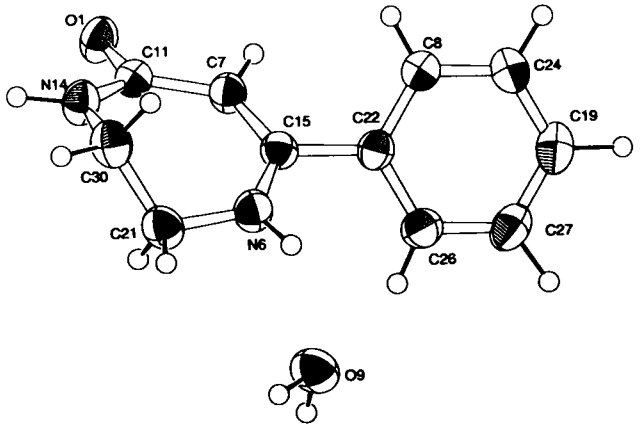
Crystal structure of 7-phenyl-1,4-diazepin-5-one monohydrate, $C_{11}H_{12}N_2O \cdot H_2O$

M. Chammache[I], E. M. Essassi[I] and M. Pierrot*,[II]

[I] Université Mohamed V, Laboratoire de Chimie Organique Hétérocyclique, Faculté des Sciences, Rabat, Maroc
[II] LBS-UMR 6517, Centre Scientifique Saint-Jérôme, F-13397 Marseille, Cedex 20, France

Received June 30, 2000, CCDC-No. 1267/488



Abstract

$C_{11}H_{14}N_2O_2$, triclinic, $P\bar{1}$ (No. 2), $a = 7.1014(4)$ Å, $b = 8.6896(7)$ Å, $c = 10.1265(8)$ Å, $\alpha = 70.175(3)°$, $\beta = 88.517(5)°$, $\gamma = 66.283(4)°$, $V = 533.7$ Å^3, $Z = 2$, $R_{gt}(F) = 0.044$, $wR_{ref}(F^2) = 0.064$, $T = 298$ K.

Source of material

A solution of (0.1 mol) of ethyl benzoylacetate and 10 ml of xylene was added, drop wise, over 40 min. to a refluxing solution of 0.1 mol ethylene diamine and 100 ml of xylene. During this time an oily layer separated. On cooling, the oil solidified to a hard mass. The xylene layer was decanted and discarded. The solid was suspended in about 100 ml of chloroform and the mixture was filtered. The solid was recrystallized from ethanol to give 50 % of product with mp 483 K – 485 K. The melting point was taken in a capillary tube. Chemical analysis for $C_{11}H_{12}N_2O$: C, 69.70; H, 6.43; N, 15.09 (calculated: C, 70.18; H, 6.43 ; N, 14.88).

Discussion

The interest carried to derivatives of the 1,4-diazepine is due to their remarkable pharmacological activity. Let's note for instance their antitumoral [1], and anticonvulsant [2,3] actions. In the course of our research in the 1,4-diazepine series [4,5], we were interested in the synthesis of the 7-phenyl-1,4-diazepin-5-one. In the literature [6] the synthesis of the compound is performed by condensation of ethylenediamine with ethyl benzoylacetate in xylene. The obtained diazepine can theoretically adopt one of the two tautomeric enamine or imine forms. In a previous work [5], we have shown by a study based on the ^{1}H-NMR spectral data and on the electronic impact fragmentations, that the compound should adopt, preferentially, the enaminic form.

The structure was determined to identify the tautomeric form present in the crystal and the enamine conformation was observed. The seven-membered ring is composed of a planar fragment C21N6C15C7C11 (at 136.2(2)° of the phenyl ring) with N14 at 0.4329(5) Å and C30 at 0.9566(6) Å. The organic molecule crystallizes with one structural water molecule (O9) which shows three intermolecular hydrogen bonds, one as acceptor (N6—O9 = 2.9506(6) Å) and two as donor (O1—O9 = 2.7990(6) Å and O1— O9 = 2.8975(7) Å).

Table 1. Data collection and handling.

Crystal:	colorless cube, size 0.30 × 0.35 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.9 cm^{-1}
Diffractometer, scan mode:	Kappa CCD, φ-scan
$2\theta_{max}$:	50.24°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1857, 1857
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\ \sigma(I_{obs})$, 1656
$N(param)_{refined}$:	144
Programs:	DENZO [7],SCALEPACK [7], SIR92 [8], maXus [9], ORTEP-II [10]

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

Atom	Site	x	y	z	U_{iso}
H(7)	2*i*	0.23393	–0.180201	0.251538	0.0564
H(8)	2*i*	0.192488	0.047041	0.02255	0.0658
H(19)	2*i*	0.402887	0.440645	–0.035683	0.0692
H(21A)	2*i*	–0.411958	0.153415	0.382936	0.0614
H(21B)	2*i*	–0.213158	0.003515	0.481737	0.0614
H(24)	2*i*	0.364517	0.221478	–0.106589	0.0725
H(26)	2*i*	0.084883	0.319495	0.293148	0.0621
H(27)	2*i*	0.264958	0.489384	0.16537	0.0701
H(30A)	2*i*	–0.435058	–0.097007	0.376588	0.0627
H(30B)	2*i*	–0.333358	–0.037807	0.240288	0.0627
H(6)	2*i*	–0.215(1)	0.2565(9)	0.2747(7)	0.0500
H(14)	2*i*	–0.165957	–0.354906	0.45561	0.0614
H(9A)	2*i*	–0.547(2)	0.518(1)	0.3509(8)	0.084(3)
H(9B)	2*i*	–0.348(2)	0.480(1)	0.408(1)	0.102(3)

* Correspondence author (e-mail: marcel.pierrot@lbs.u-3mrs.fr)

