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THE CRYSTAL AND MOLECULAR STRUCTURE OF AN OXODIPYRROMETHENE RELATED TO BILIRUBIN

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Abstract—The structure of 5'-oxo-3',4,4'-triethyl-3,5-dimethyl-1',5'-dihydro[2.2']-dipyrromethene 1, a model for bilirubin, has been determined from three dimensional counter data. The oxodipyrromethene skeleton shows only small deviations from planarity, and the structure assumes the *Z*-configuration with the nitrogen atoms *syn*. Bond lengths in the two rings are quite different. No intramolecular H-bonding is observed, but intermolecular H-bonded dimers are formed through the lactam oxygen with the lactam and pyrrole N–H groups. The compound crystallizes in monoclinic space group C2/c with cell dimensions a = 25.106(10)A, b - 7.132(7)A, c = 19.144(10)A, β = 112.87(3)°. There are eight molecules in the unit cell. 1423 independent reflections were measured. Of these, 600 had $I > 3\,\sigma_I$ and were used in the analysis. The structure was solved by direct methods and refined by least squares techniques to R = 0.056.

Although the structures of macrocyclic tetrapyrroles, porphyrins, have been studied extensively by crystallography,[1] there have been no reported crystallographic studies of bile pigments. The one published exception is a report on the structures of zinc complexes of a photo-oxidation product of octaethylporphyrin, octaethylformylbiliverdin.[2] Indeed, very little crystallographic work has been done for the structures of open chain polypyrroles. The structure of a monopyrrole, ethyl 4 - acetyl - 3 - ethyl - 5 - methyl - pyrrole - 2 - carboxylate, has been published,[3] and only one crystal structure of an uncomplexed dipyrrole, 5,5' - biscarboethoxy - 3,3',4,4' - tetraethyl - (2.2') - dipyrromethane 2, has been determined previous to this work.[4] Compound 2 might be viewed as a model substrate for rings II and III of bilirubin 3, an accurate structure of which is currently of wide interest in view of its importance in neonatal jaundice and the phototherapy thereof.[5] Structure 1 on the other hand, may be viewed as a model for rings I and II of bilirubin; thus, its structure too is a potentially important and relevant one. We report here the X-ray crystal structure of 1 which provides an interesting comparison with 2 and a possible insight into the conformation of bilirubin.

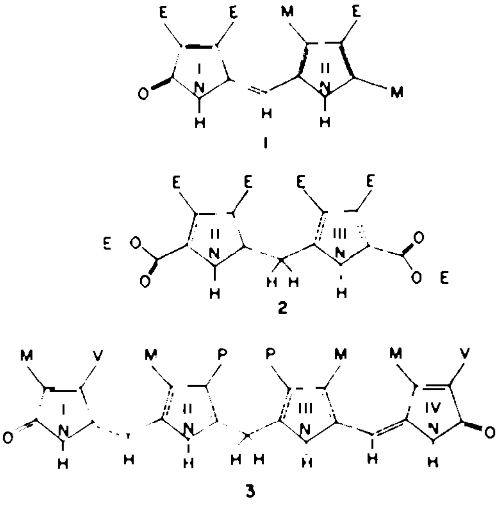


Fig. 1.

RESULTS AND DISCUSSION

Figure 2 shows the structure of the oxodipyrromethene 1. Its synthesis, characterization and properties have been discussed elsewhere.[6,7] The arbitrary numbering scheme used is also indicated. Figure 3 is a stereoview of the molecule without hydrogen atoms. An important feature in this work is that the two pyrrole rings in the molecule are in a cisoid arrangement with the *Z*-configuration. This observation is highly significant as it correlates well with the observed preference for one isomeric form in 1 and related oxodipyrromethenes during their photochemistry.[8] Other more sterically crowded configurational isomers (syn-*E*, anti-*Z*, anti-*E* of Fig. 4) which might be expected to intrude have not been found, except to a small extent.[9] With the exceptions noted below the molecule bears strong resemblances to one-half of a prophyrin ring.

