syn- and *anti*-Conformation in Oxodipyrromethenes: Crystal and Molecular Structure of 3,4-Dimethyl-2,2′-pyrromethen-5(1*H*)-one and Its *N*-Methyl Derivative

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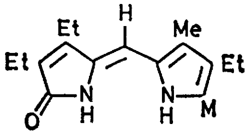
The structure of two oxodipyrromethenes have been determined from three-dimensional diffractometer data. One is 3,4-dimethyl-2,2′-pyrromethen-5(1*H*)-one, $C_{11}H_{12}N_2O$ (I), which crystallizes in the monoclinic space group $P2_1/n$ with $a = 13.597(1)$, $b = 5.809(1)$, $c = 12.558(1)$ Å, $\beta = 101.29(1)°$, $Z = 4$. The second is a derivative of this compound in which one of the pyrrole nitrogen atoms is methylated. This is 1′,3,4-trimethyl-2,2′-pyrromethen-5(1*H*)-one, $C_{12}H_{14}N_2O$, (II). It also crystallizes in $P2_1/n$ with $a = 7.122(1)$, $b = 22.873(1)$, $c = 7.012(1)$ Å, $\beta = 104.64(2)°$, $Z = 4$. Both structures were solved by direct methods and refined by full-matrix least squares. The isomers obtained both had the *Z*-configuration, but in (I), the nitrogen atoms are *syn*, while in (II), they are *anti*. Both compounds show relatively small deviation from planarity, but (II) shows larger deviations than (I). Both form hydrogen-bonded dimers between the lactam oxygen atom and pyrrole nitrogen atoms. A comparison of the structures in the solid state and in solution indicates the difference in energy between a planar and twisted conformation is small.

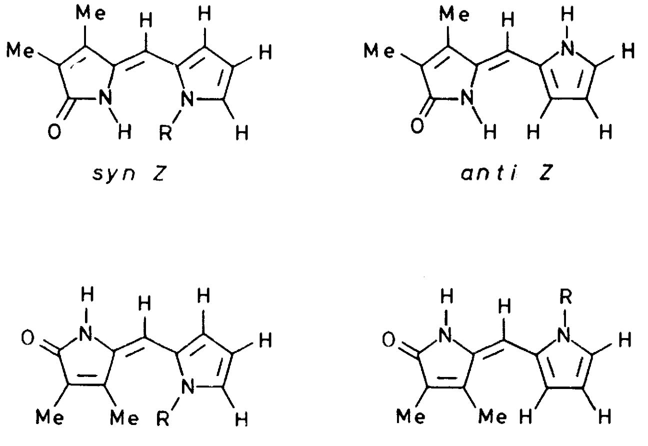
ALTHOUGH the structure of macrocyclic tetrapyrroles (*e.g.* porphyrins) have been extensively studied, it has not been until recently that much attention has been paid to the open-chain polypyrroles, a group which includes the bile pigments. The best known of the bile pigments is bilirubin, but there are several other biologically important members of this class of compounds. In bilirubin,[1] as in all the bile pigments studied thus far by *X*-ray crystallographic techniques,[2-6] adjacent rings in the dipyrromethene moieties have the *Z*-configuration with the pyrrole nitrogen atoms *syn*. This is also true for a tripyrrolic aldehyde compound,[7] the structure of which was recently reported.

Photochemistry plays an important part in the reactions of the bile pigments. It has been suggested that isomerization may account for the photo-solubilization of bilirubin.[8] It has also been postulated [9] that the spectral shift between the ' red ' and ' far-red ' forms of the chromophore of phytochrome, which is probably a bile pigment of the rhodin type,[10] may be accounted for in terms of geometrical isomerization at the methine bridge. Studies have been carried out on a number of oxodipyrromethenes which photoisomerize from the *Z*-isomer to the *E*-isomer. Among the oxodipyrromethenes which photoisomerize are 3,4-dimethyl-2,2′-pyrromethen-5(1*H*)-one (I) [11] and an *N*-methyl derivative, 1′,3,4-trimethyl-2,2′-pyrromethen-5(1*H*)-one,[12] which are the subject of this work. The four possible planar representations for these molecules are shown in Figure 1. Recently photoisomerization has been observed in aetiobiliverdin-IVγ, a bilitriene.[13]

Since these are fully conjugated systems, one expects to find a planar conformation for oxodipyrromethenes. However, studies in solutions and in the solid state indicate a much more complex situation. In an earlier *X*-ray study on a 5(1*H*)-dipyrromethene (III),[14] it was found that the molecule assumes a *syn*-*Z* conformation and shows only small deviations from planarity. In the solid state, intermolecular hydrogen-bonding between the oxygen atom and both NH-groups generates dimers. Such dimers occur in solution in non-polar solvents, but in more polar solvents monomers are present. Lanthanide shift experiments and nuclear Overhauser effect measurements [11,12] suggest the monomers have the pyrrole rings inclined at *ca.* 40°.



