

**Structures of (Z)-3,4-Diethyl-5-(phenylmethylene)-3-pyrrolin-2-one, C<sub>15</sub>H<sub>17</sub>NO(I), and (Z)(syn)-3,4-Dimethyl-5-(2-pyridylmethylene)-3-pyrrolin-2-one, C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O(II)**

BY J. K. DATTA GUPTA\* AND E. F. MEYER JR

Department of Biochemistry and Biophysics and the Texas Agricultural Experiment Station, Texas A & M University, College Station, TX 77843, USA

D. L. CULLEN

Department of Chemistry, Connecticut College, New London, CT 06320, USA

D. A. LIGHTNER

Department of Chemistry, University of Nevada, Reno, Nevada 89557, USA

H. FALK AND K. GRUBMAYR

Department of Organic Chemistry, University of Linz, A-4040 Linz, Austria

AND I. BERNAL

Department of Chemistry, University of Houston, Houston, TX 77004, USA

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**Abstract.** (I):  $M_r = 227.31$ , monoclinic,  $P2_1/n$ ,  $a = 11.392$  (2),  $b = 7.130$  (2),  $c = 15.789$  (4) Å,  $\beta = 97.76$  (2)°,  $V = 1270.7$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.188$  Mg m<sup>-3</sup>, Cu Kα,  $\lambda = 1.54184$  Å,  $\mu = 0.55$  mm<sup>-1</sup>,  $F(000) = 488$ ,  $T = 277$  (1) K,  $R = 0.040$  for 1057 observed reflections. (II):  $M_r = 200.24$ , triclinic,  $P\bar{1}$ ,  $a = 7.117$  (3),  $b = 8.223$  (6),  $c = 9.242$  (8) Å,  $\alpha = 103.59$  (6),  $\beta = 92.08$  (5),  $\gamma = 92.41$  (5)°,  $V = 524.7$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.267$  Mg m<sup>-3</sup>, Mo Kα,  $\lambda = 0.71073$  Å,  $\mu = 0.09$  mm<sup>-1</sup>,  $F(000) = 212$ ,  $T = 295$  (2) K,  $R = 0.036$  for 972 reflections. In (I) there is intermolecular hydrogen bonding so that the molecules form H-bonded dimers. There is no intermolecular hydrogen bonding in (II), but there is an intramolecular N–H...N hydrogen bond. The pyrrolic skeleton in both molecules shows relatively small deviation from planarity.

**Introduction.** Photochemistry has long been known to play an important part in the reactions of bile pigments. Irradiation with blue light is a much used therapy in neo-natal jaundice. It is now known that 'photobilirubin' is formed in this process (McDonagh, Palma & Lightner, 1980). The methylidenedipyrrole groups in bilirubin are normally in the (Z,Z) configuration with a synperiplanar conformation at the

methine single bonds (Bonnett, Davies, Hursthouse & Sheldrick, 1978) (Fig. 1). There is extensive intramolecular hydrogen bonding. It has recently been shown that aerobic irradiation of bilirubin produces a photoisomerization of the (Z,Z) configuration to produce the (Z,E) and (E,Z) diastereomers (Falk, Müller, Ratzenhofer & Winsauer, 1982; McDonagh, Palma, Trull & Lightner, 1982). Such a conversion would break the intramolecular hydrogen bonding and thus make bilirubin more water soluble and hence more easily excreted.

Work on model compounds such as the two described in this work helped, in part, to lead to the discovery of photobilirubin. (I), hereafter referred to as benzalpyrrolinone, undergoes facile Z→E conversion. On the other hand, (II), hereafter referred to as α-pyridalpyrrolinone, undergoes Z→E transformation with more difficulty (Falk, Grubmayr, Hofer &

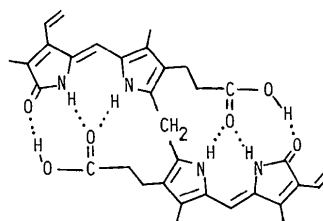


Fig. 1. (4Z,15Z)-Bilirubin IXα showing intramolecular hydrogen bonding.

\* Permanent address: Saha Institute of Nuclear Physics, 92 APC Road, Calcutta-700 009, India.