The compound is a conjugated system and the molecular structure is effectively planar. Table 4 lists the least squares planes of the two individual pyrrole rings and the skeleton of the entire molecule, excluding peripheral atoms. The maximum deviation from the plane of the dipyrromethene skeleton is 0.045A. It is important to note that the pyrrole rings each form an angle of only 1.97° with the plane of the dipyrromethene skeleton and an angle of 3.90° with each other. This contrasts with an interplanar angle of 71.9° in the dipyrromethane compound 2,[4] in which the bridging carbon atom C-5 is saturated.

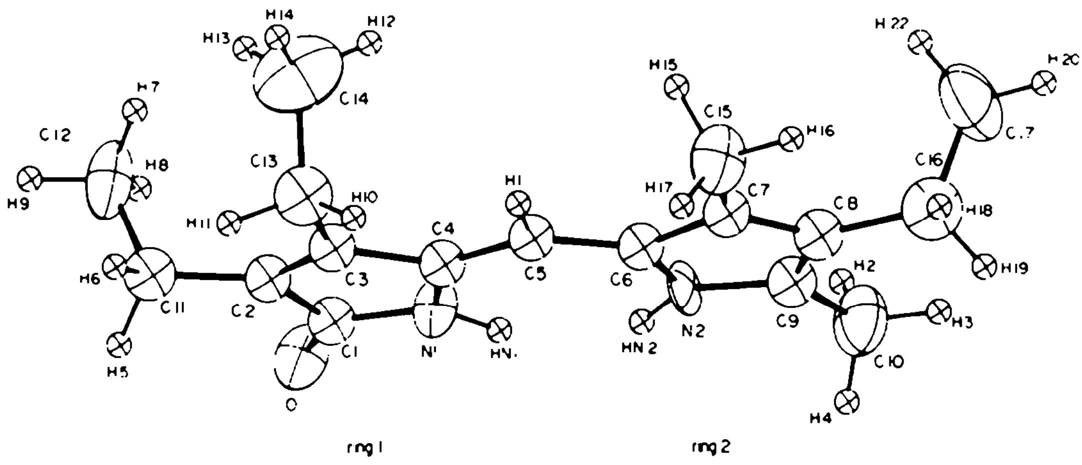


Fig. 2.

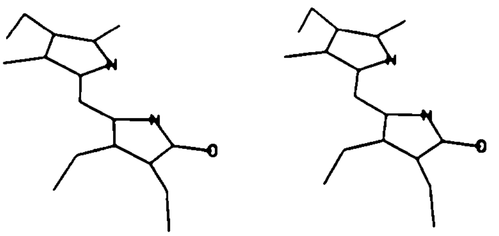
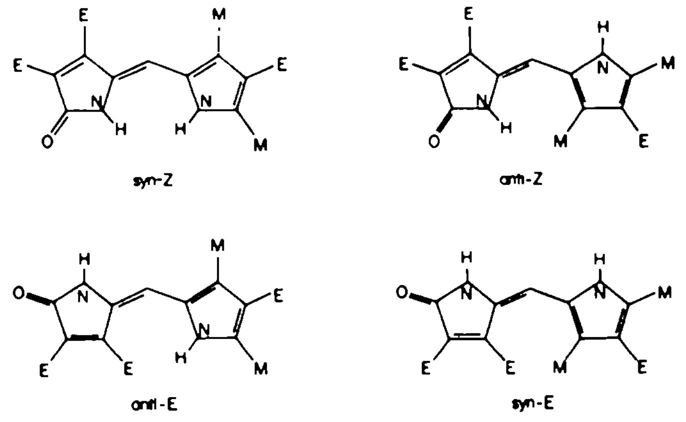


Fig. 3.

