Crystal and Molecular Structure of 3,8,12-Triethyl-14-formyl-2,7,13-trimethyl-1(15*H*)-tripyrrinone, a Tripyrrolic Aldehyde derived from Aetiobiliverdin-IVγ

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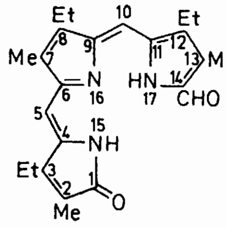
The structure of the title compound, a tripyrrolic compound derived from aetiobiliverdin-IVγ has been determined from three-dimensional *X*-ray diffractometer data. The tripyrrolic skeleton shows only small deviations from planarity. Adjacent rings assume the *Z*-configuration with the nitrogen atoms *syn*. Bond lengths in the three rings are quite different. No intra- or inter-molecular hydrogen bonding is observed. The compound crystallizes in the orthorhombic space group $Pna2_1$ with cell dimensions $a = 9.773(2)$, $b = 11.468(2)$, $c = 19.402(3)$ Å, $Z = 4$. The structure was solved by direct methods and refined by least-squares techniques to R 0.063 for 1 037 observed reflections.

UNTIL recently very little crystallographic work has been done in the field of bile pigments and open-chain polypyrroles. In the past year reports on the structures of bilirubin [1] and biliverdin dimethyl ester [2] have appeared. In addition, the structures of two zinc complexes of a synthetic formylbiliverdin [3] and the structure of the nickel complex of octaethylbilatriene [4] have been reported. The structure of a biladiene compound similar to bilirubin, but with ethoxycarbonyl groups substituted at the 1- and 19-positions instead of the oxo-groups of the bile pigments, has also been published.[5] All these show significant deviations from planarity. This is to be expected in the bilirubin-type compounds, in which the central methine carbon is saturated. The dipyrromethene moieties, planar in themselves, are mutually twisted around this methylene atom. In the case of biliverdin dimethyl ester and the other bilatrienes, which are fully conjugated, it would seem that the molecules should be planar. Yet in every case so far reported, they assume a non-planar semi-helical conformation. This is also true in the case of complexes of A/D secocorrinoid.[6] The reasons for this non-planarity are not entirely clear, although the most obvious explanation is steric hindrance. All these compounds have adjacent rings in a *syn-Z*-arrangement, thus maintaining a porphyrin-like conformation. This would bring the substituents on the 1- and 19-positions into close contact if planarity were maintained.

The recent structure determination of an oxodipyrromethene [7] has shown that molecule to be planar. The present study reports the structure of a tripyrrolic aldehyde (I) derived from the synthetic compound, aetiobiliverdin-IVγ.[7] It was of interest to determine the structure of this compound for several reasons. If the molecule were planar, it would establish that the cause of non-planarity in the tetrapyrrolic biliverdin-type compounds is primarily due to steric factors. In all the open-chain polypyrroles thus far reported, there has been considerable bond fixation and we therefore wished to observe the bonding pattern in this tripyrrolic compound. Finally, hydrogen bonding, both inter- and intra-molecular, is important in all non-complexed tetrapyrrolic species, and that in (I) would certainly be of interest for the sake of comparison.



(I)

EXPERIMENTAL

Reddish-green crystals of (I) were grown from methylene chloride–n-hexane [8] as parallelepipeds, the most prominent faces being of the form $\{0\bar{1}1\}$ and bounded by $\{100\}$ and $\{011\}$. Most crystals were elongated along *a*, but that chosen for intensity measurements was relatively equidimensional (0.16 × 0.26 × 0.26 mm). It was mounted in a glass capillary [9] at an arbitrary orientation.

Cell dimensions were determined by least-squares calculations, minimizing the differences between observed and calculated 2θ (measured at both $+$ and -2θ) for 24 reflections. Cell-constant data and the subsequent intensity data were collected using graphite-monochromated Cu-K_α radiation on a Datex–Syntex automated diffractometer.

