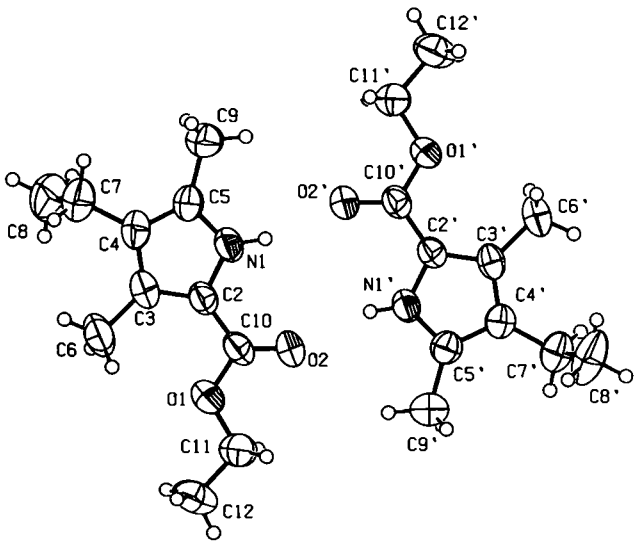
Crystal structure of 4-ethyl-3,5-dimethyl-1*H*-pyrolle-2-carboxylic acid ethyl ester, $C_{11}H_{17}NO_2$

J. A. Paixão*[I], A. Matos Beja[I], M. Ramos Silva[I], L. Alte da Veiga[I], A. J. F. N. Sobral[II], S. H. Lopes[II] and A. M. d'A. Rocha Gonsalves[II]

[I] Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, P-3004-516 Coimbra, Portugal
[II] Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, P-3004-535 Coimbra, Portugal

Received June 27, 2002, accepted and available on-line August 11, 2002; CCDC-No. 1267/893



Abstract

$C_{11}H_{17}NO_2$, monoclinic, $P12_1/n1$ (No. 14), $a = 11.8338(5)$ Å, $b = 8.2733(5)$ Å, $c = 23.700(2)$ Å, $\beta = 92.568(5)°$, $V = 2318.1$ Å^3, $Z = 8$, $R_{gt}(F) = 0.047$, $wR_{ref}(F^2) = 0.159$, $T = 293$ K.

Source of material

The 4-ethyl-3,5-dimethyl-1*H*-pyrrole-2-carboxylic acid ethyl ester was prepared by the classical Knorr reaction [1] from the oxime of ethyl acetoacetate and 3-ethyl-2,4-pentanedione, giving the title compound in 60% yield. The compound was recrystallised by slow evaporation from a dichloromethane/hexane (1:1) solution giving crystals with a melting point of 358(1) K. Elemental analysis: calculated for $C_{11}H_{17}NO_2$: C, 67.66%; H, 8.78%; N, 7.17%; found: C, 67.58%; H, 8.70%; N, 7.10%. CG/MS: $C_{11}H_{17}NO_2$ needs 195, found: M^+ (m/z) = 195. ^{1}H-NMR results are included in the deposited CIF-file.

Experimental details

The coordinates of the H atoms were placed at idealized positions and refined as riding using the SHELXL-97 defaults [2]. The final structure was examined with PLATON [3] showing that there are no solvent-accessible voids in the crystal lattice. The crystal was weakly diffracting with only 40% of the reflections up to 25° satisfying the criteria $I > 2\sigma(I)$. This probably accounts for the somewhat large R_w value.

There are two symmetry independent molecules in the asymmetric unit of the monoclinic cell. We have carefully checked for the presence of any missed crystallographic symmetry element relating the two molecules using the ADDSYM and NEWSYM tools of PLATON [3] but none was found.

