

2-Pyrrolyl 3-Thienyl Ketone

BY W. BECKER AND W. S. SHELDRIK*

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

AND J. ENGEL AND D. HEILIGER

Pharmaforschung des Chemiewerks Homburg, ZN DEGUSSA, Daimlerstrasse 25, D-6000 Frankfurt/Main, Federal Republic of Germany

(Received 4 December 1978; accepted 16 January 1979)

Abstract. C₉H₇NOS, orthorhombic, *Pbca*, $a = 11.132(2)$, $b = 19.350(4)$, $c = 7.786(3)$ Å, $M_r = 177.2$, $Z = 8$, $D_x = 1.27$ Mg m⁻³. The heterocyclic rings display an *anti*,twisted-*syn* conformation (-170.5 , 35.2°) with respect to the central ketone bridge. The molecules are linked into centrosymmetric dimers through two N—H...O hydrogen bonds of length 2.87 Å. The bond-length distribution in the pyrrole ring indicates a significant mesomeric contribution from a dipolar structure.

Introduction. As part of our systematic study of the structures of polyheterocyclic compounds, we have reported the structures of di-2-pyrrolyl ketone (II) (Sheldrick, Becker & Engel, 1978*a*) and di-3-thienyl ketone (III) (Sheldrick, Becker & Engel, 1978*b*). Here we present the analysis of a mixed derivative, 2-pyrrolyl 3-thienyl ketone (I) (Figs. 1, 2).

Cell dimensions were determined by a least-squares fit to the settings for 15 reflexions $\pm(hkl)$ on a Syntex P2₁ diffractometer (Cu K α , $\lambda = 1.54178$ Å). Intensity measurements were carried out in the $\theta-2\theta$ mode ($3.0 < 2\theta < 135.0^\circ$). After application of the observation criterion $F \geq 3.0\sigma(F)$, 1437 unique reflexions were retained. The structure was solved by the automatic centrosymmetric direct-methods routine of *SHELX* (G. M. Sheldrick) and refined to $R = 0.052$, $R_w =$

0.047.† The H-atom positional parameters were refined with individual isotropic temperature factors under the bond-length constraints C—H = 1.08 ± 0.02 , N—H = 1.01 ± 0.02 Å. The weights were given by the counting statistics. Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). Table 1 gives the final positional parameters for the nonhydrogen atoms, Fig. 2 the bond lengths and angles.

Discussion. The heterocyclic rings display an *anti*,twisted-*syn* conformation with interplanar angles

† Lists of structure factors, thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34196 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

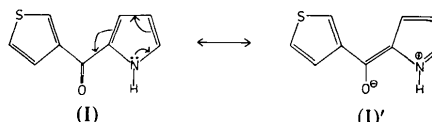


Fig. 2. Mesomeric forms of (I).

* Author to whom correspondence should be addressed.

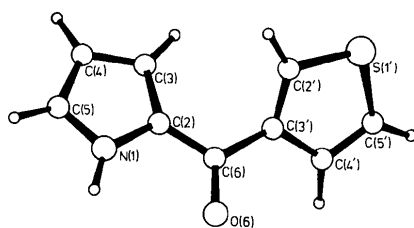


Fig. 1. A molecule of (I) showing the numbering system.

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

| | x | y | z |
|-------|----------|----------|----------|
| N(1) | 778 (2) | 5437 (1) | 7806 (3) |
| C(2) | 1058 (2) | 4839 (1) | 6939 (3) |
| C(3) | 1628 (2) | 5034 (1) | 5428 (3) |
| C(4) | 1703 (3) | 5753 (1) | 5419 (4) |
| C(5) | 1170 (3) | 5986 (1) | 6907 (3) |
| C(6) | 680 (2) | 4182 (1) | 7581 (3) |
| O(6) | 5 (1) | 4134 (1) | 8848 (2) |
| S(1') | 2406 (1) | 2631 (1) | 5299 (1) |
| C(2') | 2222 (2) | 3446 (1) | 6057 (3) |
| C(3') | 1105 (2) | 3544 (1) | 6738 (3) |
| C(4') | 395 (2) | 2932 (1) | 6628 (3) |
| C(5') | 983 (2) | 2399 (1) | 5862 (3) |