(III)



syn Z *anti Z* *anti E* *syn E*

FIGURE 1 The four possible planar conformations for (I) and (II). For (I) R = H; for (II) R = Me

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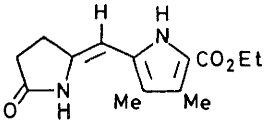
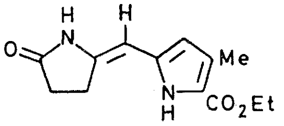
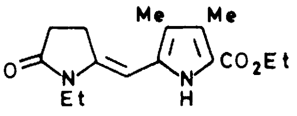
The complexity of these dipyrromethene systems is further indicated by a recent *X*-ray study on a series of compounds in which the C_b–C_b bond in the pyrroleneone ring is saturated.[15] These compounds also photoisomerize. Of particular interest are (IV)—(VI), which assume twisted *anti-Z*, planar *anti-E* and twisted *anti-E* conformations, respectively, thus differing in isomeric form and in the degree of planarity from their fully conjugated analogue.



(IV)



(V)



(VI).

The ease of deformation of the dipyrromethene group from planarity is also shown by the various fully conjugated bilitrienes which have been studied.[2-6] These tetrapyrrolic compounds cannot be planar because of steric constraints. Hence they assume a helical shape and adjacent pyrrole rings are not co-planar. On the other hand, the previously mentioned tripyrrole,[7] which is a fully conjugated system, is planar. In this compound, the steric constraints which affect the tetrapyrroles are not present.

It was decided to undertake the structure determination of the *Z*-isomers (I) and (II) in order to observe the effect of *N*-substitution on the conformation of the oxodipyrromethene. Because of steric considerations (II) cannot assume a planar *syn-Z* conformation. Unlike (I), only one ring in (II) can be involved in hydrogen bonding, a factor which could affect the planarity of the molecule. In addition, the availability of excellent crystals, especially those of (I), made it possible to obtain accurate bond parameters. In the earlier study[14] on (III), the limited amount of data made it difficult to assess the significance of differences among supposedly chemically equivalent bonds.

EXPERIMENTAL

Crystals of both (I) and (II) were grown from water–methanol. Those of (I) grew as nicely formed yellow wedge-shaped crystals with the most prominent faces being {100}. The crystal used for intensity measurements was 0.17 × 0.37 × 0.32 mm in the direction of *a*, *b*, and *c*, respectively. Crystals of (II), the *N*-methyl derivative, grew as yellow elongated plates. It was obvious under polarized light that these crystals were twinned. An irregular, roughly triangularly shaped fragment was obtained by cleaving one of these crystals. This fragment subsequently proved to contain no more than 5% of the twin. This fragment had the approximate dimensions 0.37 × 0.31 × 0.17 mm.

Crystal data for both compounds are listed in Table 1.

TABLE 1

Crystal data and experimental conditions[a]

	$C_{11}H_{12}N_2O$ (I)	$C_{12}H_{14}N_2O$ (II)
a/Å	13.957(1)	7.122(1)
b/Å	5.809(1)	22.873(3)
c/Å	12.558(1)	7.012(1)
β/°	101.29(1)	104.64(2)
Volume/Å^3	998	1 105
Room temp./°C	20	23
D_c/g cm^{-3}	1.25	1.21
D_m/g cm^{-3}	1.19(2)	1.17(2)
M/Daltons	188.2	202.1
Z	4	4
Space group	$P2_1/n$[b]	$P2_1/n$
μ (CuK_α radiation) cm^{-1}	6.70	6.39
Systematic absences	$h0l$ ($h + 1$ odd) $0k0$ (k odd)	Same
Scan rate/° min^{-1}	2.93—29.3 (depending on intensity)	2.0
Scan range/°	2.0—2.6 (depending on 2θ)	2.25°
Max. sinθ/λ	0.56 (130° in 2θ)	0.50 (100° in 2θ)
Total reflections	1 859	1 174
Reflections with $I \geqslant 2\sigma_I$	1 596	972
Stability constant (k)	0.02	0.02
$R = \dfrac{\Sigma\|\|F_o\| - \|F_c\|\|}{\Sigma\|F_o\|}$	0.051	0.063
$R_w = \dfrac{\Sigma w\|\|F_o\| - \|F_c\|\|^2}{E_w F_a{}^2}$	0.068	0.075
$\text{SEF} = \left(\dfrac{\Sigma w\|\|F_o\| - \|F_c\|\|^2}{N_{obs.} - N_{var.}}\right)^{1/2}$	4.30	3.01