Discussion

Porphyrins are important compounds with many uses in materials science [4-6] and in medicine as photosensitizers for photodynamic therapy [7]. Pyrroles are relevant intermediates in the synthesis of porphyrins [8,9] which have a core built of four pyrrole rings. Following our studies on porphyrin synthesis [10,11] we have prepared several pyrrole derivatives with different substituents on the β-positions. We report here the crystal structure of one of these derivatives, the 4-ethyl-3,5-dimethyl-1*H*-pyrrole-2-carboxylic acid ethyl esther. Bond distances and angles within the molecules are unexceptional and very similar for the two molecules. The 2-carboxyl acid ethyl ester groups are planar and lie in the same plane of the pyrrole ring in both molecules. The 3,5-dimethyl groups form an angle of ≈100° with the pyrrole ring. This small deviation from the ideal value of 90°, determined by an ab-initio HF-LCAO quantum-mechanical calculation of the geometry of the isolated molecule using the GAMESS program [12] and a 631G(d,p) basis set, is probably due to packing effects. The molecules are stacked in the unit cell with the pyrrole rings lying perpendicular to the (001) plane. The two symmetry independent molecules are joined in pairs through two moderately strong hydrogen bonds between the amine N-H and the bare carbonyl O atom of the carboxyl acid ethyl ester substituent [d(N···O) = 2.874(3) Å]

Table 1. Data collection and handling.

Crystal:	colourless, tabular, size 0.11 × 0.28 × 0.37 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.77 cm^{-1}
Diffractometer, scan mode:	Enraf Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4286, 4075
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1597
$N(param)_{refined}$:	261
Programs:	SHELXS-97 [13], SHELXL-97 [1], PLATON [2], ORTEPII [14]

* Correspondence author (e-mail: jap@pollux.fis.uc.pt)

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.3035	0.7822	–0.0082	0.073
H(2)	4*e*	0.0301	0.9006	–0.1615	0.136
H(3)	4*e*	0.0830	1.0735	–0.1660	0.136
H(4)	4*e*	0.0074	1.0311	–0.1154	0.136
H(5)	4*e*	0.3960	1.0648	–0.1681	0.113
H(6)	4*e*	0.2735	1.1311	–0.1813	0.113
H(7)	4*e*	0.3515	0.8285	–0.2175	0.185
H(8)	4*e*	0.3280	0.9777	–0.2571	0.185
H(9)	4*e*	0.2273	0.8896	–0.2292	0.185
H(10)	4*e*	0.4945	0.8222	–0.0369	0.122
H(11)	4*e*	0.5062	0.9850	–0.0700	0.122
H(12)	4*e*	0.5024	0.8204	–0.1028	0.122
H(13)	4*e*	–0.1162	0.7955	0.0252	0.094
H(14)	4*e*	–0.1119	0.6366	–0.0112	0.094
H(15)	4*e*	–0.2285	0.9197	–0.0453	0.138
H(16)	4*e*	–0.2873	0.7585	–0.0278	0.138
H(17)	4*e*	–0.2208	0.7658	–0.0835	0.138
H(1')	4*e*	0.1963	0.6225	0.0883	0.069
H(2')	4*e*	0.4775	0.3283	0.1954	0.111
H(3')	4*e*	0.4113	0.3423	0.2510	0.111
H(4')	4*e*	0.4801	0.4904	0.2296	0.111
H(5')	4*e*	0.2217	0.2590	0.2579	0.092
H(6')	4*e*	0.0995	0.3238	0.2437	0.092
H(7')	4*e*	0.2606	0.4915	0.3119	0.170
H(8')	4*e*	0.1587	0.3948	0.3352	0.170
H(9')	4*e*	0.1363	0.5510	0.2990	0.170
H(10')	4*e*	–0.0036	0.5830	0.1804	0.122
H(11')	4*e*	–0.0076	0.4168	0.1486	0.122
H(12')	4*e*	0.0062	0.5777	0.1146	0.122
H(13')	4*e*	0.6140	0.7113	0.0733	0.089
H(14')	4*e*	0.6017	0.5418	0.0434	0.089
H(15')	4*e*	0.7307	0.5976	0.1441	0.132
H(16')	4*e*	0.7822	0.5639	0.0855	0.132
H(17')	4*e*	0.7164	0.4270	0.1159	0.132