Neufingerl, 1975; Falk, Grubmayr, Hofer, Neufingerl & Ribo, 1976; Lightner & Park, 1977). IR and H NMR measurements have shown that intramolecular hydrogen bonding is present in (II), and that this stabilizes the *Z* configuration (Falk & Grubmayr, 1977). In (I), intermolecular hydrogen bonding is probably more important. To clarify the structural reasons for the differences in the properties of these two compounds, an X-ray diffraction analysis of the two compounds was initiated.

**Experimental.** (I): white needles recrystallized from pyridine-water, cell dimensions from precession photographs at 298 K, later more accurately at 277 (1) K on four-circle diffractometer using 15 reflections,  $45 < 2\theta < 67^\circ$ ; systematic absences  $0k0$  for  $k$  odd and  $h0l$  for  $h + l$  odd indicated  $P2_1/n$ ; Syntex  $P\bar{1}$  diffractometer,  $Cu K\alpha$  radiation, graphite monochromator; crystal  $0.2 \times 0.2 \times 0.5$  mm, 1139 reflections measured,  $2\theta \leq 120^\circ$ ,  $2\theta/\omega$  scan, three standard reflections measured after every 97 reflections, no significant change in intensity, 1063 reflections unique, 1057 considered observed [ $I \geq 3\sigma(I)$ ] used for structure determination and refinement. (II): needle-shaped white transparent crystals from slow evaporation of the solution of the compound in methanol, cell dimensions measured on CAD-4 diffractometer by least-squares refinement of 25 centered reflections; crystal  $0.3 \times 0.3 \times 0.4$  mm,  $2\theta/\omega$  scan, graphite-monochromatized  $Mo K\alpha$ , three standard reflections monitored after every 2 h of X-ray exposure, no significant variation in intensities, 1779 independent reflections,  $2 < 2\theta \leq 50^\circ$ ; 972 with  $I \geq 3\sigma(I)$  classified as observed and used in structure determination and refinement, no systematic absences in the data set. Corrections for Lorentz and polarization, not for absorption; both structures solved by direct methods with *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refined by least squares, first isotropically then anisotropically;  $\sum w [|F_o| - (1/k)|F_c|]^2$  minimized,  $w = 1/\sigma^2(F)$ , all H atoms, except the one bonded to imino nitrogen of (I), located from difference Fourier syntheses and included in refinement; starting  $B$  for H atoms  $4.0 \text{ \AA}^2$ , refined isotropically; scattering factors those of Cromer & Waber (1974), corrections ( $f'$  and  $f''$ ) for anomalous dispersion for every non-hydrogen atom (Cromer, 1974); calculations on a PDP 11/40 computer using Enraf-Nonius structure determination package (Frenz, 1978); use was also made of the PDP 11/40 Vector General graphics system (Morimoto & Meyer, 1976; Cole, Meyer, Swanson & White, 1979); for (I),  $R = 0.040$ ,  $R_w = 0.061$ ,  $S = 2.01$ ,  $(\Delta/\sigma)_{\max} = 0.45$ ,  $(\Delta/\sigma)_{\text{av}} = 0.08$ ; for (II),  $R = 0.036$ ,  $R_w = 0.042$ ,  $S = 0.999$ ,  $(\Delta/\sigma)_{\max} = 0.34$ ,  $(\Delta/\sigma)_{\text{av}} = 0.08$ ;  $\Delta\rho$  excursions in final difference syntheses  $0.20 \text{ e \AA}^{-3}$  (I) and  $0.15 \text{ e \AA}^{-3}$  (II).

Table 1. Fractional coordinates derived from least-squares refinement for benzalpyrrolinone (I)

