# Synthesis and *X*-Ray Crystal Structure of Two Stereoisomeric Derivatives of of 3,4-Dihydropyrromethen-5(1*H*)-one

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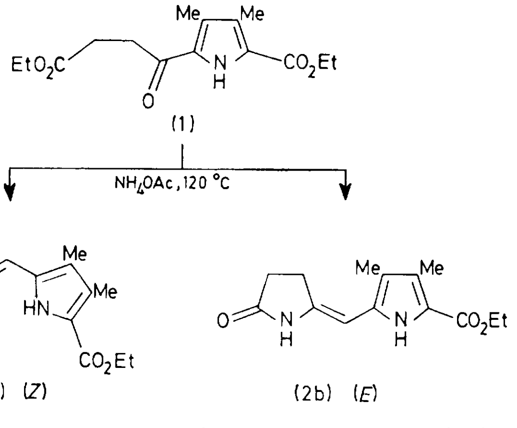
*Summary* Stable *Z*- and *E*-isomers of ethyl 1,3,4,5-tetrahydro-3',4'-dimethyl-5-oxopyrromethene-5'carboxylate have been prepared and their configurations determined by *X*-ray diffraction.

The occurrence of *Z,E*-isomerism at the exocyclic double bond of some α-vinyl pyrroles is well documented[1]. Particularly interesting within this class of compounds are pyrromethen-5(1*H*)-one derivatives as many of them may be employed as starting materials in the synthesis of bile pigments for which no known *Z,E*-isomers have been obtained.[2] Recently, Falk *et al.*[3] succeeded in transforming a *Z*-pyrromethen-5(1*H*)-one into the thermodynamically less stable *E*-isomer which could be isolated by preparative t.l.c. On theoretical grounds, however, a greater stability of both *E*- and *Z*-stereoisomers would be expected in the 3,4-dihydropyrromethen-5(1*H*)-one series. As the latter compounds can be easily transformated into bile pigments of the rhodin type,[4] to which the chromophore of the plant photomorphogenic pigment, phytochrome, probably belongs,[5] we have recently investigated the synthesis of derivatives stable enough to be isolated and characterized by usual analytical methods. Now we report the cyclisation in the presence of ammonium acetate[4] of the δ-(pyrrol-2-yl)-laevulinic ester derivative (**1**),† obtained from ethyl δ-diazolaevulinate[6] and ethyl 3,4-dimethylpyrrole-2-carboxylate,[7] to the two isomeric 3,4-dihydropyrromethen-5(1*H*)-ones (**2a**)† (m.p. 160 °C) and (**2b**)† (m.p. 202 °C) which were separated by t.l.c.



The configuration at the exocyclic double bond of each stereoisomer has been conclusively established by *X*-ray diffraction. Crystals of (**2a**) are monoclinic, space group $P2_1/c$ with $a = 12{\cdot}705(3)$, $b = 7{\cdot}425(2)$, $c = 15{\cdot}356(4)$ Å, $\beta = 102{\cdot}82(2)°$, $Z = 4$; those of (**2b**) are monoclinic, space group $P2_1/c$ with $a = 6{\cdot}275(2)$, $b = 8{\cdot}068(2)$, $c = 26{\cdot}651(8)$ Å, $\beta = 94{\cdot}74(2)°$, $Z = 4$. The structures were solved by direct methods and refined to $R = 0{\cdot}077$ for (**2a**) and 0·078 for (**2b**), for 1346 and 1366 reflections, respectively $[F \geqslant 3{\cdot}0\,\sigma(F)]$. Hydrogen atoms were located and refined together with isotropic temperature factors in both cases. Dihedral angles of 48·5° (**2a**) and 3·4° (**2b**) between the planes of the pyrrolidine and pyrrole rings are observed. The C(5)–C(6) bond distances of 1·466(5) and 1·444(7) Å, respectively, suggest that the degree of π-delocalisation involving the pyrrole ring system and the C(4)–C(5) double bond is greater in the latter isomer, indicating a virtually planar pyrromethenone system. Other bond lengths and angles in the two isomers are similar. Both molecules are