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)	2*i*	0.19420(6)	-0.43687(5)	0.41247(4)	0.0411(2)	0.0304(2)	0.0569(3)	-0.0141(2)	0.0098(2)	-0.0111(2)
N(6)	2*i*	-0.16927(8)	0.14163(6)	0.29777(5)	0.0428(3)	0.0317(2)	0.0501(3)	-0.0116(2)	0.0137(2)	-0.0133(2)
C(7)	2*i*	0.10653(9)	-0.13080(7)	0.28554(6)	0.0361(3)	0.0327(3)	0.0416(3)	-0.0134(2)	0.0100(2)	-0.0117(2)
C(8)	2*i*	0.1995(1)	0.13784(7)	0.05225(6)	0.0549(4)	0.0390(3)	0.0444(3)	-0.0236(3)	0.0132(3)	-0.0170(2)
O(9)	2*i*	-0.41198(8)	0.49325(6)	0.32548(5)	0.0484(3)	0.0568(3)	0.0570(3)	-0.0173(2)	0.0158(2)	-0.0256(2)
C(11)	2*i*	0.05250(9)	-0.27685(7)	0.36560(5)	0.0369(3)	0.0334(3)	0.0361(3)	-0.0155(2)	0.0063(2)	-0.0128(2)
N(14)	2*i*	-0.14046(7)	-0.25171(6)	0.39211(5)	0.0377(3)	0.0376(2)	0.0493(3)	-0.0186(2)	0.0101(2)	-0.0113(2)
C(15)	2*i*	0.00821(8)	0.05132(6)	0.25527(5)	0.0355(3)	0.0335(3)	0.0321(3)	-0.0134(2)	0.0034(2)	-0.0102(2)
C(19)	2*i*	0.3147(1)	0.37084(8)	0.01792(6)	0.0520(4)	0.0484(3)	0.0483(4)	-0.0299(3)	0.0032(3)	-0.0051(3)
C(21)	2*i*	-0.29176(9)	0.06041(7)	0.38654(6)	0.0392(3)	0.0409(3)	0.0459(3)	-0.0114(2)	0.0117(3)	-0.0145(2)
C(22)	2*i*	0.11277(8)	0.16489(6)	0.17173(5)	0.0357(3)	0.0287(2)	0.0353(3)	-0.0111(2)	0.0013(2)	-0.0071(2)
C(24)	2*i*	0.2990(1)	0.24108(8)	-0.02399(6)	0.0610(4)	0.0508(3)	0.0449(3)	-0.0290(3)	0.0172(3)	-0.0157(3)
C(26)	2*i*	0.1279(1)	0.29750(7)	0.21225(6)	0.0507(4)	0.0380(3)	0.0385(3)	-0.0181(2)	0.0020(3)	-0.0132(2)
C(27)	2*i*	0.2295(1)	0.39938(8)	0.13587(6)	0.0584(4)	0.0424(3)	0.0504(3)	-0.0275(3)	-0.0043(3)	-0.0117(3)
C(30)	2*i*	-0.31846(9)	-0.07941(8)	0.34179(6)	0.0320(3)	0.0483(3)	0.0493(3)	-0.0161(2)	0.0063(3)	-0.0131(3)

References

1. Kuo-Hsing, L.; Thoshiro I.: Antitumor agents. Helenanin sym-dimethyl-ethylenediamine reaction products and related derivatives. J. Med. Chem. **21** (1978) 698-701.
2. Fiakpui, C. Y.; Phillips, O. A.; Murthy, K. S. K.; Knauss, E. E.: Synthesis and anticonvulsant activities of 5-[2-chlorophenyl]-7*H*-pyrido [4,3-*f*][1,2,4]triazolo[4,3-*a*][1,4]diazepines. J. Heter. Chem. **36** (1999) 377-380.
3. Phillips, O. A.; Murthy, K. S. K.; Fiakpui, C. Y.; Knauss, E. E.: Synthesis of 5-phenyl-10-methyl-7*H*-pyrimido[4,5-*f*][1,2,4]triazolo[4,3-a][1,4]diazepine and its evaluation as an anticonvulsant agent. Canad. J. Chem. **77** (1999) 216-222.
4. Chammache, M.; Essassi, E. M.; Salem, M.; Zniber, R.: New methods of synthesis of pyrazole and isoxazole derivatives from 7-phenyl-1,4-diazepine-5-thione. Bull. Soc. Belg. **99** (1990) 351-356.
5. Chammache, M.; Essassi, E. M.; Zniber, R.: Reactivity of 7-phenyl-1,4-diazepin-5-one. Bull. Soc. Belg. **102** (1993) 89-98.
6. Hofmann, C. M.; Safir, S. R.: Synthesis and structure of 7-methyl-and-7-phenyl-1,2,3,4-tetrahydro-1,4-diazepin-5-ones. J. Org. Chem. **27** (1962) 3565-3568.
7. Otwinowski, Z.; Minor, W.: Processing of X-ray Diffraction Data Collected in Oscillation Mode. Methods in Enzymology. Vol. 276. Macromolecular Crystallography part A, Edits. C.W. Carter, Jr. & R. M. Sweet, pp. 307-326, New York: Academic Press (1997).
8. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M.: Sir92 - A program for automatic solution of crystal structures by direct methods. J. Appl. Cryst. **27** (1994) 435-436.
9. Mackay, S.; Gilmore, C. J.; Edwards, C.; Stewart, N.; Shankland, K.: maXus Computer Program for the Solution and Refinement of Crystal Structures. Nonius, The Netherlands, MacScience, Japan & The University of Glasgow 1999.
10. Johnson, C. K.: ORTEP-II. A Fortran Thermal-Ellipsoid Plot Program. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA 1976.