For non-hydrogen atoms,  $B_{\text{eq}} = \frac{4}{3} \sum_j \beta_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j)$ . The hydrogen atoms were refined isotropically and the value given is the refined isotropic parameter. H(N1) was not located and was not included in any of the calculations.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}/B (\text{\AA}^2)$
O(1)	0.3464 (2)	0.4404 (2)	0.9809 (1)	4.64 (5)
N(1)	0.4329 (2)	0.7073 (3)	0.9345 (1)	3.29 (4)
C(1)	0.3379 (2)	0.6022 (4)	0.9524 (2)	3.44 (5)
C(2)	0.2308 (2)	0.7148 (4)	0.9327 (2)	3.27 (6)
C(3)	0.2635 (2)	0.8854 (4)	0.9070 (1)	3.12 (5)
C(4)	0.3923 (2)	0.8865 (4)	0.9072 (2)	2.98 (5)
C(5)	0.4548 (2)	1.0316 (4)	0.8837 (2)	3.37 (6)
C(6)	0.5805 (2)	1.0511 (4)	0.8741 (2)	3.39 (6)
C(7)	0.6205 (2)	1.2286 (4)	0.8542 (2)	4.37 (7)
C(8)	0.7362 (3)	1.2606 (5)	0.8420 (2)	5.61 (8)
C(9)	0.8155 (3)	1.1142 (6)	0.8500 (2)	6.09 (9)
C(10)	0.7784 (3)	0.9395 (5)	0.8698 (2)	5.84 (8)
C(11)	0.6632 (3)	0.9068 (4)	0.8816 (2)	4.76 (7)
C(12)	0.1110 (2)	0.6403 (4)	0.9420 (2)	4.21 (6)
C(13)	0.0467 (3)	0.5597 (5)	0.8602 (2)	5.46 (8)
C(14)	0.1848 (2)	1.0468 (4)	0.8783 (2)	3.88 (6)
C(15)	0.1554 (3)	1.0581 (4)	0.7812 (2)	5.07 (7)
H(5)	0.405 (2)	1.138 (3)	0.870 (1)	3.3 (5)
H(7)	0.567 (2)	1.330 (3)	0.850 (2)	4.5 (6)
H(8)	0.766 (3)	1.384 (5)	0.824 (2)	8.5 (9)
H(9)	0.899 (3)	1.145 (5)	0.838 (2)	7.8 (8)
H(10)	0.832 (2)	0.830 (4)	0.873 (2)	6.2 (7)
H(11)	0.637 (2)	0.782 (4)	0.894 (2)	5.4 (7)
H(12)A	0.058 (2)	0.744 (4)	0.963 (2)	5.2 (7)
H(12)B	0.123 (3)	0.537 (4)	0.988 (2)	5.9 (7)
H(13)A	-0.025 (3)	0.502 (4)	0.872 (2)	6.2 (7)
H(13)B	0.033 (3)	0.658 (5)	0.811 (2)	8.1 (8)
H(13)C	0.091 (3)	0.456 (5)	0.837 (2)	8.1 (9)
H(14)A	0.222 (2)	1.165 (3)	0.899 (1)	3.6 (5)
H(14)B	0.115 (2)	1.041 (3)	0.903 (2)	4.4 (6)
H(15)A	0.237 (3)	1.073 (5)	0.750 (2)	10.0 (10)
H(15)B	0.101 (2)	1.156 (4)	0.763 (2)	5.6 (7)
H(15)C	0.117 (3)	0.935 (4)	0.754 (2)	6.8 (8)

Table 2. Fractional coordinates derived from least-squares refinement for  $\alpha$ -pyridalpyrrolinone (II)

For non-hydrogen atoms,  $B_{\text{eq}} = \frac{4}{3} \sum_j \beta_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j)$ . The hydrogen atoms were refined isotropically and the value given is the refined isotropic parameter.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}/B (\text{\AA}^2)$
O(1)	0.7123 (2)	0.2310 (2)	0.5647 (2)	5.57 (4)
N(1)	0.6429 (2)	0.4580 (2)	0.7501 (2)	3.91 (4)
N(2)	0.1917 (3)	0.3032 (3)	0.0115 (2)	4.67 (5)
C(1)	0.6002 (3)	0.3304 (3)	0.6264 (2)	3.97 (5)
C(2)	0.3985 (3)	0.3393 (3)	0.5882 (2)	3.66 (5)
C(3)	0.3316 (3)	0.4690 (3)	0.6859 (2)	3.53 (5)
C(4)	0.5140 (3)	0.4512 (3)	0.2083 (2)	3.34 (5)
C(5)	0.5188 (3)	0.3178 (3)	0.0924 (2)	3.72 (5)
C(6)	0.3635 (3)	0.2406 (3)	-0.0105 (2)	3.75 (5)
C(7)	0.0511 (4)	0.2298 (4)	0.9152 (3)	5.89 (7)
C(8)	0.0704 (4)	0.0969 (4)	0.7955 (3)	6.27 (7)
C(9)	0.7553 (4)	0.9651 (3)	0.2269 (3)	5.63 (7)
C(10)	0.3932 (4)	0.1062 (3)	0.8698 (3)	4.65 (6)
C(11)	0.2994 (4)	0.2168 (3)	0.4598 (3)	5.12 (7)
C(12)	0.1372 (3)	0.5299 (3)	0.6921 (3)	5.09 (7)
H(N1)	0.250 (3)	0.514 (3)	0.202 (2)	5.2 (5)
H(5)	0.638 (3)	0.265 (2)	0.078 (2)	3.9 (5)
H(7)	0.938 (3)	0.280 (3)	0.934 (2)	6.4 (6)
H(8)	0.962 (3)	0.051 (3)	0.733 (2)	6.5 (6)
H(9)	0.739 (3)	0.059 (3)	0.307 (2)	5.9 (6)
H(10)	0.521 (3)	0.063 (3)	0.862 (2)	5.4 (6)
H(11)A	0.323 (4)	0.102 (3)	0.463 (3)	8.2 (7)
H(11)B	0.167 (4)	0.211 (3)	0.466 (3)	9.9 (8)
H(11)C	0.341 (4)	0.228 (3)	0.366 (3)	9.1 (8)
H(12)A	0.049 (4)	0.439 (3)	0.638 (3)	7.4 (7)
H(12)B	0.869 (4)	0.371 (4)	0.340 (3)	11.2 (9)
H(12)C	0.909 (4)	0.450 (3)	0.206 (3)	8.7 (8)