The presence of a conjugated system has other effects. There is a large difference in the bond lengths and angles in the two rings which indicates the resonance form as shown in Fig. 1 overwhelmingly predominates. However the short lengths of the C_a-N bonds indicate a significant amount of double bond character, so resonance forms involving the nitrogen atoms in each ring undoubtedly contribute. Bond lengths and angles are tabulated in Table 5 and are illustrated in Fig. 5. That figure also shows the nomenclature used for different types of carbon atoms. The C_b-C_b distances of 1.30(1) and 1.38(1) in rings 1 and 2 respectively indicate the former bond has a much greater double bond character. Similarly, the average C_a-C_b distance of 1.46A in ring 1 indicates these bonds have less double bond character than the analogous bonds in ring 2, for which the average distance is 1.38A. The two C_m-C_a distances are also different (1.35(1)A and 1.40(1)A).

The dimensions of ring II are closer to those found by microwave studies for pyrrole itself[10] and those found in the dipyrromethane compound 2[4] than are the dimesnions of ring I, which can be described as a pyrrolenone moiety. However the C_b-C_b distance in ring II in the dipyrromethane is 0.03A shorter than the 1.41A found in the other compounds. It is not clear if this difference is real. Hoard[1] has postulated that use of a high percentage of data from the lower half of the copper sphere causes an underestimation in the C_b-C_b distances in porphyrins. In this regard it is interesting to note the analogous distance in ring I (1.30A) is approximately 0.02–0.03A shorter than normally found for pure sp^2-sp^2 double bonds. For example the average C=C distance is 1.323(6)A in spiro - [5,5] - undeca - 1,4,7,10 - tetraene - 3,9 - dione.[11] Other comparable bond parameters in this compound are in better agreement with the present study. For example the average C=O distance in this quinone compound[11] is 1.227(1)A, in good agreement with the 1.22(1)A found in the dipyrromethene.

In the dipyrromethane compound 2[4] the bond lengths in the individual pyrrole rings indicate significant deviations from C_2V symmetry. The authors attribute these differences to contributions from other resonance forms. While there are also deviations from C_2V symmetry in both rings of the dipyrromethene compound, the relatively large standard deviations makes it difficult to assess the significance of the differences, and thus attribute them to the existence of contributions from other resonance forms.



syn-Z anti-Z

anti-E syn-E

Fig. 4.

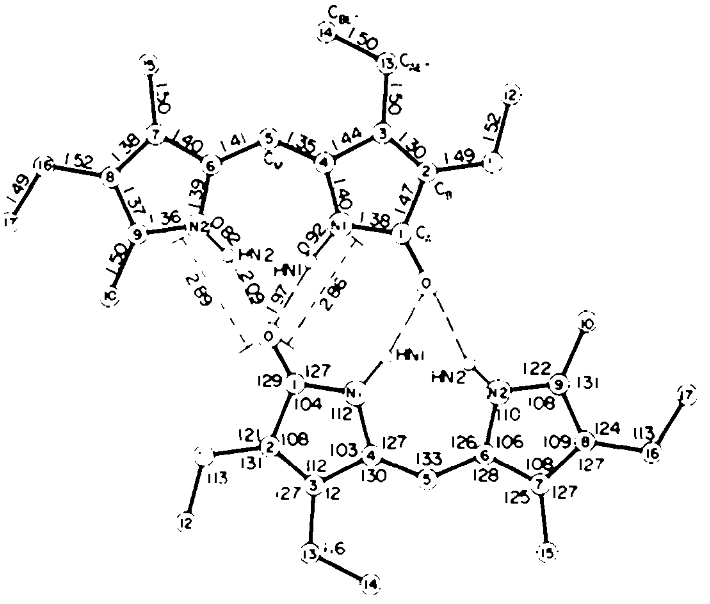


Fig. 5.

The $C_{\alpha et}$–$C_{\beta et}$ distances are usually short. However this is a common observation for terminal C–C bonds of aliphatic peripheral groups (e.g. various octaethylporphyrin complexes).[12] This apparent shortening generally is attributed to neglect of the relatively large thermal motion of the terminal carbon atoms.