Crystal Data.—$C_{24}H_{29}N_3O_2$, $M = 391.5$. Orthorhombic, $a = 9.772(2)$, $b = 11.468(2)$, $c = 19.402(3)$ Å, $U = 2\,174.3$ Å^3, $D_c = 1.20$ g cm^{-3}, $Z = 4$, $D_m = 1.19$ g cm^{-3}. Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) = 6.16 cm^{-1}. Systematic absences ($0kl$ for $k + l$ odd, $h0l$ for h odd) indicated space group $Pna2_1$ (# 33) or $Pnam$ (# 62, standard setting $Pnma$), but for $Z = 4$ the non-centrosymmetric space group, $Pna2_1$, seemed to be more likely. The centric space group would require a disordered model. The solution of the structure and the subsequent successful

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[1] R. Bonnett, J. E. Davies, and M. B. Hursthouse, *Nature*, 1976, **262**, 326.

[2] W. S. Sheldrick, *J.C.S. Perkin II*, 1976, 1457.

[3] G. Struckmeyer, U. Thewalt, and J. H. Fuhrhop, *J. Amer. Chem. Soc.*, 1976, **98**, 278.

[4] J. V. Bonfiglio, R. Bonnett, M. B. Hursthouse, and K. M. A. Malik, *J.C.S. Chem. Comm.* 1977, 83.

[5] G. Struckmeyer, U. Thewalt, and J. Engel, *J.C.S. Chem. Comm.*, 1976, 963.

[6] M. Currie and J. D. Dunitz, *Helv. Chim. Acta*, 1971, **54**, 98.

[7] D. L. Cullen, P. S. Black, E. F. Meyer, jun., D. A. Lightner, G. B. Quistad, and C. S. Pak, *Tetrahedron*, 1977, **33**, 477.

[8] F. Eivazi, M. F. Hudson, and K. M. Smith, *Tetrahedron Letters*, 1976, 3837; *Tetrahedron*, 1977, in press.

[9] E. F. Meyer, jun., *J. Appl. Cryst.*, 1973, **6**, 45.

refinement verified the choice of the non-centrosymmetric cell.

Intensity data were collected by the θ—2θ scan method, monitoring the intensity scale by remeasuring a group of five standard reflections periodically. The intensities of these standard reflections fluctuated by $\pm 6\%$ in a systematic manner that could be correlated with likely fluctuations in line voltage. Intensities of all reflections were corrected by a factor calculated from the weighted mean of the intensities of the check reflections. The scan rate was 2° min^{-1} while the scan range was 2.25°. Backgrounds at either end of the scan range were collected for half the scan time. Independent reflections (1 302) were measured out to a $\sin\theta/\lambda$ of 0.50 or 50° in θ, which is the machine limit. A total of 1 037 reflections had a net intensity $I > 2\sigma_I$ and were used in the analysis. The standard deviation was defined in terms of the statistical variances of the counts as $\sigma_I^2 = \sigma_I^2$ (count) $+ K^2(S + B_1 + B_2)^2$, where S, B_1, and B_2 are the observed counts for the scans and two backgrounds respectively, and σ_I^2(count) is the variance determined solely from counting statistics. An empirically determined value of 0.025 was used.

The intensities were corrected for coincidence[10] ($\tau = 2.81 \times 10^{-7}$ counts^{-1}). No absorption correction was applied in view of the small linear absorption coefficient and the relatively equidimensional shape of the crystal. Structure factors were calculated in the usual way assuming an ideally imperfect monochromator for the polarization factor.

Structure Solution and Refinement.—The structure was solved by use of the tangent refinement procedure, employing the MULTAN package, which besides the phasing program MULTAN, also includes a program to calculate normalized structure factors, a fast Fourier-transform program and programs to search for molecular fragments.[11] It proved necessary to hand select a set of origin reflections, as all attempts using the automatically chosen origin reflections failed. Two $hk0$ reflections (580, 210) and one $hk1$ reflection (251) were chosen. This is analogous to the procedure suggested for $P2_1$.[12] Two reflections (204, 205), chosen by the program, were in the starting set. Of the 8 sets of phases generated, the one having the highest combined figure-of-merit (2.43) proved to be the correct solution. Twelve atoms were definitely identified in the subsequent E map, including those in two of the three pyrrole rings. The remaining 17 non-hydrogen atoms were found from a series of difference-Fourier syntheses.