**Discussion.** The positional parameters of the atoms with their e.s.d.'s are given in Tables 1 and 2.\* Structures of the two molecules are shown in Figs. 2 and 3. Also shown is the crystallographic numbering system used. Both molecules have the *Z* configuration. (II),  $\alpha$ -pyridalpyrrolinone, has a synperiplanar conformation at the methine single bond [C(5)—C(6)].

Both compounds show only small deviations from planarity. The dihedral angle between the plane of the pyrrolinone ring and the plane of the phenyl or pyridyl ring is 9.5 and 2.8° for (I) and (II), respectively. The larger angle in (I) can probably be attributed to non-bonded repulsive interactions between H(N1) of the pyrrolinone ring and H(C11) of the phenyl ring. Assuming H(N1) to be in an idealized position (N—H = 1.0 Å), the H...H distance is 1.84 Å. The N(1)—C(11) distance is 3.194 (2) Å. This type of steric hindrance is not a factor in (II).

The planarity of (II) is also stabilized by the existence of a N(1)—H(N1)...N(2) intramolecular hydrogen bond. The N(1)...N(2) and H(N1)...N(2) distances are

2.771 (3) and 2.18 (3) Å, respectively, while the N(1)—H(N1)...N(2) angle is 126 (2)°.

The effects of steric interaction in (I) and the intramolecular hydrogen bond in (II) are also seen in certain of the bond angles in the two molecules. Bond lengths and angles are given in Tables 3 and 4. Most notably the angle at the methine carbon atom is bigger in (I). The values found for this angle agree with those found respectively in protonated (Becker, Sheldrick & Engel, 1978) and free-base methylidynedipyrroles (Sheldrick, Borkenstein, Struckmeier & Engel, 1978). In addition, the C(5)—C(6)—C(11) angle in (I) is larger than the analogous angle C(5)—C(6)—N(2) in (II).

Intermolecular hydrogen bonding is found for (I) but not for (II). Packing diagrams of the two molecules are shown in Figs. 4 and 5. The molecules in (I) form hydrogen-bonded dimers between the lactam oxygen atom and pyrrolinone nitrogen atom on a centrosymmetrically related molecule. The N...O distance is 2.882 (2) Å.

\* Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38813 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

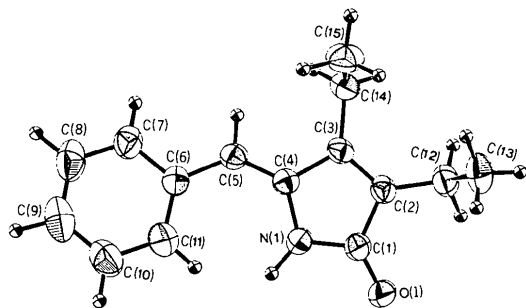


Fig. 2. ORTEP (Johnson, 1965) drawing of the structure of benzalpyrrolinone (I). Thermal ellipsoids are drawn for 50% probability. Hydrogen atoms are numbered the same as the atom to which they are bonded. Thermal ellipsoids for hydrogen atoms are not drawn to scale. H(N1) was not found in the analysis, but is shown here in an idealized position for illustrative purposes.