The significance of differences in the bond angles is also difficult to assess. It would appear the average N–C_a–C_b angle in ring I (103.6°) is less than the average angle in ring II (106.6°). The C_a–C_m–C_a angle of 133.3° is quite large and probably arises because of the intramolecular repulsions between the hydrogen atoms bonded to the nitrogen atoms. The N–N distance is 3.17A while the H(N1)–H(N2) separation is approximately 2.19A. In compound 2 which is non-planar,[4] the N–N distance is 3.50A and the distance between the hydrogen atoms on these nitrogen atoms is 2.55A. Thus, hydrogen–hydrogen atom repulsion is not a factor and the C_a–C_m–C_a angle is 113.8°, which is close to the value normally found for methylene carbon atoms.

A similar expansion of the C_a–C_m–C_a angle is also seen when the bond parameters of porphyrin diacids are compared. In H_4OEP^{+2} (OEP = octaethylporphyrin),[13] a molecule showing relatively small deviations from planarity, the average C_a–C_m–C_a angle is 127.5°, while in the diacid cations of tetraphenylporphyrin (H_4TPP^{+2}) and tetrapyridylporphyrin (H_4TPyP^{+2}), in which the macrocycle assumes a highly ruffled configuration to relieve the strain caused by intramolecular hydrogen–hydrogen repulsion, the analogous angles are 120° and 123° respectively.[14] The macrocyclic configuration probably keeps the angle in H_4OEP^{+2} from increasing to larger values.

The N–H stretching frequencies for dipyrromethenes and dipyrromethanes with alkyl substituents at all alpha-carbon atom positions differ significantly with γ_{N-H} being 3280 cm^{-1} and 3453 cm^{-1} respectively.[15] This has been postulated as being due to an intramolecular NH . . . . N bond in the latter. The IR spectra of 1 in CCl_4 and in KBr have a band attributable to N–H stretch at 3400 cm^{-1} with a much weaker band at 3200 cm^{-1}. The X-ray structure determination results reveal no evidence of an *intra*-molecular hydrogen bond. This is to be expected since, as in the dipyrromethanes, both nitrogen atoms in 1 carry hydrogen atoms, rather than only one as in the cited[15] alkyl-substituted dipyrromethenes.

Instead the molecules are arranged in the crystal lattice so as to form *inter*molecular hydrogen-bonded dimers. This arrangement is shown in Fig. 5. The interaction is between a given molecule and that related by the symmetry operation $x' = 1.5 - x$, $y' = 1.5 - y$, $z' = -z$. The nitrogen atoms of one molecule are hydrogen bonded to the oxygen atoms of the other. The N(1)–O And N(2)–O distances are 2.895 and 2.856A respectively. A similar hydrogen bonding dimer has been observed in the dipyrromethane compound 2.[4] In this compound the interaction is between the carbonyl oxygen of one of the diethoxycarbonyl groups and the pyrrole N–H atoms of the other molecule.

Figure 6 shows the packing in the unit cell. Besides the hydrogen bonding just described, there are no other short intermolecular contacts. Only three contacts are less than 3.5A. These are N(1)–C(5)'', 3.44A; N(2)–C(3)'', 3.45A; and C(4)–C(5)'', 3.48A. The doubly primed atoms indicate those related to those on the given molecule by the symmetry operation $x'' = 1.5 - x$, $y = 0.5 - y$, $z'' = z$. None of these contacts is considered of any significance. These distances are within the range of typical van der Waals contacts.

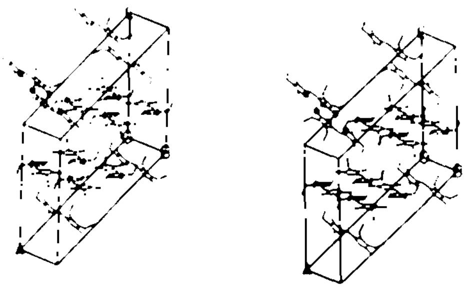


Fig. 6.

CONCLUSIONS

The X-ray crystallographic structure of oxodipyrromethene 1 shows a preference for the *syn-Z* configuration about the central carbon–carbon double bond. The data also reveal the ability of the amide carbonyl oxygen and N–H groups of one molecule of 1 to H-bond in a reciprocal way with another molecule of 1. This information is entirely in keeping with the required *syn-Z* configuration in bilirubin for the H-bonded structure of Kuenzle *et al.*[16] and the more recent one proposed by Knell, Hancock and Hutchinson.[17] A recent communication has given experimental support to the latter model.[18] The present work also supports the propensity for H-bonding to the amide oxygen and N–H groups as required by those structures of bilirubin.

