

## 5-Ethoxycarbonyl-3,4'-diethyl-4,3',5'-trimethyl-2,2'-dipyrrolyl Ketone

BY W. S. SHELDRIK\* AND W. BECKER

*Gesellschaft für Biotechnologische Forschung mbH, Mascheroder Weg 1, D-3300 Braunschweig-Stöckheim, Federal Republic of Germany*

AND J. ENGEL†

*Institut für Organische Chemie der Technischen Universität Schleinitzstrasse, D-3300 Braunschweig, Federal Republic of Germany*

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**Abstract.**  $C_{19}H_{26}N_2O_3$ ,  $M_r = 331.4$ , monoclinic,  $P2_1/c$ ,  $a = 9.861$  (4),  $b = 16.825$  (6),  $c = 12.348$  (4) Å,  $\beta = 113.89$  (2)°,  $D_x = 1.16$  g cm<sup>-3</sup>. The pyrrole rings display a twisted *syn,anti* conformation [48.6, -167.3] with respect to the central ketone bridge and are both linked through N—H...O hydrogen bonds (the first to an ethoxycarbonyl, the second to a ketone carbonyl group) to molecules related by a centre of symmetry. The bond-length distribution in the second pyrrole ring indicates a significant mesomeric contribution from a dipolar structure.

**Introduction.** Cell dimensions were determined by a least-squares fit to settings for 15 reflexions ( $\pm hkl$ ) on a Syntex  $P2_1$  four-circle diffractometer (Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å). Intensity measurements were carried out in the  $\theta$ - $2\theta$  mode ( $3.5 < 2\theta < 55.0^\circ$ ) with graphite-monochromated Mo  $K\alpha$  radiation, at scan speeds varying linearly between 2.93 (150 counts s<sup>-1</sup> and below) and 29.30° min<sup>-1</sup> (5000 counts s<sup>-1</sup> and above). Scan and background times were equal. After application of the criterion  $I \geq 2.5\sigma(I)$ , 1883 unique reflexions were retained for use in the structure analysis. No absorption correction [ $\mu(\text{Mo } K\alpha) = 0.46$  cm<sup>-1</sup>] was applied. The positions of all the non-hydrogen atoms were revealed by multiresolution tangent refinement ( $E_{\min} = 1.5$ , 7 multiresolution phases, second best  $E$  map) using *SHELX* (G. M. Sheldrick). Refinement was by a blocked full-matrix least-squares method,  $\sum w\Delta^2$  being minimized, with anisotropic temperature factors for the non-hydrogen atoms. The H-atom positional parameters were freely refined with a joint isotropic temperature factor for the methyl protons and individual temperature factors for others. The terminal value of  $R_w$  ( $= \sum w^{1/2}\Delta / \sum w^{1/2}|F_o|$ ) was 0.048 with  $R = 0.054$ . The weights were  $w = k[\sigma^2(F_o)]^{-1}$

where  $k$  and  $g$  refined to 2.1320 and 0.000201 respectively. Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). Table 1 gives the final positional parameters for the non-hydrogen atoms, Tables 2 and 3 give bond lengths and angles.‡

**Discussion.** Pyrroketones (2,2'-dipyrrolyl ketones) are useful starting materials for porphyrin synthesis (Jackson, Kenner, McGillivray & Sach, 1965). Their

‡ Lists of structure factors, anisotropic thermal parameters and hydrogen atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33621 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters ( $\times 10^4$ ) for the non-hydrogen atoms

	x	y	z
N(1)	3263 (3)	5301 (1)	3136 (2)
C(1)	2299 (3)	5641 (2)	3545 (2)
C(2)	1106 (3)	5942 (2)	2576 (2)
C(3)	1387 (3)	5787 (2)	1568 (2)
C(4)	2720 (3)	5373 (2)	1938 (2)
C(5)	3467 (3)	5023 (2)	1233 (3)
O(5)	3605 (2)	5430 (1)	452 (2)
N(2)	4868 (3)	3938 (2)	912 (2)
C(6)	3971 (3)	4212 (2)	1441 (2)
C(7)	3677 (3)	3569 (2)	2032 (2)
C(8)	4438 (3)	2913 (2)	1847 (3)
C(9)	5174 (3)	3162 (2)	1161 (3)
C(11)	2713 (3)	5641 (2)	4812 (3)
O(11)	3905 (2)	5423 (1)	5523 (2)
O(12)	1647 (2)	5898 (1)	5121 (2)
C(13)	2003 (5)	5911 (4)	6388 (3)
C(14)	618 (6)	5955 (3)	6565 (4)
C(21)	-254 (4)	6344 (3)	2587 (3)
C(31)	440 (4)	6033 (2)	319 (3)
C(32)	554 (5)	6921 (2)	133 (4)
C(71)	2712 (4)	3536 (2)	2697 (3)
C(81)	4460 (5)	2076 (2)	2271 (4)
C(82)	3379 (6)	1538 (3)	1344 (5)
C(91)	6185 (5)	2721 (2)	746 (4)

\* To whom correspondence should be addressed.