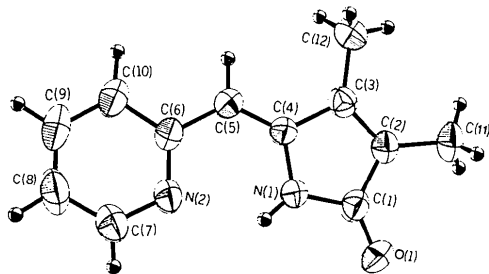


Fig. 3. ORTEP drawing of the structure of  $\alpha$ -pyridalpyrrolinone (II).

Table 3. Interatomic distances (Å) and angles (°) for benzalpyrrolinone (I)

O(1)—C(1)	1.237 (2)	C(5)—C(6)	1.465 (3)
N(1)—C(1)	1.377 (3)	C(6)—C(7)	1.395 (3)
N(1)—C(4)	1.407 (3)	C(6)—C(11)	1.389 (3)
C(1)—C(2)	1.458 (3)	C(7)—C(8)	1.377 (4)
C(2)—C(3)	1.351 (3)	C(8)—C(9)	1.375 (4)
C(2)—C(12)	1.490 (3)	C(9)—C(10)	1.365 (4)
C(3)—C(4)	1.467 (3)	C(10)—C(11)	1.370 (4)
C(3)—C(14)	1.491 (3)	C(12)—C(13)	1.509 (4)
C(4)—C(5)	1.337 (3)	C(14)—C(15)	1.526 (3)
N(1)—C(1)—C(2)	108.4 (2)	N(1)—C(4)—C(3)	106.4 (2)
C(1)—N(1)—C(4)	108.8 (2)	C(6)—C(5)—C(4)	131.8 (2)
O(1)—C(1)—N(1)	123.8 (2)	C(7)—C(6)—C(11)	116.9 (2)
O(1)—C(1)—C(2)	127.8 (2)	C(7)—C(6)—C(5)	117.5 (2)
C(1)—C(2)—C(3)	107.6 (2)	C(11)—C(6)—C(5)	125.6 (2)
C(1)—C(2)—C(12)	122.3 (2)	C(6)—C(7)—C(8)	122.0 (3)
C(3)—C(2)—C(12)	130.1 (2)	C(7)—C(8)—C(9)	119.4 (3)
C(2)—C(3)—C(4)	108.7 (2)	C(8)—C(9)—C(10)	119.6 (3)
C(2)—C(3)—C(14)	127.4 (2)	C(9)—C(10)—C(11)	121.2 (3)
C(4)—C(3)—C(14)	123.8 (2)	C(6)—C(11)—C(10)	120.9 (3)
C(5)—C(4)—C(3)	125.0 (2)	C(3)—C(14)—C(15)	112.8 (2)
C(5)—C(4)—N(1)	128.5 (2)	C(2)—C(12)—C(13)	113.4 (2)

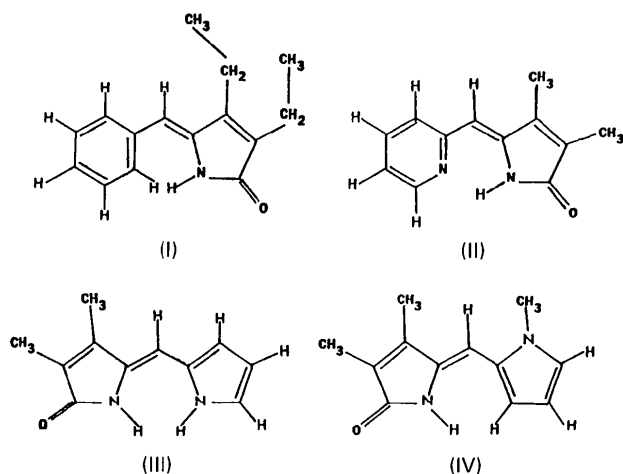
Average C—H = 1.00 Å

Table 4. Interatomic distances (Å) and angles (°) for  $\alpha$ -pyridalpyrrolinone (II)