[a] In this and subsequent tables, estimated standard deviations for the least significant figures are in parentheses.
[b] Non-standard aspect of $P2_1/c$ (C^5_{2h}, # 14).

Also listed are some of the experimental conditions used in the intensity measurements. The cell dimensions of both compounds were refined by least squares. In the case of (I) they were obtained by minimizing the differences between observed and calculated values of the setting angles for 15 reflections. For (II) they were obtained by minimizing the differences between observed and calculated 2θ values for 24 reflections measured at both + and − settings of the 2θ angle. Cu-K_α radiation (λ = 1.541 78 Å), monochromatized by pyrolitic graphite, was used for both compounds in the determination of cell dimensions and intensity data. The densities were determined by flotation in an aqueous zinc nitrate solution. For both compounds the choice of the space group ($P2_1/n$) was uniquely determined by the systematic absences.

All data for (I) were measured on a Syntex $P2_1$ diffractometer. For (II) a Datex-Syntex diffractometer was used. The data in each case were collected by the θ—2θ scan method, the intensity scale being monitored by remeasuring the group of five reflections periodically. In neither case were there any significant trends in the intensities of these check reflections and no corrections were made. Backgrounds at either end of the scan range were collected for half the scan time. The standard deviation in the intensities, σ_I, was determined in terms of the statistical variances of the counts as $\sigma_I{}^2 = \sigma_I{}^2(\text{count}) + (kA)^2$, where $\sigma_I{}^2$(count) is the variance determined purely from counting statistics. The values of k, the so-called stability constant, are given in Table 1. For (1), A is the observed intensity. For (II), it is the sum of the scan and background counts.

Only reflections with $I \geqslant 2\sigma_I$ were used in the analysis. The intensities were corrected for coincidence using the alogarithm supplied by Syntex in the case of (I) and the method of Sletten, Sletten, and Jensen[16] ($\tau = 4.0 \times 10^{-7}$ counts^{-1}) for (II). Absorption corrections were not applied.

Determination and Refinement of the Structure.—The structures of both compounds were solved by an automatic multisolution technique which is part of the SHELX-76 system of programs.[17] 2^{12} Sign permutations were expanded by the Σ_2 formula. All non-hydrogen atoms were found in the subsequent E-maps.

Least-squares refinement using full-matrix methods was carried out. The function minimized was $\Sigma w(F_o - F_c)^2$ where $w = 1/\sigma_F^2$. Initially isotropic temperature factors were used, but in later refinement cycles, all non-hydrogen atoms were assumed to have anisotropic thermal motion. After several cycles of refinement, ΔF syntheses were calculated in an attempt to locate hydrogen atoms. For (*I*), all but four of the hydrogen atoms could be found. Positions for the remainder were calculated. For (II) all hydrogen atoms could be located. In both cases all hydrogen atoms positions were refined, assuming isotropic thermal motion. Both refinements converged. The final R values are given in Table 1.

After the final cycles, all shifts were well below 1σ. Corrections were made for anomalous dispersion for the non-hydrogen atoms.[18] Scattering factors were from ref. 19. There was some evidence of secondary extinction. In (I) the most intense reflection (311) was affected. For (II) the five most intense reflections ($\bar{2}11$, $\bar{2}00$, $\bar{1}40$, 020, $01\bar{1}$) were considered to be affected. These were not included in the final refinements.

On the final difference-Fourier synthesis, the largest peaks were 0.18 and 0.26 e/A^3 for (I) and (II) respectively. No physical significance is attributed to any of the peaks on these final difference maps.