EXPERIMENTAL

Crystals of the title compound, obtained from a pyridine-water mixture,[6,7] grow as greenish yellow rods, elongated along *b* and bounded by {100} and {001}. The crystals obtained were generally small. The one selected for intensity measurements was 0.03 × 0.26 × 0.08 mm in the directions of a, b, and c respectively. The crystal was mounted in a thin-walled glass capillary[19] with the b axis approximately parallel to the spindle axis.

Cell data are summarized in Table 1. Cell dimensions were determined by least squares, minimizing the differences between the observed and calculated 2θ values for 18 reflections measured on a Datex-Syntex automatic diffractometer at both $+2\theta$ and -2θ. The same instrument was used for the intensity measurements. Cu Kα radiation ($\lambda = 1.54178$), monochromatized by pyrolitic graphite, was used for all measurements. The ambient temperature was 18°C. The density was measured by flotation in an aqueous zinc nitrate solution. The successful completion of the structure confirmed the choice of the centrosymmetric space group C2/c rather than the acentric space group Cc. There is one independent molecule in the asymmetric unit.

Table 1. Crystal data

$a = 25.106(10)$ Å	$D_c = 1.145$ g/cm^3
$b = 7.132(7)$ Å	$D_m = 1.13(1)$ g/cm^3
$c = 19.144(10)$ Å	M.W. 272.3 daltons ($C_{17}H_{24}N_2O$)
$\beta = 112.87(3)°$	$Z = 8$
$V = 3158$ Å^3	μ(CuKα radiation) $= 5.66$ cm^{-1}

Systematic absences: hkl (h + k odd); h0l (l odd)

Space Group. C2/c (C^6_{2h})

The intensity data were collected by the $\theta - 2\theta$ scan method, the intensity scale being monitored by periodic measurement of a group of five standard reflections. The intensities of these reflections varied by ±2%. These fluctuations were attributed to statistical variations and no corrections were applied. The scan rate was 1°/min, while the scan range was 2°. Backgrounds were measured for half the scan time at each end of the scan range. The standard deviation of the intensity, σ_I, was defined in terms of the statistical variances of the counts as $\sigma_I^2 = \sigma_I^2\,(\text{count}) + K^2(S - B1 + B2)^2$ where S, B1, and B2 are the observed counts for the scan and two backgrounds respectively. σ_I (count) is the standard deviation derived purely from counting statistics. A value of 0.02 was used for K.

1423 independent reflections were measured out to a $\sin\theta/\lambda$ of 0.46 or 45° in θ. Because of the small size of the crystal, virtually no reflections above this limit were of sufficient intensity to be considered observed. 600 reflections had $I \geq 3\sigma_I$ and were used in the analysis. Structure factors were calculated in the normal way assuming an ideally imperfect monochromator for the polarization correction.

Because of the small crystal size and the small linear absorption coefficient, correction for absorption effects was considered unnecessary. No correction for coincidence losses was applied, as the strongest observed peak intensities were in the range of 3000–4000 counts/sec. Previous experience has shown measurements of this magnitude are not affected by coincidence losses.

Determination and refinement of the structure

The structure was solved by use of the tangent refinement procedure, employing the MULTAN package,[20,21] 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. It was feared the large number of unobserved reflections in the shell $80° < 2\theta \leq 90°$ would improperly bias the statistics for the normalized structure factors, hence only data with $2\theta \leq 80°$ were used. Attempts to solve the structure using only reflections with $2 \leq 70°$ failed. 250 E values having $E \geq 1.02$ were used. The program was allowed to choose the two necessary origin defining reflections (5 1 −4, 7 1 −5) and four reflections for the starting set (10 2 9, 10 4 5, 1 5 −5, 7 3 2). In addition the phase of the 10 2 −8 reflection was known to be 0° from Σ_1 relationships. Of the 16 solutions generated, the one having both the highest absolute figure of merit (1.06) and the highest combined figure of merit

