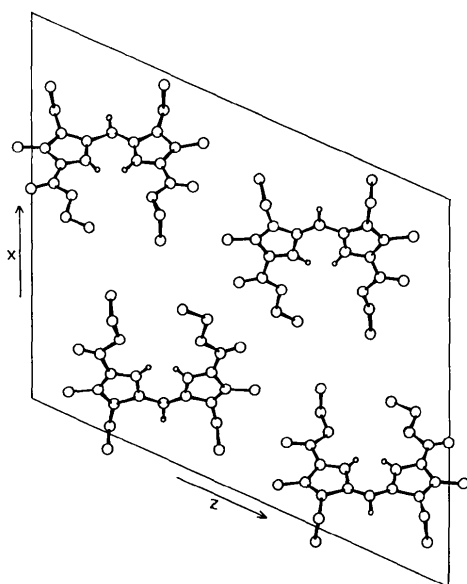


Fig. 2. The unit-cell contents of (I) perpendicular to [010].

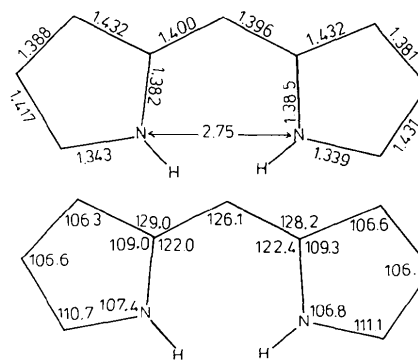


Fig. 3. Bond lengths (Å) and angles (°) in (I). Standard deviations are 0.002–0.003 Å and 0.1–0.2°.

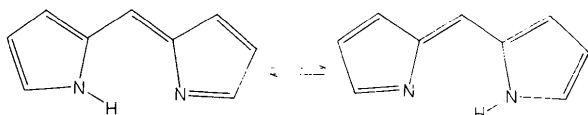


Fig. 4. Pyrromethene valence tautomers.

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.

Acta Cryst. (1978). **B34**, 332–335

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

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(Received 31 May 1977; accepted 8 September 1977)

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)°; $Z = 4$, $D_x = 1.346$, $D_m = 1.350$ 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 photopolymerizable 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 photopolymerizable crystals of symmetrical diolefinic com-

- References**
- COTTON, F. A., DE BOER, B. G. & PIPAL, J. R. (1970). *Inorg. Chem.* **9**, 783–788.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- ELDER, M. & PENFOLD, B. R. (1969). *J. Chem. Soc. A*, pp. 2556–2559.
- FALK, H., GERGELY, S. & HOFER, O. (1974a). *Monatsh. Chem.* **105**, 853–862.
- FALK, H., GERGELY, S. & HOFER, O. (1974b). *Monatsh. Chem.* **105**, 1004–1018.
- FALK, H. & HOFER, O. (1974). *Monatsh. Chem.* **105**, 995–1003.
- FALK, H., HOFER, O. & LEHNER, E. (1974). *Monatsh. Chem.* **105**, 366–378.
- MARCH, F. C., COUCH, D. A., EMERSON, K., FERGUSON, J. E. & ROBINSON, W. T. (1971). *J. Chem. Soc. A*, pp. 440–448.
- SHELDRICK, W. S. (1976). *J. Chem. Soc. Perkin Trans. 2*, pp. 1457–1462.
- SHELDRICK, W. S., BORKENSTEIN, A., BLACHA-PULLER, M. & GOSSAUER, A. (1977). *Acta Cryst.* **B33**, 3625–3635.
- STRUCKMEIER, G. & ENGEL, J. (1977). Unpublished results.

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