The structures were solved using an Amdahl 470 V/6 computer. Some other calculations were also done on this machine using programs as previously listed,[7] but the majority of the calculations were performed on a PDP 11/40 computer using the Enraf–Nonius Structure Determination Package. Use was made of the PDP 11/40-Vector General Graphics System.[20]

TABLE 2

Final fractional atom co-ordinates for (I) derived from the least-squares refinement

Atom	*X*	*Y*	*Z*
O(1)	0.590 3(1)	0.721 1(3)	0.480 0(1)
N(1)	0.522 8(1)	0.648 3(3)	0.630 2(1)
N(2)	0.384 0(1)	0.322 9(2)	0.739 7(1)
C(1)	0.579 3(1)	0.768 5(3)	0.573 8(1)
C(2)	0.622 7(1)	0.959 0(3)	0.642 3(1)
C(3)	0.590 9(1)	0.945 8(3)	0.736 5(1)
C(4)	0.525 6(1)	0.748 5(3)	0.731 9(1)
C(5)	0.478 9(1)	0.677 7(3)	0.810 9(1)
C(6)	0.416 6(1)	0.484 9(3)	0.818 3(1)
C(7)	0.379 6(1)	0.421 2(3)	0.908 2(1)
C(8)	0.325 7(1)	0.219 0(4)	0.883 4(1)
C(9)	0.329 3(1)	0.162 7(3)	0.778 7(1)
C(10)	0.690 4(1)	1.127 8(4)	0.605 7(2)
C(11)	0.617 3(1)	1.017 4(3)	0.832 4(2)
H(N1)	0.481(1)	0.530(3)	0.606(1)
H(N2)	0.396(1)	0.315(3)	0.672(1)
H(C5)	0.486(1)	0.769(3)	0.878(1)
H(C7)	0.395(1)	0.506(3)	0.985(1)
H(C8)	0.289(1)	0.127(3)	0.927(1)
H(C9)	0.305(1)	0.032(3)	0.734(1)
H(101)	0.752(1)	1.153(5)	0.656(2)
H(102)	0.667(1)	1.273(4)	0.624(1)
H(103)	0.668(1)	1.169(5)	0.532(2)
H(111)	0.565(1)	1.148(4)	0.864(1)
H(112)	0.627(1)	1.256(6)	0.810(2)
H(113)	0.682(2)	1.075(5)	0.872(2)

TABLE 3

Final fractional atom co-ordinates for (II) derived from the least-squares refinement

Atom	*X*	*Y*	*Z*
O(1)	0.029 2(4)	0.574 3(1)	−0.421 9(4)
N(1)	0.144 8(4)	0.495 0(1)	−0.221 8(4)
N(2)	0.315 3(4)	0.330 4(1)	0.123 8(4)
C(1)	0.113 3(5)	0.553 7(2)	−0.258 4(5)
C(2)	0.197 1(5)	0.584 7(2)	−0.076 2(5)
C(3)	0.267 9(4)	0.545 5(2)	0.063 5(5)
C(4)	0.235 4(4)	0.487 1(2)	−0.023 7(5)
C(5)	0.289 1(5)	0.436 4(2)	0.072 7(5)
C(6)	0.269 7(4)	0.377 5(2)	−0.004 8(5)
C(7)	0.217 1(5)	0.355 5(2)	−0.191 2(5)
C(8)	0.230 4(6)	0.294 2(2)	−0.178 6(6)
C(9)	0.288 8(5)	0.280 5(2)	0.014 3(6)
C(10)	0.195 2(6)	0.650 3(2)	−0.064 7(6)
C(11)	0.363 2(6)	0.556 6(2)	0.274 0(6)
C(12)	0.373 2(7)	0.332 9(2)	0.335 3(6)
H(N1)	0.083(4)	0.465(1)	−0.351(4)
H(C5)	0.340(3)	0.440(1)	0.211(3)
H(C7)	0.169(4)	0.377(1)	−0.320(4)
H(C8)	0.200(5)	0.267(1)	−0.305(4)
H(C9)	0.304(4)	0.243(1)	0.096(3)
H(101)	0.132(5)	0.664(1)	0.053(5)
H(102)	0.307(5)	0.667(1)	0.006(4)
H(103)	0.131(7)	0.669(2)	−0.209(6)
H(111)	0.308(5)	0.539(1)	0.366(4)
H(112)	0.356(5)	0.595(1)	0.296(5)
H(113)	0.492(5)	0.539(1)	0.316(5)
H(121)	0.278(5)	0.357(1)	0.384(4)
H(122)	0.379(6)	0.296(1)	0.392(5)
H(123)	0.516(6)	0.350(1)	0.377(5)

The final positional parameters are given in Tables 2 and 3. The thermal parameters, the root-mean-square component of thermal displacement along the principal axes of the thermal ellipsoids, and the observed and calculated structure factors are available as a Supplementary publication [No. SUP 22483 (17 pp.)*].