Table 2. Fractional coordinates and thermal motion parameters derived from the least squares refinement. In this and subsequent tables estimated standard deviations for the least significant figure are in parentheses. The Debye–Waller factor for anisotropic temperature factors is defined as:

$$T = \exp[-2\pi^2\Sigma_i\Sigma_j a_i^* a_j^* h_i h_j U_{ij}]$$

The values for U have been multiplied by 10^4. Isotropic B's, defined by $T = \exp[-B(\sin^2\theta/\lambda^2)]$ are given in the column labeled U(11). These have been multiplied by 10.

ATOM	X	Y	Z	U(11)	U(22)	U(33)	U(12)	U(13)	U(23)
O	0.6775(2)	0.7725(9)	-0.0795(3)	416(41)	355(53)	702(51)	-81(37)	153(35)	175(43)
N(1)	0.7129(2)	0.5347(10)	0.0096(3)	302(49)	210(54)	461(51)	-137(44)	39(41)	47(49)
N(2)	0.8149(2)	0.3980(10)	0.1599(3)	386(48)	410(64)	237(46)	74(48)	30(38)	212(46)
C(10)	0.9105(3)	0.4947(15)	0.2571(4)	469(69)	723(97)	633(76)	-145(68)	63(59)	22(78)
C(12)	0.5320(3)	0.6704(14)	-0.1315(5)	430(68)	642(91)	681(78)	-48(64)	-40(54)	110(73)
C(14)	0.5633(4)	0.1839(15)	0.0070(6)	915(98)	672(107)	1484(120)	-321(77)	631(89)	32(91)
C(15)	0.7704(3)	-0.0567(14)	0.2100(4)	562(73)	395(81)	666(77)	-15(64)	138(57)	147(64)
C(17)	0.8815(4)	0.1742(15)	0.3927(5)	1093(94)	916(114)	496(74)	178(80)	213(67)	193(78)
C(1)	0.6731(4)	0.6198(14)	-0.0540(5)	29(2)					
C(2)	0.6247(3)	0.4868(13)	-0.0818(4)	27(2)					
C(3)	0.6381(3)	0.3405(13)	-0.0377(4)	28(2)					
C(4)	0.6943(3)	0.3583(14)	0.0230(4)	27(2)					
C(5)	0.7221(3)	0.2422(13)	0.0814(4)	26(2)					
C(6)	0.7754(3)	0.2524(14)	0.1435(4)	26(2)					
C(7)	0.7989(3)	0.1230(14)	0.2025(5)	29(2)					
C(8)	0.8511(3)	0.1921(13)	0.2521(4)	31(2)					
C(9)	0.8610(3)	0.3610(14)	0.2255(5)	32(2)					
C(11)	0.5713(3)	0.5327(14)	-0.1492(4)	34(2)					
C(13)	0.6011(4)	0.1717(14)	-0.0425(5)	44(2)					
C(16)	0.8914(3)	0.1035(15)	0.3257(5)	48(2)					

(2.97) proved to be the correct one. All 20 non-hydrogen atoms were found in the subsequent E-map.

Most of the least squares refinement was performed using block diagonal methods. The function minimized was $\Sigma w|Fo-Fc|^2$, where $w = 1/\sigma_F^2$. Initially isotropic temperature factors were used. The limited number of data precluded anisotropic refinement of all atoms, hence only the oxygen atom, the nitrogen atoms, and the terminal carbon atoms (C(10), C(12), C(14), C(15), C(17)) were refined anisotropically. It was felt the temperature factors of the terminal atoms would show the most marked anisotropy.