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4*e*	–0.0228(2)	0.8182(3)	–0.04248(9)	0.058(1)	0.093(2)	0.065(1)	0.009(1)	–0.009(1)	0.008(1)
O(2)	4*e*	0.0980(2)	0.7152(3)	0.02317(9)	0.068(2)	0.113(2)	0.063(1)	0.008(2)	–0.010(1)	0.029(2)
N(1)	4*e*	0.2799(2)	0.8291(3)	–0.03891(9)	0.062(2)	0.075(2)	0.046(1)	0.008(2)	–0.009(1)	0.004(1)
C(2)	4*e*	0.1678(3)	0.8520(4)	–0.0551(1)	0.057(2)	0.067(2)	0.046(2)	0.008(2)	–0.007(2)	0.001(2)
C(3)	4*e*	0.1656(3)	0.9338(4)	–0.1064(1)	0.074(2)	0.066(2)	0.053(2)	0.009(2)	–0.013(2)	0.005(2)
C(4)	4*e*	0.2783(3)	0.9572(4)	–0.1204(1)	0.083(3)	0.073(3)	0.047(2)	–0.002(2)	–0.002(2)	0.006(2)
C(5)	4*e*	0.3473(3)	0.8907(4)	–0.0779(1)	0.072(2)	0.066(2)	0.046(2)	0.000(2)	0.002(2)	–0.002(2)
C(6)	4*e*	0.0621(3)	0.9898(5)	–0.1404(1)	0.095(3)	0.104(3)	0.070(2)	0.019(2)	–0.022(2)	0.021(2)
C(7)	4*e*	0.3172(3)	1.0338(5)	–0.1737(1)	0.107(3)	0.113(4)	0.062(2)	–0.002(3)	0.006(2)	0.015(2)
C(8)	4*e*	0.3049(4)	0.9223(6)	–0.2239(2)	0.134(4)	0.175(5)	0.062(2)	0.026(4)	0.019(2)	–0.002(3)
C(9)	4*e*	0.4741(3)	0.8784(5)	–0.0713(1)	0.063(2)	0.109(3)	0.072(2)	–0.006(2)	0.002(2)	0.002(2)
C(10)	4*e*	0.0817(3)	0.7895(4)	–0.0206(1)	0.056(2)	0.074(3)	0.054(2)	0.012(2)	–0.014(2)	–0.002(2)
C(11)	4*e*	–0.1167(3)	0.7535(5)	–0.0131(1)	0.061(2)	0.100(3)	0.073(2)	0.002(2)	0.004(2)	–0.003(2)
C(12)	4*e*	–0.2229(3)	0.8039(5)	–0.0453(2)	0.060(2)	0.114(4)	0.101(3)	0.008(2)	–0.012(2)	–0.019(3)
O(1')	4*e*	0.5208(2)	0.5545(3)	0.11579(8)	0.049(1)	0.089(2)	0.056(1)	0.007(1)	–0.005(1)	0.008(1)
O(2')	4*e*	0.3984(2)	0.6649(3)	0.05277(8)	0.060(1)	0.116(2)	0.056(1)	0.011(1)	–0.000(1)	0.027(1)
N(1')	4*e*	0.2190(2)	0.5713(3)	0.11824(9)	0.058(2)	0.066(2)	0.047(1)	0.008(2)	–0.004(1)	0.006(1)
C(2')	4*e*	0.3301(2)	0.5403(4)	0.1338(1)	0.050(2)	0.052(2)	0.045(2)	0.006(2)	–0.005(1)	–0.004(2)
C(3')	4*e*	0.3315(3)	0.4570(4)	0.1845(1)	0.068(2)	0.046(2)	0.043(2)	0.006(2)	–0.009(2)	–0.004(2)
C(4')	4*e*	0.2185(3)	0.4375(4)	0.1992(1)	0.065(2)	0.051(2)	0.050(2)	0.000(2)	0.003(2)	–0.003(2)
C(5')	4*e*	0.1508(3)	0.5093(4)	0.1571(1)	0.061(2)	0.058(2)	0.055(2)	0.000(2)	0.004(2)	–0.002(2)
C(6')	4*e*	0.4344(3)	0.3993(4)	0.2182(1)	0.087(3)	0.077(3)	0.057(2)	0.006(2)	–0.018(2)	0.009(2)
C(7')	4*e*	0.1775(3)	0.3564(4)	0.2511(1)	0.093(3)	0.069(3)	0.069(2)	–0.003(2)	0.009(2)	0.016(2)
C(8')	4*e*	0.1839(4)	0.4576(5)	0.3041(1)	0.188(5)	0.088(3)	0.068(3)	0.012(3)	0.049(3)	0.010(2)
C(9')	4*e*	0.0252(3)	0.5229(5)	0.1495(2)	0.060(2)	0.097(3)	0.086(2)	0.001(2)	0.008(2)	0.006(2)
C(10')	4*e*	0.4164(3)	0.5922(4)	0.0972(1)	0.057(2)	0.064(2)	0.044(2)	0.005(2)	–0.009(2)	–0.003(2)
C(11')	4*e*	0.6122(3)	0.5956(5)	0.0797(1)	0.058(2)	0.097(3)	0.068(2)	0.003(2)	0.005(2)	0.002(2)
C(12')	4*e*	0.7200(3)	0.5412(5)	0.1089(2)	0.058(2)	0.111(3)	0.094(3)	0.005(2)	–0.009(2)	–0.008(3)