RESULTS AND DISCUSSION

Figure 2 shows the ORTEP[21] drawings of the oxodipyrromethenes (I) and (II). The numbering scheme used is shown. Also shown in Figure 2(a) is the nomenclature for the various types of carbon atoms. From this Figure it can be seen that both molecules assume a *Z*-configuration. However, in (I) the nitrogen atoms are *syn*, thus resembling half of a porphyrin ring, while in (II), the nitrogen atoms are *anti*. A shift from the *syn*- to *anti*-conformation would correspond to a rotation around the C(5)–C(6) bond, which is essentially a single bond. These conformations could be expected from simple steric considerations. If (II) had a *syn*-conformation, there would be impossibly close contacts between the methyl group on N(2) and the hydrogen atom on N(1). The *anti-Z*-isomer would be the most sterically favoured planar conformation for (II).

The near-planarity of these compounds is of interest. Least-squares planes of interest are given in Table 4. As is usually found, the individual pyrrole rings are planar. The interplanar angle between the pyrrole

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.

rings are 4.9° and 10.0° for (I) and (II) respectively. The angle in (I) agrees well with the value of 3.9° found in an earlier study on (III).[14] This might be expected since the two differ only in alkyl substituents.

TABLE 4

Least-squares planes

(a) Deviations (Å × 10^3) from planes

	(I)			(II)		
	(1)	(2)	(3)	(1)	(2)	(3)
O(1)	−42	9	−413	−200	−43	−626
N(1)	3	−3	−233	−77	15	−309
N(2)	62	−27	1	−103	−118	3
C(1)	−29	1	−342	−100	−15	−395
C(2)	−37	2	−352	37	9	−155
C(3)	−11	−3	−251	85	0	12
C(4)	25	4	−161	1	−9	−93
C(5)	57	1	−48	29	−10	33
C(6)	44	−44	−3	9	39	−1
C(7)	−31	−153	4	116	254	−2
C(8)	−73	−218	−3	73	234	3
C(9)	−10	−133	1	70	4	−4
C(10)	−79	−3	−470	101	36	−126
C(11)	−31	−20	−243	193	−11	254
C(12)				−274	−401	−31

(b) Angles (°) between planes

(I): (1)—(2) 1.5, (1)—(3) 3.4, (2)—(3) 4.9
(II): (1)—(2) 4.6, (1)—(3) 5.8, (2)—(3) 10.0

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

Plane 1: Dipyrrole skeleton, N(1), N(2), C(1)—(9)

$$\text{(I)}: 10.128X - 3.236Y + 2.690Z = 4.894$$
$$\text{(II)}: -7.025X - 1.653Y + 2.753Z = -2.523$$

Plane 2: Pyrrole ring 1, N(1), C(1)—C(4)

$$\text{(I)}: 9.891X - 3.310Y + 2.921Z = 4.863$$
$$\text{(II)}: -6.930X - 1.166Y + 3.250Z = -2.286$$

Plane 3: Pyrrole ring 2, N(2), C(6)—C(9)

$$\text{(I)}: 10.599Z - 3.113Y + 2.078Z = 4.603$$
$$\text{(II)}: -7.105X - 1.106Y + 2.119Z = -2.311$$