After several cycles of refinement, ΔF syntheses were calculated to locate hydrogen atoms. 19 of the 24 hydrogen atoms could be found. However many of the bond lengths and angles were chemically unreasonable. It was clear that a set of idealized hydrogen atom positions, calculated assuming a N–H or C–H distance of 1.0A and a staggered configuration for the methyl hydrogen atoms, would be a good approximation to the observed values. Refinement was continued, including the contribution of the calculated hydrogen atoms positions ($B_H = 4.0$) to the structure factors. However in this and subsequent refinements, the hydrogen atom parameters were not refined. After several cycles of refinement another difference synthesis was calculated. All but three of the hydrogen atoms were located. There was some improvements in the observed bond lengths and angles, but not enough to justify the use of the observed positions in subsequent analysis, except for the hydrogen atoms bonded to the pyrrole nitrogen atoms. In the final cycles of refinement, carried out using full-matrix least squares methods, the observed positions of these two hydrogen atoms were used. The idealized positions of the other hydrogen atoms were recalculated and used.

After the final cycle the shifts on all refined parameters were well below one standard deviation. The final conventional R index, defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ was 0.056, while the weighted index, R_w defined as $\Sigma w||F_o| - |F_c||^2/\Sigma wF_o^2$ was 0.048. A structure factor calculation using all reflections, including those with $I < 3\sigma_I$ gave a conventional R of 0.162 (0.133 when reflections with $I = 0$ were excluded). R_w was 0.067. The error in an observation of unit weight, defined as $[\Sigma w||F_o| - |F_c||^2/(N_o - N_v)]^{1/2}$ was 1.65 for $N_o = 600$ reflections and $N_v = 121$ variables. A final difference Fourier synthesis showed a maximum electron density of 0.17 e/A^3. The highest peaks were close to atoms which were assumed to have isotropic thermal motion.

No evidence of secondary extinction was found. No correction for anomalous dispersion was applied. Scattering factors were from the *International Tables of Crystallography*.[22]

The final positional and thermal parameters for non-hydrogen atoms are given in Table 2. A list of hydrogen atoms positions is given in Table 3. A listing of the final observed calculated

Table 3. Fractional coordinates for hydrogen atoms*

	x	y	z
H(N1)	0.740	0.609	0.026
H(N2)	0.810	0.494	0.126
H(1)	0.700	0.117	0.081
H(2)	0.897	0.627	0.267
H(3)	0.942	0.456	0.306
H(4)	0.930	0.521	0.219
H(5)	0.581	0.590	-0.192
H(6)	0.547	0.416	-0.172
H(7)	0.521	0.614	-0.092
H(8)	0.554	0.789	-0.112
H(9)	0.496	0.700	-0.178
H(10)	0.625	0.045	-0.026
H(11)	0.573	0.138	-0.099
H(12)	0.588	0.205	0.058
H(13)	0.537	0.299	-0.015
H(14)	0.537	0.073	-0.001
H(15)	0.731	-0.036	0.214
H(16)	0.794	-0.128	0.258
H(17)	0.762	-0.146	0.166
H(18)	0.887	-0.038	0.324
H(19)	0.934	0.130	0.336
H(20)	0.907	0.117	0.441
H(21)	0.886	0.315	0.396
H(22)	0.839	0.146	0.385

*H(N1) and H(N2) are from difference Fourier synthesis. Others are "idealized" calculated positions. The isotropic temperature factor was assumed to be 4.0 Å^2 for all hydrogen atoms.

Table 4. Deviations (A) from least-squares planes

Plane 1: (N(1), N(2), C(1)–C(9))
$-17.879x + 3.159y + 14.906z = -10.899$
Plane 2: (N(1), C(1)–C(4))
$-17.503x + 3.072y + 15.296z = -10.697$
Plane 3:
$-18.073x + 3.299y + 14.484z = -11.100$

	Plane 1 Dipyrrolic Skeleton	Plane 2 Pyrrole Ring 1	Plane 3 Pyrrole Ring 2
N(1)	-0.016	0.007	0.118
C(1)	0.017	-0.007	0.197
C(2)	0.048	0.006	0.231
C(3)	0.004	-0.002	0.145
C(4)	-0.039	-0.002	0.068
C(5)	-0.033	0.047	0.028
N(2)	-0.028	0.104	0.003
C(6)	-0.027	0.096	-0.002
C(7)	0.022	0.188	-0.000
C(8)	0.046	0.245	0.002
C(9)	0.007	0.184	-0.003
C(10)	0.015	0.212	0.001
O	0.040	-0.005	0.251

Note: All planes are unweighted. x, y, z are in triclinic fractional coordinates.