Initial refinements were carried out using block-diagonal techniques on an IBM 360/65.* Subsequent refinements and calculations were performed on a PDP 11/40 computer using the Enraf–Nonius Structure Determination Package (SDP). In least-squares calculations the function minimized was $\Sigma w(F_o - F_c)^2$, where $w = 1/\sigma_F^2$. Because $Pna2_1$ is a polar space group, the z co-ordinate of one atom [chosen to be O(1)] had to be held constant. Initially isotropic temperature factors were used. The data–parameter ratio was not large enough to allow full anisotropic refinement. The atoms in the pyrrole skeleton, and those in the oxo- and formyl-groups were refined anisotropically. Those in the peripheral methyl and ethyl groups were refined isotropically.

TABLE 1

Final fractional atom co-ordinates derived from the least-squares refinement. The z co-ordinate of O(1) was not refined. Here and in subsequent Tables estimated standard deviations for the least significant figure are in parentheses

Atom	x	y	z
O(1)	0.011 8(6)	0.068 9(4)	0.042 3
O(2)	−0.229 1(7)	0.003 8(5)	−0.086 5(4)
C(1)	0.068 3(7)	−0.017 8(6)	0.066 0(4)
C(2)	0.178 6(7)	−0.024 3(5)	0.119 1(4)
C(3)	0.209 0(6)	−0.134 6(5)	0.129 0(4)
C(4)	0.122 1(6)	−0.209 2(5)	0.083 6(3)
C(5)	0.122 4(6)	−0.326 9(5)	0.077 5(4)
C(6)	0.031 8(7)	−0.394 1(5)	0.035 2(3)
C(7)	0.036 4(7)	−0.523 1(5)	0.036 9(4)
C(8)	−0.063 6(7)	−0.558 8(5)	−0.004 4(4)
C(9)	−0.126 3(6)	−0.451 7(5)	−0.032 2(3)
C(10)	−0.232 2(6)	−0.448 6(5)	−0.078 3(4)
C(11)	−0.292 1(6)	−0.348 8(5)	−0.108 8(3)
C(12)	−0.395 0(7)	−0.340 5(6)	−0.160 4(3)
C(13)	−0.414 1(6)	−0.222 9(5)	−0.173 3(3)
C(14)	−0.330 4(7)	−0.161 4(5)	−0.131 6(4)
N(15)	0.040 2(5)	−0.132 3(5)	0.049 1(3)
N(16)	−0.063 9(5)	−0.353 7(4)	−0.005 5(2)
N(17)	−0.254 7(5)	−0.238 5(4)	−0.093 2(2)
C(18)	−0.314 5(8)	−0.038 8(8)	−0.125 7(4)
C(19)	0.235 2(8)	0.083 7(7)	0.150 4(4)
C(20)	0.309 3(7)	−0.186 8(6)	0.179 0(4)
C(21)	0.237 7(10)	−0.219 6(8)	0.245 1(4)
C(22)	0.136 2(7)	−0.595 6(6)	0.076 2(4)
C(23)	−0.106 7(7)	−0.679 8(6)	−0.023 7(4)
C(24)	−0.034 8(8)	−0.725 8(7)	−0.087 8(5)
C(25)	−0.462 0(8)	−0.442 9(6)	−0.195 6(4)
C(26)	−0.386 2(9)	−0.475 9(7)	−0.262 1(4)
C(27)	−0.517 3(8)	−0.173 6(7)	−0.223 4(4)

The positions of most of the hydrogen atoms could be discerned from difference syntheses, but many of the bond lengths and angles were chemically unreasonable. Therefore, except for the hydrogen atoms bonded to the pyrrole nitrogen atoms for which the difference synthesis positions were used, a set of idealized hydrogen atoms positions were calculated and their contribution added to the structure factors (B_H 4.0 Å^2). A C–H distance of 1.0 Å and a staggered configuration for the methyl hydrogen atoms were assumed. No hydrogen-atom parameters were re-