† Current address: Chemiewerk Homburg, ZN DEGUSSA, Daimlerstrasse 25, D-6000 Frankfurt/Main, Federal Republic of Germany.

Table 2. Bond lengths (Å)

C(1)–N(1)	1.369 (4)	C(4)–N(1)	1.359 (4)
C(2)–C(1)	1.390 (3)	C(11)–C(1)	1.449 (4)
C(3)–C(2)	1.404 (5)	C(21)–C(2)	1.508 (5)
C(4)–C(3)	1.390 (4)	C(31)–C(3)	1.502 (4)
C(5)–C(4)	1.473 (5)	O(5)–C(5)	1.235 (4)
C(6)–C(5)	1.439 (4)	C(6)–N(2)	1.374 (5)
C(9)–N(2)	1.348 (4)	C(7)–C(6)	1.399 (4)
C(8)–C(7)	1.405 (4)	C(71)–C(7)	1.488 (6)
C(9)–C(8)	1.385 (5)	C(81)–C(8)	1.499 (5)
C(91)–C(9)	1.490 (6)	O(11)–C(11)	1.206 (3)
O(12)–C(11)	1.327 (4)	C(13)–O(12)	1.459 (5)
C(14)–C(13)	1.470 (8)	C(32)–C(31)	1.523 (5)
C(82)–C(81)	1.509 (6)		

Table 3. Bond angles (°)

C(4)–N(1)–C(1)	109.7 (2)	C(2)–C(1)–N(1)	107.9 (3)
C(11)–C(1)–N(1)	117.7 (2)	C(11)–C(1)–C(2)	134.4 (3)
C(3)–C(2)–C(1)	107.1 (3)	C(21)–C(2)–C(1)	127.0 (3)
C(21)–C(2)–C(3)	126.0 (2)	C(4)–C(3)–C(2)	107.5 (2)
C(31)–C(3)–C(2)	126.5 (3)	C(31)–C(3)–C(4)	126.0 (3)
C(31)C(4)–N(1)	107.8 (3)	C(5)–C(4)–N(1)	122.5 (2)
C(5)–C(4)–C(3)	129.7 (2)	O(5)–C(5)–C(4)	118.6 (3)
C(6)–C(5)–C(4)	119.5 (3)	C(6)–C(5)–O(5)	121.8 (3)
C(9)–N(2)–C(6)	110.1 (3)	N(2)–C(6)–C(5)	118.3 (3)
C(7)–C(6)–C(5)	134.2 (3)	C(7)–C(6)–N(2)	107.4 (2)
C(8)–C(7)–C(6)	106.6 (3)	C(71)–C(7)–C(6)	129.1 (3)
C(71)–C(7)–C(8)	124.3 (3)	C(9)–C(8)–C(7)	108.0 (3)
C(81)–C(8)–C(7)	127.9 (4)	C(81)–C(8)–C(9)	124.1 (3)
C(8)–C(9)–N(2)	107.9 (3)	C(91)–C(9)–N(2)	121.6 (3)
C(91)–C(9)–C(8)	130.5 (3)	O(11)–C(11)–C(1)	123.5 (3)
O(12)–C(11)–C(1)	113.6 (2)	O(12)–C(11)–O(11)	122.9 (3)
C(13)–O(12)–C(11)	116.0 (3)	C(14)–C(13)–O(12)	109.0 (3)
C(32)–C(31)–C(3)	111.9 (3)	C(82)–C(81)–C(8)	113.1 (3)

chemical and spectroscopic properties reflect the conjugation of the two pyrrole nuclei through the carbonyl group and are largely determined by the mesomeric contributions of dipolar structures such as (I'). For instance, reaction with hydrazine and its derivatives may only be achieved under forcing conditions (Fischer & Orth, 1934), whereas mono-pyrrolyl ketones react normally. Particularly characteristic for the pyrroketones and indicative of an extended conjugated system are their UV spectra and basicity. Their principal absorption band is at *ca* 350 nm (depending on the substituents) compared with that of *ca* 300 nm for simple 2-acylpyrroles (Cookson, 1953), and it is shifted to *ca* 420 nm with some intensification by addition of strong acid to a solution in an organic solvent (Ballantine, Jackson, Kenner & McGilivray, 1966). As part of our systematic study of the structures of linear polypyrrolic compounds, we present here the results of the first X-ray analysis of a pyrroketone, the title compound (I).