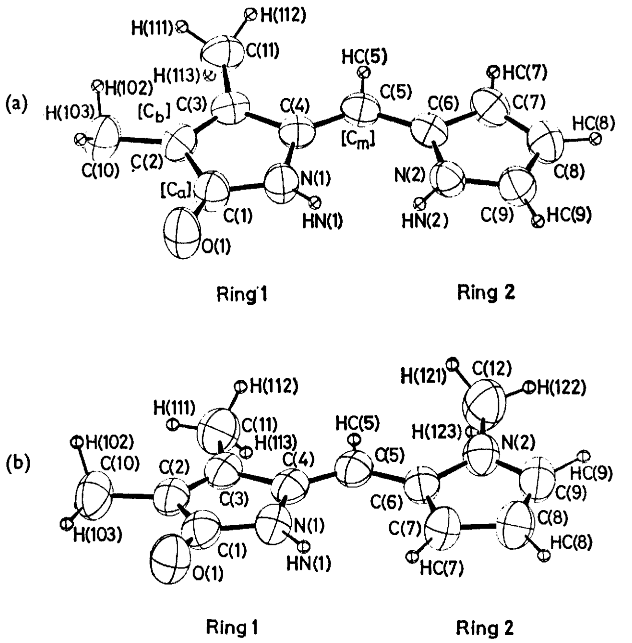

FIGURE 2 (a) ORTEP[21] drawing of the structure of (I). The numbering scheme used is also shown. The thermal ellipsoids are drawn for 50% probability except those of the hydrogen atoms which are not drawn to scale. The nomenclature for various types of carbon atoms is shown in brackets. (b) ORTEP drawing of the structure of (II)

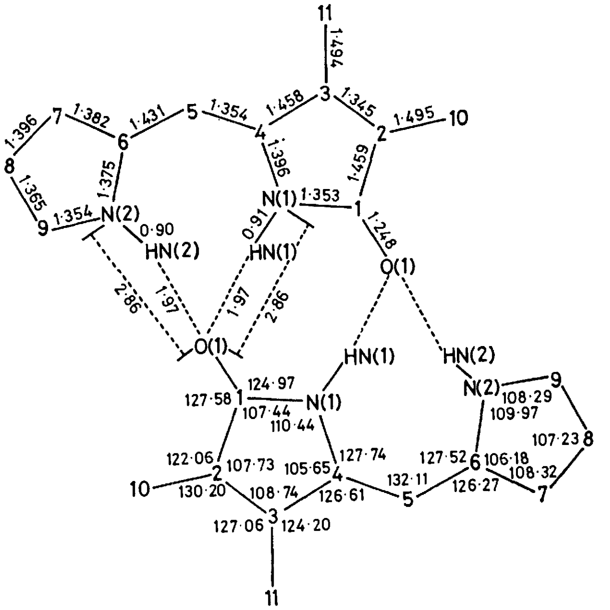

FIGURE 3 Schematic drawing showing the hydrogen-bonded dimer in (I). The intermolecular contact distances are shown. Also shown are the intramolecular bond distances and angles for non-hydrogen atoms. E.s.d.'s are *ca.* 0.001 Å for C–O, C–N, C–C bonds; 0.005 Å for N–H bonds; 0.03—0.04° for bond angles not involving hydrogen atoms

The probable reason for the planarity of these systems in the solid state is intermolecular hydrogen bonding. As was found for (III), (I) forms a hydrogen-bonded dimer between the two pyrrole nitrogen atoms and the lactam oxygen atom on a centrosymmetrically related molecule. A schematic drawing of this dimer is shown in Figure 3. The N · · · O distances are both 2.86 Å. The N–H · · · O angles are 164° and 175°. A similar dimer exists in the solid state for (II), although obviously only N(1) and O(1) may be involved, since N(2) is the methyl substituted atom. Thus there are only two hydrogen bonds per dimer rather than the four found in (I). A hydrogen-bonding scheme similar to that found in (II) has been observed in biliverdin dimethyl ester.[2] The N(1) · · · O(1) distance in (II) is 2.95 Å, while the O(1) · · · C(7) distance is 3.25 Å. The N(1)–H(NN1) · · · O(1) angle is 172°. A schematic drawing of this dimer is shown in Figure 4.

It is clear that for (I), a planar conformation is the most favourable for hydrogen-bonding, but the case for (II) is less clear, since ring 2 is not involved in the hydrogen bonding. The larger dihedral angle between pyrrole rings in (II) may partially be due to attempts to increase the H(C7) · · · O(1) intermolecular distance and the H(C7) · · · H(N1) intramolecular distance.

Hydrogen bonding is also found in compounds (IV)—(VI).[15] Compound (VI), like (II), is also an *N*-alkyl substituted derivative, but in this case it is the nitrogen atom on the pyrroleneone ring that is methylated. This compound is non-planar with a dihedral angle of 30°. However, it should be remembered that the C(2)–C(3) bond is essentially a single bond. The degree of conjugation is less than in either (I) or (II), and this fact, coupled with the differing nitrogen atom substitution, makes it less likely that a planar conformation would be maintained.