Table 5. Bond lengths and angles

O(1)-C(1)	1.216(10)Å	C(1)-N(1)-C(4)	112.2(7)°
N(1)-C(1)	1.380(10)	C(6)-N(2)-C(9)	109.9(8)
N(1)-C(4)	1.401(10)	N(1)-C(1)-O(1)	126.9(9)
N(2)-C(6)	1.384(9)	N(1)-C(1)-C(2)	104.4(8)
N(2)-C(9)	1.362(9)	O(1)-C(1)-C(2)	128.6(10)
C(1)-C(2)	1.469(10)	C(1)-C(2)-C(3)	108.2(8)
C(2)-C(3)	1.303(10)	C(1)-C(2)-C(11)	120.7(9)
C(2)-C(11)	1.491(10)	C(3)-C(2)-C(11)	131.0(9)
C(3)-C(4)	1.443(10)	C(2)-C(3)-C(4)	112.2(9)
C(3)-C(13)	1.501(11)	C(2)-C(3)-C(13)	127.2(8)
C(4)-C(5)	1.347(10)	C(4)-C(3)-C(13)	120.5(9)
C(5)-C(6)	1.405(10)	N(1)-C(4)-C(3)	102.9(8)
C(6)-C(7)	1.399(11)	N(1)-C(4)-C(5)	127.1(8)
C(7)-C(8)	1.376(10)	C(3)-C(4)-C(5)	130.0(10)
C(7)-C(15)	1.502(12)	C(4)-C(5)-C(6)	133.3(9)
C(8)-C(9)	1.367(10)	N(2)-C(6)-C(5)	126.4(9)
C(8)-C(16)	1.516(11)	N(2)-C(6)-C(7)	105.7(7)
C(9)-C(10)	1.496(11)	C(5)-C(6)-C(7)	127.8(10)
C(11)-C(12)	1.520(12)	C(6)-C(7)-C(8)	108.1(9)
C(13)-C(14)	1.504(12)	C(6)-C(7)-C(15)	124.9(9)
C(16)-C(17)	1.489(12)	C(8)-C(7)-C(15)	126.9(10)
		C(7)-C(8)-C(9)	108.7(9)
		C(7)-C(8)-C(16)	127.1(10)
		C(9)-C(8)-C(16)	124.2(9)
		N(2)-C(9)-C(8)	107.5(9)
		N(2)-C(9)-C(10)	121.7(9)
		C(8)-C(9)-C(10)	130.8(9)
		C(2)-C(11)-C(12)	113.1(8)
		C(3)-C(13)-C(14)	115.5(9)
		C(8)-C(16)-C(17)	112.8(8)

structure factors is available from the authors at Texas A & M. Calculations were carried out on the CDC 7600 computer at Brookhaven National Laboratory using the CRYSNET system, and the IBM 360/65 and Amdahl 470 v/6 computers at Texas A & M University.† Use was made of the PDP 11/40-Vector General graphics system which is part of the CRYSNET Network.[23,24]

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†Besides those programs already mentioned, the following programs were used: TRACER, a cell reduction program by Lawton, LSLAT (least-squares cell-parameter refinement), BDLR4 (block-diagonal least squares program), FOURIER (version of the Zalkin Fourier summation program modified by Robinson and Dellaca), NUCLS (version of the ORFLS[25] least squares program, modified by Ibers and Doedens), HOW and XANADU (molecular geometry programs, the latter by Roberts and Sheldrick), ORFFE (function and error program written by Busing, Martin and Levy[26] and modified by Brown, Johnson and Thiessen), ORTEP (Thermal ellipsoid plot program of Johnson)[27] and LIST by Snyder for listing structure factors. Several other local data handling programs were used as well as the autoindexing and least-squares cell parameter refinement program written by Sparks for the Nova computer.[28] Data collection programs used were those written by Stanford for the Varian 620i computer.

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