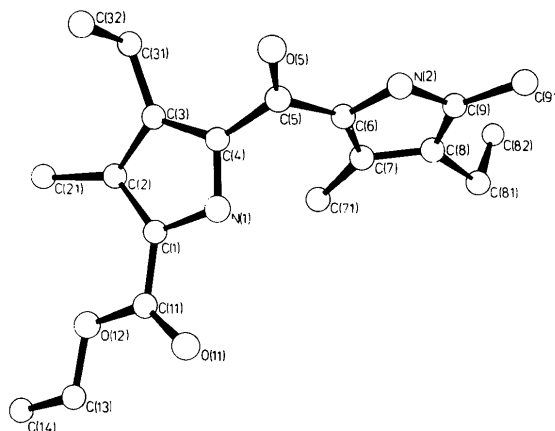


Fig. 1. Molecule (I) in perspective with the numbering system.

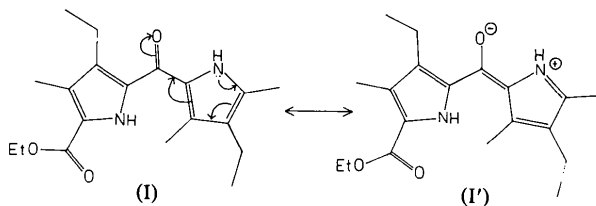


Fig. 1 is a perspective drawing showing the numbering scheme. As depicted in Fig. 2 for derivative (I), asymmetrical pyrroketones may be represented by four planar conformations, which we may denominate as *syn,syn*; *syn,anti*; *anti,syn* and *anti,anti* [with respect to the C(5)–C(6) and C(5)–C(4) bonds]. For symmetrically substituted pyrroketones the *syn,anti* and *anti,syn* forms are equivalent. An alternative means of notation, which also enables the concise description of intermediate systems, is to use the dihedral angles  $\delta_1$  and  $\delta_2$  (Fig. 2) at the central ketone bridge. Using the *syn,syn* form as the reference [0,0], the *syn,anti* form will be, for example, [0,180]. Although it appears to have been common practice in the past to depict pyrroketones in

the [180,180] form, this conformation would be expected to be less energetically favourable for substituted pyrroketones than other representatives, even after significant twisting, as a result of steric contacts between the C(3) and C(7) substituents, *e.g.* between C(31) and C(71) in (I). The observation of a particular conformation for (I) in the crystalline state will be the result of the relative energetic significance of four potential contributing factors. (1) The electronic stabilization to be achieved by  $p_\pi$ -delocalization over the whole pyrroketone skeleton, which will be optimized by a planar conformation. (2) The minimization of intramolecular steric repulsions between the two pyrrole ring systems. Fig. 2 indicates that the [0,0] conformation should be preferred over other planar representations in the absence of intermolecular interactions. Steric contacts between an N–H proton and an alkyl  $\beta$ -pyrrole substituent in the [0,180] and [180,0]

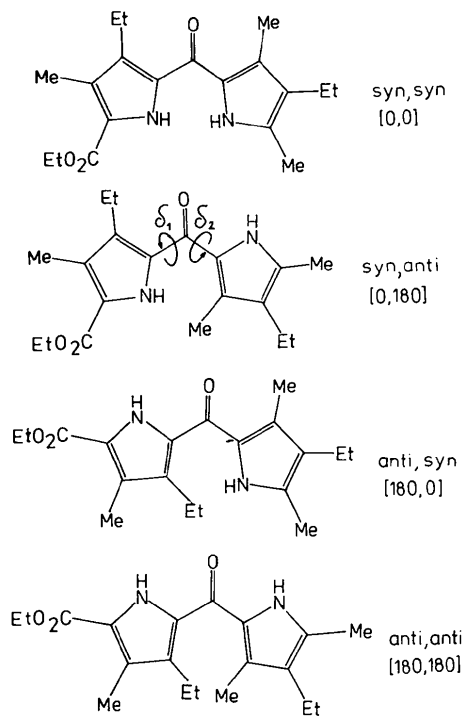


Fig. 2. Planar representations of (I)