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* The structure was solved by use of the CDC 7600 computer at Brookhaven National Laboratory *via* remote hook-up on the CRYSNET system. Those programs used on the IBM 360/65 and its successor at Texas A & M, the Amdahl 470V/6, included: TRACER, a cell reduction program by S. Lawton, LSLAT (least-squares cell parameter refinement), BDLR4 (block-diagonal least-squares program), FOURIER (version of the A. Zalkin Fourier summation program modified by W. Robinson and R. Dellaca), HOW and XANADU (molecular geometry programs, the latter by P. Roberts and G. Sheldrick) and ORTEP (thermal ellipsoid plot program of C. K. Johnson).[13] Several other local data handling programs were used as well as the autoindexing and least-squares cell parameter refinement program written by R. A. Sparks for the NOVA computer.[14] Data collection programs used were those written by R. Stanford for the Varian 620i computer. Use was also made of the PDP 11/40 Vector General graphics system, also a part of the CRYSNET system.[15,16]

[10] E. Sletten, J. Sletten, and L. H. Jensen, *Acta Cryst.*, 1969, **B25**, 1330.

[11] M. M. Woolfson, in 'Crystallographic Computing Techniques,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1976, pp. 85—96.

[12] I. L. Karle, in ref. 11, p. 54.

[13] C. K. Johnson, ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, Report ORNL 3794, Revised, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[14] R. A. Sparks in ref. 11, pp. 452—467.

[15] E. F. Meyer, C. N. Morimoto, J. Villarreal, H. M. Berman, H. L. Carrel, R. K. Stodola, T. F. Koetzle, L. C. Andrews, F. C. Bernstein, and H. J. Bernstein, *Fed. Proc.*, 1974, **33**, 2402.

[16] C. N. Morimoto and E. F. Meyer, jun., in ref. 11, pp. 488—496.

fined in the least-squares procedure, but before the final cycles, new positions for the hydrogen atoms bonded to nitrogen atoms were taken from a difference synthesis, and new positions were calculated for the remaining hydrogen atoms.

After the final cycle the shifts on all refined parameters were well below 1σ. The final conventional R was 0.063, while R', defined as $\Sigma w||F_o| - |F_c||^2/\Sigma wF_o^2$ was 0.064. A structure-factor calculation using all 1 302 reflections gave R 0.082. The error in an observation of units weight, defined as $\Sigma w||F_o| - |F_c||^2/(N_o - N_v)$ was 2.43 for N_o = 1 037 reflections and N_v = 216 variables. A final difference-Fourier synthesis showed a maximum electron density of 0.22 eÅ^{-3}.

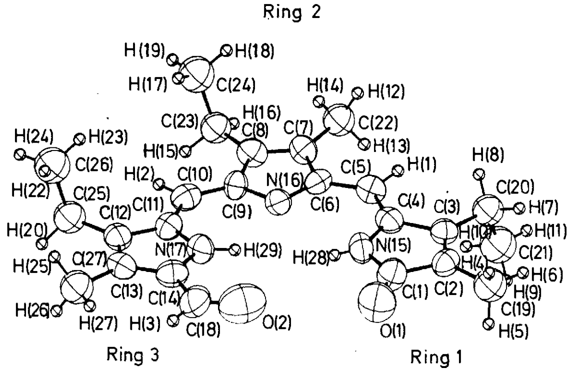

FIGURE 1 ORTEP [13] Drawing of the structure of (I) showing the arbitrary atom numbering scheme used. Thermal ellipsoids are drawn for 50% probability, except those of the hydrogen atoms which are not drawn to scale. H(21) is hidden behind C(25)

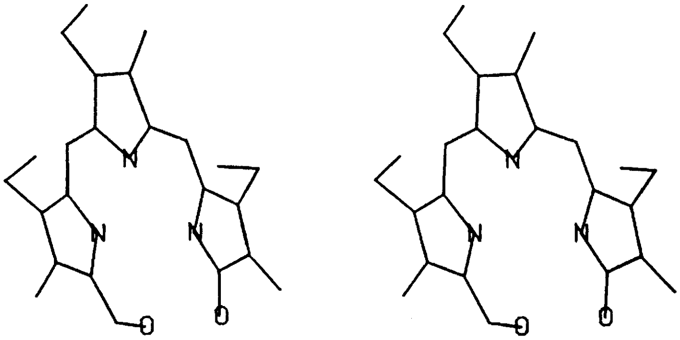

FIGURE 2 Stereoview of a single molecule, with hydrogen atoms omitted for clarity

No evidence of secondary extinction was found. Corrections for anomalous dispersion were applied to all non-hydrogen atoms.[17] Scattering factors were taken from ref. 18.