O(1)—C(1)	1.224 (3)	C(4)—C(5)	1.344 (4)
C(1)—N(1)	1.373 (3)	C(5)—C(6)	1.453 (3)
N(1)—C(4)	1.385 (3)	C(6)—N(2)	1.350 (3)
C(1)—C(2)	1.475 (3)	N(2)—C(7)	1.338 (3)
C(2)—C(11)	1.496 (3)	C(7)—C(8)	1.376 (4)
C(2)—C(3)	1.342 (3)	C(8)—C(9)	1.366 (4)
C(3)—C(12)	1.490 (4)	C(9)—C(10)	1.376 (4)
C(3)—C(4)	1.468 (3)	C(6)—C(10)	1.397 (3)
C(1)—N(1)—C(4)	110.6 (2)	C(3)—C(4)—N(1)	106.3 (2)
C(6)—N(2)—C(7)	117.3 (2)	C(3)—C(4)—C(5)	128.2 (2)
C(2)—C(1)—N(1)	106.4 (2)	N(1)—C(4)—C(5)	125.4 (2)
O(1)—C(1)—N(1)	124.7 (2)	C(4)—C(5)—C(6)	127.2 (2)
O(1)—C(1)—C(2)	128.9 (2)	N(2)—C(6)—C(10)	121.2 (2)
C(1)—C(2)—C(3)	108.3 (2)	C(5)—C(6)—N(2)	118.5 (2)
C(1)—C(2)—C(11)	121.9 (2)	C(5)—C(6)—C(10)	120.3 (2)
C(3)—C(2)—C(11)	129.8 (3)	C(8)—C(7)—N(2)	124.5 (3)
C(2)—C(3)—C(4)	108.3 (2)	C(7)—C(8)—C(9)	118.0 (3)
C(2)—C(3)—C(12)	128.4 (2)	C(8)—C(9)—C(10)	119.4 (3)
C(4)—C(3)—C(12)	123.2 (2)	C(6)—C(10)—C(9)	119.6 (3)

Average C—H = 0.96 Å

The effects of hydrogen bonding on the structural parameters in these compounds have also been reported in bile pigments as well as model dipyrrolic compounds. In the oxomethylidenedipyrrole (*Z*)-3,4-dimethyl-5-(2-pyrrolylmethylene)pyrrol-2(1*H*)-one (III) (Cullen, Pépe, Meyer, Falk & Grubmayr, 1979), the nitrogen atoms in both rings are hydrogen bonded, not intramolecularly as found in (II), but to the same lactam oxygen atom on a centrosymmetrically related molecule. The *N*-methyl derivative of this compound (IV) has intermolecular hydrogen bonding similar to that found in (I), and in biliverdin dimethyl ester (Sheldrick, 1976). As in (I), only the nitrogen atom from the pyrrolinone ring is hydrogen bonded to a lactam oxygen atom on a neighboring molecule. (IV) shows greater deviation from planarity than (II), just as (I) shows greater deviation than (II).



The hydrogen bonding in these two compounds is one of the factors contributing to the greater thermodynamic stability of the *Z* isomer in (II). A *Z*→*E* transformation in (I) would change the intermolecular hydrogen-bonding arrangement, but the number of hydrogen bonds would remain constant, as was found when (III) was photoisomerized to the *E* configuration (Hori *et al.*, 1981). In (II), however, a *Z*→*E* transformation would disrupt the intramolecular hydrogen bond. The influence of the intramolecular hydrogen bond can be seen by comparison of (II) with 4-pyridalpyrrolinone. The quantum efficiency of the *Z*→*E* transformation is higher in the latter (Falk & Neufingerl, 1979).

The difference in hydrogen bonding also affects the melting points of (I) and (II), which are 406–408 K and 409 K, respectively. This can be seen by comparisons with related compounds. The melting point of the pyridyl analog of (I) is 337 K (Lightner & Park, 1977). The *E* isomer of (II) melts at 430–433 K, while the 4-pyridyl analog, in which intermolecular hydrogen

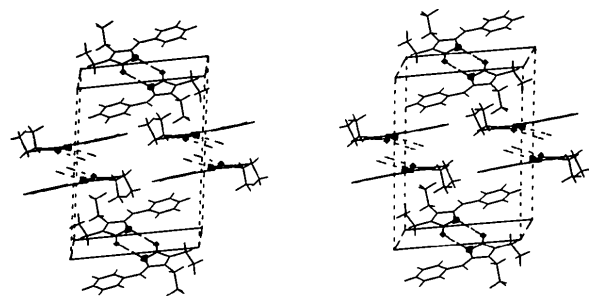


Fig. 4. Stereoview of the packing in the unit cell of (I). Nitrogen atoms are marked by tetrahedra; oxygen atoms are marked by filled octahedra. The view is approximately parallel to *b*. The *a*, *b* and *c* axes are indicated by solid, long-dashed and short-dashed lines, respectively. Hydrogen bonding is denoted by dashed lines between atoms.