Bond lengths and angles for both compounds are given in Figures 3 and 4. The bond parameters for (I) agree with those found in (III),[14] as far as the rather large standard deviations in the latter will allow comparison. The estimated standard deviations in both compounds (I) and (II), especially (I), are quite good. While the bond parameters in (II) generally agree with those found in (III), the C_a–C_m–C_a and C_m–C_a–C_b angles are an exception. In (I) the C_a–C_m–C_b angle [C(4)–C(5)–C(6)] is 132.11 (4)° agreeing with the angle of 133° found in (III). This rather large angle probably arises because of intramolecular repulsions between the imino-hydrogen atoms which in the case are involved in hydrogen-bonding to the same atom. The H(N1)–H(N2) distance is 2.01 Å. In contrast the C_a–C_m–C_a angle in (II) is 128.7 (2)°, but the C(5)–C(6)–C(7) angle is 133.0 (2)°, much larger than either the C(5)–C(6)–C(7) angle [126.27 (4)°] or the C(5)–C(6)–N(2) angle [127.522 (3)°] in (I). The latter angle would be the geometrically analogous angle. These differences are again probably due to non-bonded repulsive interactions. In (II), it is desirable to increase both the separation between H(C7) and the oxygen atom involved in hydrogen bonding. This can be accomplished by increasing the C(5)–C(6)–C(7) angle. In (I), however, opening of the C(4)–C(5)–C(6) angle would increase the separation between the imino hydrogen atoms and yet allow both hydrogen-bonding contact distances to be minimized.

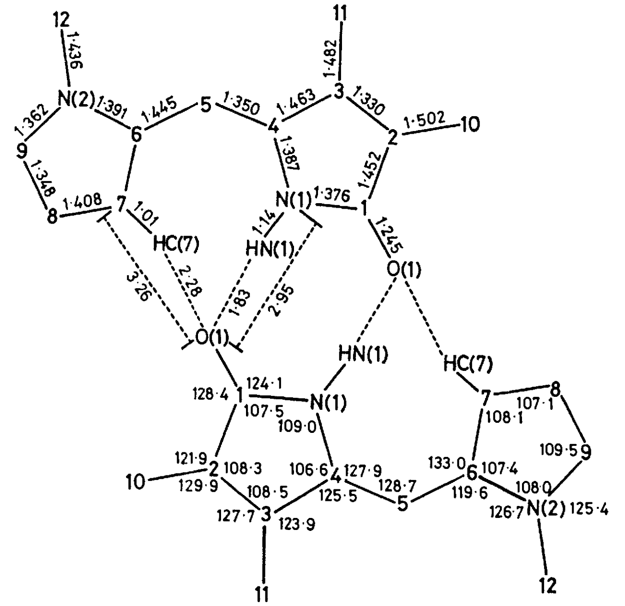

FIGURE 4 Schematic drawing of the hydrogen-bonded dimer in (II). See Figure 3 for explanation. E.s.d.'s are *ca.* 0.003—0.004 Å for C–O, C–N, C–C bonds; 0.02 Å for N–H and C–H bonds; and 0.2—0.3° for bond angles not involving hydrogen atoms

A C_a–C_m–C_a angle of 133° has also been found in a protonated dibromo-pyrromethene, where both nitrogen atoms carry hydrogen atoms and are hydrogen-bonded to a bromide ion.[22] On the other hand, in the free base of a pyrromethene, where there is only one imino-hydrogen atom, the angle is 126°.[23]

As far as has been observed for virtually all the open chain polypyrroles so far studied, there is a considerable degree of bond fixation in both compounds, though to a considerably less degree than has been observed in bilirubin.[1] The bond lengths indicate that for both (I) and (II) the resonance form as shown in Figure 1 predominates. This is particularly true for ring 1, which is a pyrroleneone moiety. This ring is primarily present as the lactam form as indicated by the C–O distance of 1.24 Å. The short C_b–C_b and relatively long C_a–C_b distances in ring 1 indicates these bonds can be considered essentially double and single bonds respectively.

The observation that the lactam form is predominant in the solid state is in agreement with all the other *X*-ray diffraction data available. This is also confirmed by *X*-ray photoelectron spectroscopy.[24] In solution the lactam–lactim equilibrium is shifted to the lactam form by at least four to six orders of magnitude.

In both compounds the N(1)–C(1) distance is significantly shorter than the N(1)–C(4) distance. This difference was also noted in (III), but the data for that compound, like the data available for other tripyrrolic or tetrapyrrolic compounds, is not of sufficient quality to assess the significance of these differences.