Final positions for non-hydrogen atoms are given in Table 1. Final hydrogen-atom positions, root-mean-square components of thermal displacement along the principal axes of the thermal ellipsoids, thermal parameters, and observed and calculated structure factors are available as Supplementary Publication No. SUP 22162 (11 pp.).*

RESULTS AND DISCUSSION

Figure 1 shows the structure of (I), which confirms the original formulation;[8] the numbering scheme used is also indicated. Figure 2 is a stereoview of the molecule without hydrogen atoms. Adjacent rings in the tripyrrolic moiety are in a cisoid arrangement with the Z-configuration. Thus the molecule bears strong resemblance to three-quarters of a porphyrin ring.

The compound is a conjugated system and the molecular structure is effectively planar, unlike the tetrapyrrolic skeleton in biliverdin dimethyl ester[2] and the zinc(II) and nickel complexes of synthetic biliverdins.[3,4] Table 2 lists least-squares planes of the individual pyrrole rings and also that of the tripyrrolic skeleton, excluding the peripheral methyl and ethyl groups. The maximum deviation of an atom from this last plane is 0.01 Å [for C(10)]. The dihedral angles between planes of individual pyrrole rings are 4.6 and 4.9°. It is clear from these results, as well as those obtained for a planar oxodipyrromethene compound,[7] that the non-planar helical conformation observed in the tetrapyrrolic bilatrienes is primarily the result of steric effects. A planar tetrapyrrole would bring the groups substituted at the 1- and 19-positions (the C_a positions on the terminal rings) into impossibly close contact.

TABLE 2

Least-square planes

(a) Deviations (A × 10^3) from planes

	(1)	(2)	(3)	(4)	(5)
O(1)	84	65	−12	254	116
O(2)	−97	−132	−170	−146	−18
N(15)	19	14	10	167	−48
N(16)	−14	−14	70	2	−150
N(17)	18	−2	51	−94	−7
C(1)	51	41	−7	246	26
C(2)	56	55	2	340	−5
C(3)	9	16	3	292	−111
C(4)	−33	−28	−8	161	−160
C(5)	−103	−91	−27	63	−282
C(6)	−78	−69	25	3	−260
C(7)	−65	−49	94	−7	−309
C(8)	31	43	205	8	−199
C(9)	46	47	172	−6	−117
C(10)	108	103	232	−24	−21
C(11)	68	51	147	−95	2
C(12)	32	7	106	−214	3
C(13)	−39	−72	−16	−281	−7
C(14)	−25	−56	−27	−186	9
C(18)	−68	−105	−123	−193	179

(b) Angles (°) between planes

(1)–(2) 0.4, (1)–(3) 2.2, (1)–(4) 3.6, (1)–(5) 2.6, (2)–(3) 1.9, (2)–(4) 3.4, (2)–(5) 3.1, (3)–(4) 4.6, (3)–(5) 4.7, (4)–(5) 4.9.

(c) Equations of planes. All planes are unweighted. X, Y, and Z are in orthorhombic fractional co-ordinates

Plane 1: O(1), O(2), N(15)—(17), C(1)—(14), C(18)
$-6.727X - 0.154Y + 14.072Z = 0.4218.$

Plane 2: Pyrrolic Skeleton, N(15)—(17), C(1)—(14)
$-6.689X - 0.214Y + 14.142Z = 0.439$

Plane 3: Pyrrole ring 1, N(15), C(1)—(4)
$-6.711X - 0.588Y + 14.069Z = 0.489$

Plane 4: Pyrrole ring 2, N(16), C(6)—(9)
$-6.290X + 0.044Y + 14.849Z = 0.303$

Plane 5: Pyrrole ring 3, N(17), C(11—(14)
$-6.886X + 0.306Y + 13.759Z = 0.406$

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1977, Index issue.