Acknowledgments. The authors would like to thank Chymiotechnon and FCT (Sapiens POCTI/QUI/42536/2001) for financial support.

References

1. Paine, J. B.: The Porphyrins (Ed. D. Dolphin), Ac. Press, Vol. 1 (1978), chp. 4, p. 101-234.
2. Sheldrick, G. M.: SHELXL-97. A program for refining crystal structures. University of Göttingen, Germany 1997.
3. Spek, A. L.: PLATON. Molecular Geometry Program. University of Utrecht, Utrecht, The Netherlands 2002).
4. Grieve, M. B.; Richardson, T.; Hudson, A. J.; Johnstone, R. A. W.; Sobral, A. J. F. N; Rocha Gonsalves, A. M. d'A.: The molecular electronic properties of a novel tetraphenylporphyrin derivative. Int. J. Electronics **77** (1994) 957-962.
5. Smith, V. C.; Batty, S. V.; Richardson, T.; Foster, K. A.; Johnstone, R. A. W.; Sobral, A. J. F. N.; Rocha Gonsalves, A. M. d'A. : Chlorine sensing properties of porphyrins thin films. Thin Solid Films **284-285** (1996) 911-914.
6. Richardson, T.; Smith, V. C.; Johnstone, R. A. W.; Sobral, A. J. F. N.; Rocha Gonsalves, A. M. d'A.: Optical response of monolayer films of a metal-free sulphonamido-porphyrin. Thin Solid Films **327-329** (1998) 315-320.
7. Bonnet, R.: Photosensitizers of the porphyrin and phtalocyanine series for photodynamic therapy. Chem. Soc. Rev. **24** (1995) 19-33.
8. Jones, A.: The synthesis and the physical and chemical aspects of the pyrrolic ring. In: *The Chemistry of Heterocycle Compounds* (Ed. Edward C. Taylor) Wiley, Vol. 48 (1990), Part 1.
9. Battersby, A. R.; McDonald, E.: Biosynthesis of porphyrins, chlorins and corrins in Porphyrins and Metalloporphyrins (Ed. Kevin M. Smith) Elsevier (1976)., Chap. 3, p. 61-122.
10. Sobral, A. J. F. N.; Rocha Gonsalves, A. M. d'A.: The manganese complex of 2,3,7,8,12,13,17,18-octaphenylporphyrin as epoxydation catalyst. J. Porphyrins Phtalocyanines **5** (2001) 428-430.
11. Sobral, A. J. F. N.; Rocha Gonsalves, A. M. d'A.: 5,15-Diaryl-β-substituted-porphyrinato-manganese (III) chlorides as probes for structure-activity relashionships in porphyrin based epoxydation catalysts. J. Porphyrins Phtalocyanines **5** (2001) 861-866.
12. Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Hensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen K.A.; Su S.J.; Windus, T. L.; Dupuis; M.; Montgomery, J. A. : The General Atomic and Molecular Electronic Structure System. J. Comput. Chem. **14** (1993) 1347-1363.
13. Sheldrick, G. M.: SHELXS-97. A program for determining crystal structures. University of Göttingen, Germany 1997.
14. Johnson, C. K.: ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA, USA 1976.