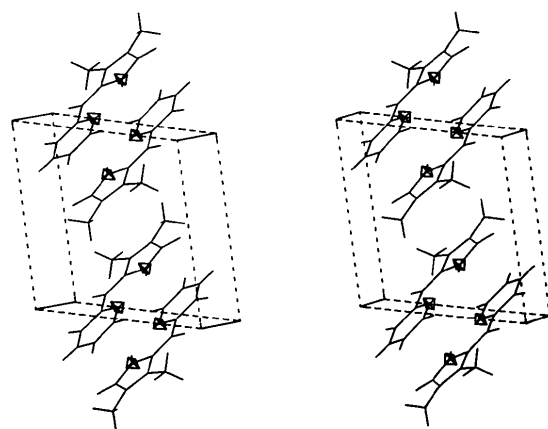


Fig. 5. Stereoview of the packing in the unit cell of (II). View is approximately parallel to *a*. This figure (and Fig. 4) were drawn with the aid of the computer graphics program *PACK* (Swanson, Rosenfield & Meyer, 1982).

bonding would be more likely, melts at 519–520 K (Falk & Grubmayr, 1977).

Molecules of (II) pack in layers, as has been found for a number of these planar dipyrrolic compounds (Sheldrick, Borkenstein, Blacha-Puller & Gossauer, 1977). Dispersion forces between layers are believed to stabilize the planarity of the molecules. The average interplanar spacing is approximately 3.5 Å.

Bond lengths and angles in the pyrrolinone ring for both compounds agree well with those found in bile pigments, other tetrapyrroles, tripyrroles, and oxomethylidenedipyrroles (Hori, Mangani, Pépe, Meyer, Cullen, Falk & Grubmayr, 1981, and references therein). As is the general case, this ring is in the lactam form. This observation is verified by X-ray photoelectron spectroscopy (Falk, Gergely, Grubmayr & Hofer, 1977) and by *pK* measurements (Falk & Grubmayr, 1977). Some bond localization has been found in all the bile pigments and related model

compounds. The resonance form as drawn in (I)–(IV) predominates. The effect is more pronounced in the present case, especially in the C(4)–C(5) and C(5)–C(6) bonds, which have lengths typical of a pure double bond and a pure  $sp^2$ – $sp^2$  carbon atom single bond, respectively. Bond angles in the phenyl and pyridyl rings are as expected.

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### Third ( $\gamma$ ) Polymorph of Tri-*tert*-butylmethyl *p*-Nitrobenzoate, C<sub>20</sub>H<sub>31</sub>NO<sub>4</sub>

BY WINNIE WONG-NG,\* PEI-TAK CHENG AND STANLEY C. NYBURG

*Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1*

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**Abstract.**  $M_r = 349.5$ , monoclinic,  $P2_1/c$ ,  $a = 12.655$  (6),  $b = 26.523$  (5),  $c = 12.134$  (6) Å,  $\beta = 105.8$  (2)°,  $U = 3919$  (3) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.194$  g cm<sup>-3</sup>,  $\lambda(\text{Cu K}\alpha) = 1.5418$  Å,  $\mu = 6.7$  cm<sup>-1</sup>.  $F(000) = 1520$ ;  $T = 298$  K. Final  $R = 0.087$  for 3453 significant reflections. The two independent molecules of this polymorph have virtually identical structures. They differ from that of the  $\alpha$  polymorph in that the central C(1)–C(7)–O(1)–C(8) system has a torsional angle of 178° in the former and 162° in the latter.

\* Present address: JCPDS-International Center for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19081, USA.

**Introduction.** Molecular overcrowding caused by bulky substituents on *p*-nitrobenzoate esters such as the title compound increases their rate of solvolysis (Cheng, Nyburg, Thankachan & Tidwell, 1977). The strain found in molecules of the  $\alpha$  polymorph of the title compound has been reported (Cheng & Nyburg, 1978). This paper reports structural results for the molecules of the  $\gamma$  polymorph.

**Experimental.** The first crystals to form from acetone–water solutions were colorless and of the  $\gamma$  polymorph. Crystals deposited later consist of pale-yellow clusters composed of two mutually-imbedded different poly-