[17] D. T. Cromer, 'International Tables for X-Ray Crystallography,' vol. IV, Kynoch Press, Birmingham, 1974, pp. 149—150.

[18] D. T. Cromer and J. T. Waber, ref. 17, pp. 99—101.

The molecule is definitely present in the lactam form. The C(1)–O(1) distance is 1.227(7) Å, in good agreement with the C=O distance in the formyl group [C(18)–O(2)] and with the values found in the oxodipyrromethene, biliverdin methyl ester,[2] and bilirubin.[1] Ring 1 is thus best described as a pyrrolenone moiety.

Bond lengths and angles are summarized in Table 3, and a stereoview of the molecule is shown in Figure 3.

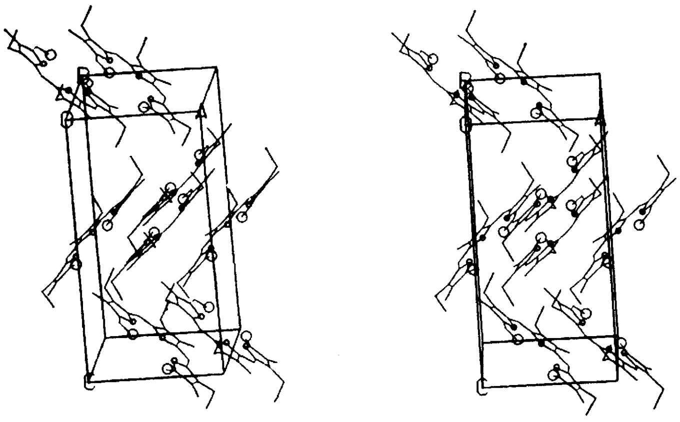


FIGURE 3 Stereoview of the packing in the unit cell, with hydrogen atoms omitted; small circles represent oxygen atoms

TABLE 3

Bond lengths (Å) and angles

(*a*) Distances

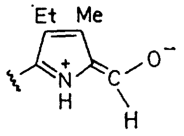
O(1)–C(1)	1.227(7)	C(7)–C(8)	1.328(7)
O(2)–C(18)	1.229(8)	C(7)–C(22)	1.492(8)
N(15)–C(1)	1.380(7)	C(8)–C(9)	1.475(6)
N(15)–C(4)	1.367(6)	C(8)–C(23)	1.498(7)
N(16)–C(6)	1.308(6)	C(9)–C(10)	1.362(7)
N(16)–C(9)	1.379(6)	C(10)–C(11)	1.418(7)
N(17)–C(11)	1.352(6)	C(11)–C(12)	1.421(7)
N(17)–C(14)	1.373(6)	C(12)–C(13)	1.384(7)
C(1)–C(2)	1.492(7)	C(12)–C(25)	1.508(8)
C(2)–C(3)	1.315(7)	C(13)–C(14)	1.350(7)
C(2)–C(19)	1.486(8)	C(13)–C(27)	1.511(8)
C(3)–C(4)	1.492(7)	C(14)–C(18)	1.419(9)
C(3)–C(20)	1.503(7)	C(20)–C(21)	1.508(8)
C(4)–C(5)	1.356(7)	C(23)–C(24)	1.523(8)
C(5)–C(6)	1.433(7)	C(25)–C(26)	1.535(8)
C(6)–C(7)	1.480(7)		