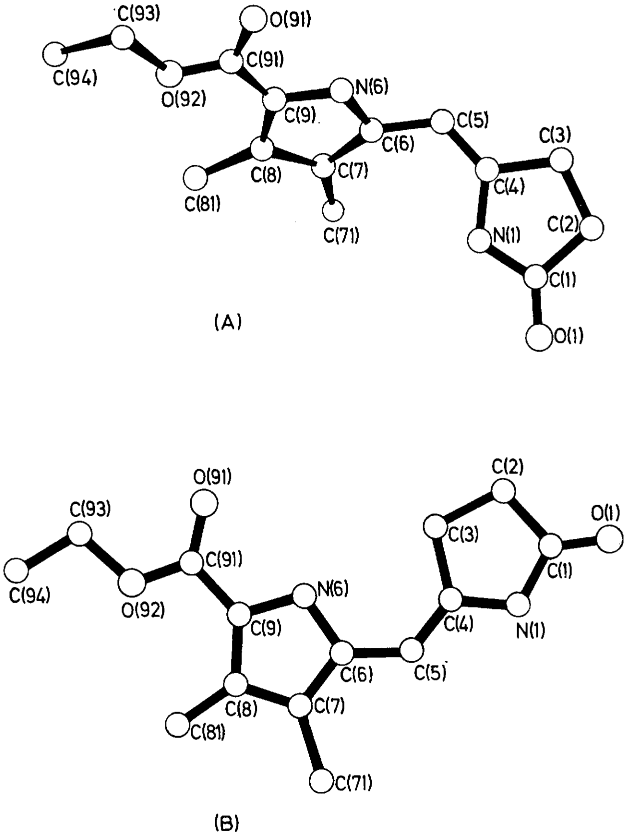


Figure. Bond lengths (e.s.d.s. 0·005—0·008 Å) for the molecules (**2a**) (A) and (**2b**) (B), respectively are: C(1)–O(1) 1·223, 1·241; N(1)–C(1) 1·359, 1·346; N(1)–C(4) 1·398, 1·417; C(1)–C(2) 1·506, 1·495; C(2)–C(3) 1·522, 1·529; C(3)–C(4) 1·519, 1·502; C(4)–C(5) 1·321, 1·324; C(5)–C(6) 1·466, 1·444; N(6)–C(6) 1·373, 1·360; N(6)–C(9) 1·386, 1·385; C(6)–C(7) 1·409, 1·394; C(7)–C(8) 1·412, 1·411; C(8)–C(9) 1·387, 1·378 Å.

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† These compounds gave satisfactory analysis, and mass, u.v., and n.m.r. spectral data.

linked into chains through linear N–H ··· O hydrogen bonds involving O(1). However, these bridges involve the pyrrole N–H proton in (**2a**) [N(6)–H ··· O(1) 2·824, N(6)–H 1·09(5), H ··· O(1) 1·74 Å] and the pyrrolidine N–H proton in (**2b**) [N(1)–H ··· O(1) 2·872, N(1)–H 1·00(5), H ··· O(1) 1·88 Å]. Whereas the involvement of N(1)–H in hydrogen bonding is clearly favourable for a planar *E*-configuration, steric interactions may be assumed to prevent the formation of N(1)–H ··· O(1) bonds in the *Z*-configuration. The large dihedral angle between the ring systems in (**2a**) with a consequently smaller degree of $\pi$-delocalisation is necessary for N(6)–H to participate in hydrogen bonding.

Addition of zinc acetate to a methanolic solution of (**2b**) (*E*-isomer) does not affect the u.v. absorption ($\lambda_{max}$ = 324 nm), while (**2a**) (*Z*-isomer) shows a bathochromic shift ($\lambda_{max}$ = 312 → 358 nm), indicating that the zinc chelate has been formed (*cf.* ref. 8). On the other hand, treatment of (**2a**) with $Et_3O^+BF_4^-$ in $CH_2Cl_2$ yields the corresponding lactim ether, whereas, under the same conditions, the *E*-isomer (**2b**) is converted without isomerization into the *N*-alkylated derivative, the structure of which has been demonstrated by *X*-ray analysis.[9]

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