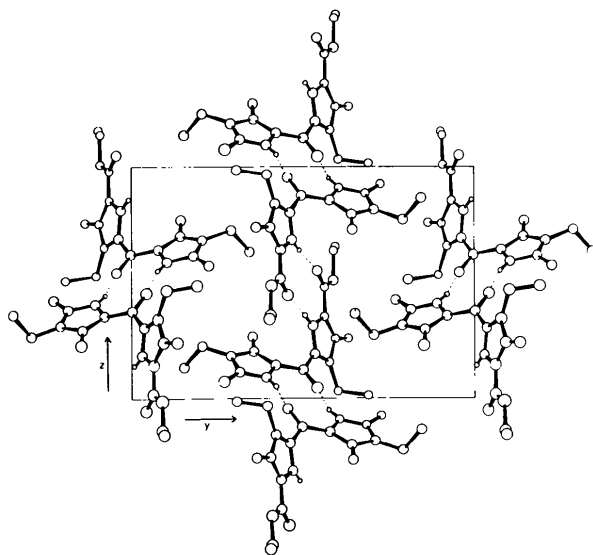


Fig. 3. Unit-cell contents viewed perpendicular to (100).

forms or between the  $\beta$ -pyrrole substituents in the [180,180] form must lead to a very significantly twisted conformation and *ipso facto* to a reduction of the electronic stabilization. The  $H(1)\cdots H(2)$  contact in the [0,0] form may, however, be minimized by either the adoption of a relatively small inter-planar angle or by a widening of the  $C(4)-C(5)-C(6)$  angle as is observed, for instance, in a protonated pyrromethene (Becker, Sheldrick & Engel, 1978). (3) Intermolecular  $N-H\cdots O$  hydrogen bonding involving the ketone O

atom. This would be expected to lead to a centrosymmetric dimerization of symmetrically substituted pyrroketones through two equivalent  $N-H\cdots O$  bonds and will only be possible for a participant N atom in a planar (or near-planar) *anti* conformation. In (I) the  $C(11)-O(11)$  carbonyl function of the ethoxycarbonyl substituent will also be expected to take part in a similar hydrogen-bonding pattern with  $N(1)$ . (4) Non-bonded interactions. Dispersion forces would be expected to enhance the stability of planar pyrroketone systems with extended  $p_\pi$ -delocalization, which are capable of stacking parallel to one another at a van der Waals distance.

The observed conformation for (I) is [48.6, -167.3].  $N(1)$  takes part in the hydrogen bond  $N(1)-H\cdots O(11)$  of 2.87 Å, the *anti*-positioned  $N(2)$  in the hydrogen bond  $N(2)-H\cdots O(5)$  of 2.87 Å, both to molecules related by a centre of symmetry (see Fig. 3). The molecular conformation is clearly determined by the intermolecular hydrogen bonding and by steric repulsions between  $C(71)$  and  $N(1)$  [ $C(71)\cdots N(1) = 3.03$ ,  $H(711)\cdots N(1) = 2.66$ ,  $H(712)\cdots N(1) = 2.89$  Å], which lead to the value of 48.6° for  $\delta_1$ . The bond-length distribution is indicative of a significant mesomeric contribution from the dipolar structure (I'). Thus the  $C(5)-C(6)$  and  $N(2)-C(9)$  bond lengths of 1.439 (4) and 1.348 (4) Å are much shorter than those of 1.473 (5) and 1.374 (5) Å for  $C(4)-C(5)$  and  $N(2)-C(6)$ . The ketone bridge  $C-C$  bond lengths are thereby similar to those of 1.440 (5) and 1.481 (5) Å in octaethylxanthoporphinogen dihydrate (II), in which the chromophore has crystallographic  $S_4$  symmetry with local pyrroketone units in the [41.6, -8.9] conformation (Sheldrick, 1976). The  $N-C$  distances in the second pyrrole ring of (II) are also significantly different [1.364 (4) and 1.384 (4) Å respectively]. In the first pyrrole ring of (I), the  $N(1)-C(4)$  distance of 1.359 (4) is only 0.01 shorter than that of 1.369 (4) Å for  $N(1)-C(1)$ , indicating that  $p_\pi$ -delocalization from this pyrrole system into the  $C(11)-O(11)$  carbonyl group is less significant than from the second pyrrole system into the ketone carbonyl function.

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