(*b*) Angles

C(1)–N(15)–C(4)	112.3(5)	C(7)–C(8)–C(23)	130.1(5)
C(6)–N(16)–C(9)	104.7(4)	C(9)–C(8)–C(23)	124.3(5)
C(11)–N(17)–C(14)	109.6(5)	N(16)–C(9)–C(8)	111.0(4)
O(1)–C(1)–N(15)	126.3(6)	N(16)–C(9)–C(10)	124.0(5)
O(1)–C(1)–C(2)	128.6(6)	C(8)–C(9)–C(10)	125.1(5)
N(15)–C(1)–C(2)	105.2(5)	C(9)–C(10)–C(11)	127.6(5)
C(1)–C(2)–C(3)	108.2(5)	N(17)–C(11)–C(10)	123.3(5)
C(1)–C(2)–C(19)	120.7(5)	N(17)–C(11)–C(12)	106.6(5)
C(3)–C(2)–C(19)	131.2(6)	C(10)–C(11)–C(12)	130.1(6)
C(2)–C(3)–C(4)	109.6(5)	C(11)–C(12)–C(13)	106.8(5)
C(2)–C(3)–C(20)	128.7(6)	C(11)–C(12)–C(25)	125.0(6)
C(4)–C(3)–C(20)	121.7(5)	C(13)–C(12)–C(25)	128.1(6)
N(15)–C(4)–C(3)	104.7(4)	C(12)–C(13)–C(14)	108.6(5)
N(15)–C(4)–C(5)	127.0(6)	C(12)–C(13)–C(27)	124.8(6)
C(3)–C(4)–C(5)	128.3(6)	C(14)–C(13)–C(27)	126.5(6)
C(4)–C(5)–C(6)	125.7(5)	N(17)–C(14)–C(13)	108.4(5)
N(16)–C(6)–C(5)	126.6(5)	N(17)–C(14)–C(18)	122.3(6)
N(16)–C(6)–C(7)	112.9(5)	C(13)–C(14)–C(18)	129.2(6)
C(5)–C(6)–C(7)	120.4(6)	O(2)–C(18)–C(14)	121.2(8)
C(6)–C(7)–C(8)	105.6(5)	C(3)–C(20)–C(21)	110.2(5)
C(6)–C(7)–C(22)	126.1(6)	C(8)–C(23)–C(24)	113.4(5)
C(8)–C(7)–C(22)	128.2(5)	C(12)–C(25)–C(26)	111.2(5)
C(7)–C(8)–C(9)	105.6(5)		

There is considerable bond fixation, particularly in rings 1 and 2. It is quite apparent that the resonance form shown (I) overwhelmingly predominates in these two rings. Thus in ring 1, the pyrrolenone ring, the average C_a–C_b bond length is 1.492 Å, the approximate length of a single bond between two sp^2 carbon atoms. The C_b–C_b distance is 1.315(7) Å, a distance indicative of a pure double bond. Several factors indicate that ring 2 is a pyrrolenine ring, *i.e.* the nitrogen atom bears no hydrogen atom. The C(6)–N(16) bond length is much shorter than the C(9)–N(16) distance, indicating a much greater degree of double-bond character in the former. The C–C bond lengths in this ring are very similar to those in ring 1, so that it may be postulated that the C_a–C_b bonds are essentially single and the C_b–C_b bond essentially a pure double bond. There is a large difference between the C_a–N–C_a bond angles in rings 1 and 2. The C(6)–N(16)–C(9) angle [104.7(4)°] is typical for pyrrole rings in which there is no hydrogen atom bonded to the nitrogen atom, *e.g.* in free base porphyrins and porphyrin acids [19-21] and biliverdin dimethyl ester.[2] On the other hand the angle of 112.3° in ring 1 is similar to those found for pyrrole rings which do have a N–H bond.[19]

The bond lengths and angles in ring 3 show some unusual features. It is quite clear that canonical forms such as (II) have an important effect, and that the formyl group is involved in delocalization. The C(14)–C(18) bond length [1.419(9) Å] indicates a substantial degree of double-bond character. A similar shortening has been noted in other compounds, *e.g.* 1.439 Å (mean) in a monopyrrolic [22] and a dipyrrolic compound,[23] both having ethoxycarbonyl groups substituted at the C_a positions. The C_a–C_b bond [1.384(7) Å] in ring 3 is longer than in rings 1 and 2. Both C_a–C_b distances are shorter in ring 3 than in the other rings. However the two C_a–C_b distances are significantly different in ring 3 with C(11)–C(12) 1.421(7) and C(13)–C(14) 1.350(7) Å. This difference is *ca.* 10σ and is thus significant. No satisfactory explanation for this difference is readily available, but a similar difference was noted in the monopyrrolic compound ethyl 4-acetyl-3-ethyl-5-methylpyrrole-2-carboxylate,[22] in which a



(II)

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[19] J. L. Hoard in 'Porphyrins and Metalloporphyrins,' ed. K. M. Smith, Elsevier, Amsterdam, 1975, pp. 317—380, and references therein.