Ring 2 has bond parameters more like those found in pyrrole[25] itself or in both rings of a dipyrromethane compound.[26] Thus other canonical forms also contribute. The C_b–C_b distance is slightly shorter than the 1.41 Å expected for a pure pyrrole ring. In both compounds the N(2)–C(6) bond length is significantly longer than the N(2)–C(9) distance. These observations may be explained by the existence of some contributions from canonical forms such as (VII). This may also explain the observation that the length of C(4)–C(5) is shorter than expected for a single bond. A similar observation was made for the previously mentioned dipyrromethane compound,[26] but in that case the cause was believed to be resonance forms involving ethoxycarbonyl groups substituted at the C_a positions.

(VII)

Of the four 3,4-dihydrodipyrromethen-5(1*H*)-one compounds reported by Sheldrick, Borkenstein, Blacha-Puller, and Gossauer[15] [(IV)—(VI) and one other], two are planar and two are twisted. For both the planar cases, the molecules stack in the crystal lattice parallel to one another at a van der Waals distance of

3.4—4.0 Å between molecule sheets. The authors postulate further enhancement of the electronic stability of the planar forms through dispersion forces between parallel aromatic systems. Stereoviews of the packing for (I) and (II) are shown in Figures 5 and 6. From these it can be seen that the molecules in (II) stack in layers. The separation between molecules in different layers is 3.7—3.8°. The packing in (I), the more planar molecule, is quite different. Here the molecules are arranged in a herringbone pattern, and are not stacked in parallel layers.

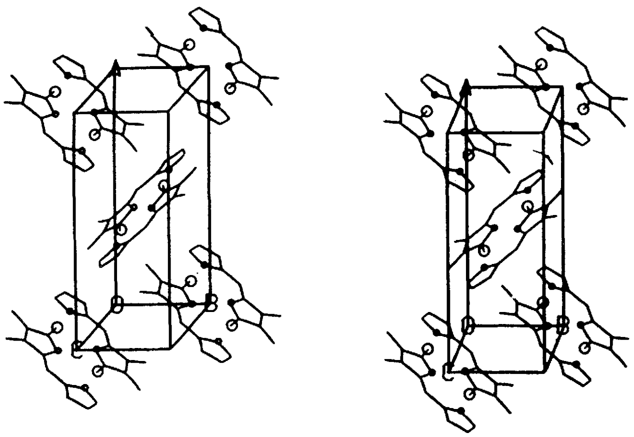

FIGURE 5 Stereoview of the packing in the unit cell of (I). Hydrogen atoms have been omitted. Smaller circles represent nitrogen atoms; larger circles represent oxygen atoms

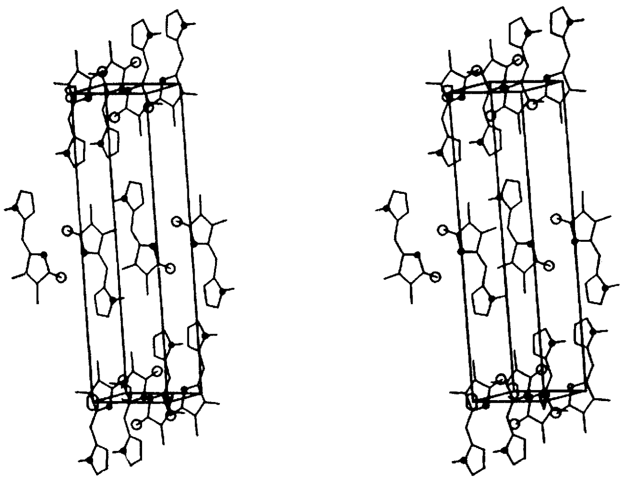

FIGURE 6 Stereoview of the packing in the unit cell of (II)

Aside from the contacts in the dimers, there are no unusually short intermolecular contacts. There are contacts of 3.48 Å between N(2) and C(11) and between C(5) and C(9) in (I). There is a contact of 3.44 Å between C(1) and C(5) in (II). No other contacts are less than 3.5 Å.

We acknowledge support of this research project by the Robert A. Welch Foundation, the National Institutes of Health, the National Science Foundation, and the Texas Agricultural Experiment Station. Thanks also are due to Dr. Shirley Chu of Southern Methodist University for use of her Syntex $P2_1$ diffractometer and for her help in data collection.

[8/890 *Received*, 15*th May*, 1978]

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