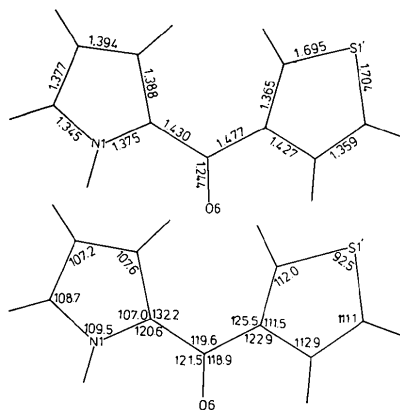


Fig. 3. Bond lengths (Å) and angles (°) for (I). The e.s.d.'s are 0.002–0.003 Å for bond lengths and 0.1–0.2° for bond angles.

of -170.5 and 35.2° with respect to the central ketone bridge.

The *anti* position of the pyrrole ring is a necessary consequence of the dimerization of (I) through N(1)—H \cdots O(6) hydrogen bonds of length 2.87 Å between equivalent molecules related by a centre of symmetry. A similar interplanar angle of -167.3° and N—H \cdots O distance of 2.87 Å is observed for that pyrrole ring in (II) which is involved in equivalent hydrogen bonding. Steric contact between the protons

on C(3) and C(2') of (I) must lead to twisting of the thiophene ring with respect to the trigonal coordination plane at C(6). In fact, an interplanar angle of 35.2° is observed for an H(3) \cdots H(2') intramolecular distance of 2.55 Å. The degree of twist in (III) is less pronounced with interplanar angles of 20.9 and 20.1° for a very much shorter intramolecular H \cdots H distance of 2.28 Å. Packing forces must presumably be responsible for this average difference of 14.7° between (I) and (III) in the conformation of the thiophene ring relative to the central ketone bridge.

The bond-length distribution is indicative of a significant mesomeric contribution from the dipolar structure (I). Thus, the N(1)—C(5) and C(2)—C(6) lengths, 1.345 (3) and 1.430 (3) Å, are much shorter than the 1.375 (3) and 1.477 (3) Å for N(1)—C(2) and C(6)—C(3').

References

- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
 SHELDRIK, W. S., BECKER, W. & ENGEL, J. (1978a). *Acta Cryst.* **B34**, 2929–2931.
 SHELDRIK, W. S., BECKER, W. & ENGEL, J. (1978b). *Acta Cryst.* **B34**, 3120–3122.

Acta Cryst. (1979). **B35**, 1270–1273

1,7-Diazaspiro[4.4]nonane-2,6-dione

BY INGEBOG CSÖREGH AND MÁTYÁS CZUGLER*

Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

AND MÁRTON KAJTÁR

Institute of Organic Chemistry, L. Eötvös University, H-1088 Budapest, Muzeum Krt. 4/B, Hungary

(Received 19 December 1978; accepted 5 February 1979)

Abstract. $C_7H_{10}N_2O_2$, $M_r = 142.16$, monoclinic, $P2_1/c$, $a = 9.601$ (2), $b = 7.815$ (1), $c = 9.498$ (2) Å, $\beta = 91.20$ (3)°, $Z = 4$, $V = 712.50$ Å³, $\mu(Cu K\alpha) = 0.80$ mm⁻¹. The envelope-shaped pyrrolidone rings are nearly perpendicular to each other. The crystal structure consists of infinite hydrogen-bonded layers linked together by normal van der Waals forces.

* Permanent address: Central Research Institute for Chemistry of the Hungarian Academy of Sciences, H-1525 Budapest, POB.17, Hungary.

Introduction. This structure determination is part of a research programme to study the conformation of the pyrrolidone ring in some isomers of spiro-bis-pyrrolidones (*i.e.* diazaspiro[4.4]nonane-diones), which show interesting chiroptical properties. The title compound was prepared at the Institute of Organic Chemistry, L. Eötvös University, Budapest (Kajtár, Hollósi & Kinsky, 1975).

The colourless crystals, generally in the shape of hexagonal plates, were preliminarily examined using X-ray photographic methods, such as the Guinier,