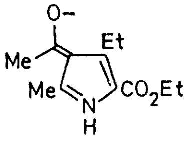
[20] N. Hirayama, A. Takenaka, Y. Sasada, E. Watanabe, H. Ogoshi, and Z. Yoshida, *J.C.S. Chem. Comm.*, 1974, 330.

[21] C. P. Hrung, M. Tsutsui, D. L. Cullen, and E. F. Meyer, jun., *J. Amer. Chem. Soc.*, 1976, **98**, 7878.

[22] R. Bonnett, M. B. Hursthouse, and S. Neidle, *J.C.S. Perkin II*, 1972, 902.

[23] R. Bonnett, M. B. Hursthouse, and S. Neidle, *J.C.S. Perkin II*, 1972, 1335.

canonical form such as (III) is stabilized by the presence of an acyl group substituted at one of the C_b positions.



(III)

It might be expected that if form (II) is important, the two C_a–N distances should be different with C(11)–N(17) being shorter than C(14)–N(17). This is indeed the case, but the difference is small [1.352(6) and 1.373(6) Å] corresponding to barely 3σ and thus just on the edge of being considered significant.

Bond angles in all three rings are as expected. While the bond angles involving the methine carbon atoms are large (125 and 127°) they are not nearly so large as that (133°) in the oxodipyrromethene compound.[6] In the dipyrromethene groups there are hydrogen atoms bonded to the nitrogen atoms in adjacent rings. Presumably, steric repulsion between these hydrogen atoms causes the large C_a–C_m–C_a angles. In the present case, where the central ring is taken as a pyrrolenine ring and has no N–H bond, such repulsion is not found and as a consequence the C_a–C_m–C_a bond angle is not as large. The N(15)–N(16) and N(16)–N(17) distances are 2.93 and 2.85 Å respectively. The N(15)–N(17) distance is 4.17 Å. It is highly unlikely that there is any intramolecular hydrogen bonding.

The bond lengths involving terminal carbon atoms in the ethyl groups are shorter than expected for a C–C single-bond distance. However this is a common observation for terminal C–C bonds of aliphatic peripheral groups (*e.g.* various octaethylporphyrin complexes).[24] This apparent shortening generally is attributed to neglect of the relatively large thermal motion of the terminal carbon atoms.

A stereoview of the packing in the unit cell is shown in Figure 3. There is no intermolecular hydrogen bonding. While there are several intermolecular contacts <3.5 Å (Table 4), the shortest is 3.32 Å for O(2) · · · C(7) contact.

TABLE 4

Intermolecular contacts (Å) <3.5 Å

O(1) · · · C(23$^{\mathrm{I}}$)	3.36	N(15) · · · C(11$^{\mathrm{III}}$)	3.48
O(1) · · · C(24$^{\mathrm{I}}$)	3.48	N(16) · · · C(3$^{\mathrm{II}}$)	3.43
O(2) · · · C(7$^{\mathrm{II}}$)	3.32	N(16) · · · C(14$^{\mathrm{III}}$)	3.35
O(2) · · · C(25$^{\mathrm{III}}$)	3.43	N(16) · · · C(10$^{\mathrm{III}}$)	3.44
N(15) · · · C(10$^{\mathrm{III}}$)	3.46	C(11) · · · C(27$^{\mathrm{III}}$)	3.50

Roman numeral superscripts denote the following equivalent positions relative to the reference molecule at x,y,z:

I $x, 1 + y, z$
II $-\frac{1}{2} + x, -\frac{1}{2} - y, z$
III $\frac{1}{2} + x, -\frac{1}{2} - y, z$

It is not believed that any of these contacts has any significant effect on the structure.

We thank Azarabadegan University (Tabriz, Iran) for financially supported leave (to F. E.). This work was supported in part by the Robert A. Welch Foundation and the Texas Agricultural Experiment Station. Much of the early computation was performed at Brookhaven National Laboratory utilizing the CRYSNET system.

[7/1164 *Received, 4th July,* 1977]

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[24] D. L. Cullen and E. F. Meyer, jun., *Acta Cryst.*, 1976, **B32**, 2259.