Instrumental Achievements

Crystal Structure of 1,5-Dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one-4-[(1*E*)-(aminomethylidenyl)]-5′-hydroxy-benzo-15-crown-5

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Benzocrown ethers have been a very useful class of host molecules, preparing the ground for the other substituted crown ether frameworks.[1,2] The crown ethers with different ring sizes and different types and numbers of substituents have been used to prepare a large number of alkaline, alkaline earth cation and neutral molecular complexes as guest.[3]

In 2-hydroxybenzocrown ethers, two types of hydrogen bonds [either N–H···O (*keto*-amine tautomer) or N···H–O (phenol-imine tautomer)] may exist, in polar solvents.[2] The present structure determination was undertaken in order to determine the type of hydrogen bonding, in the solid state, which is the first example containing 4-aminophenazone, (4-AAP), to be reported in the literature. 4-AAP and its derivatives are used as anti-inflammatory drugs.[4] The title ligand was prepared from a mixture of 4′-formyl-5′-hydroxybenzo-15-crown-5 (0.50 g, 1.60 mmol) and 4-AAP (0.32 g, 1.60 mmol) in methanol (50 ml). The mixture was refluxed for 1 h and then allowed to come to ambient temperature. The raw material was recrystallized from methanol (yield 0.43 g, 55%; m.p. 451 K).

The results of X-ray structure determination are given in Tables 1 – 3. The hydrogen atoms were located by a difference Fourier synthesis and a geometrical calculation, with the

Table 1 Crystal and experimental data

Formula: $C_{26}H_{31}N_3O_7$
Formula weight = 497.54
Crystal system: triclinic
Space group: $P\bar{1}$ $Z = 2$
a = 9.340(1)Å
b = 11.082(1)Å
c = 12.587(1)Å
α = 98.68(1)°
β = 94.97(1)°
γ = 104.09(1)°
V = 1238.7(3)Å^3
D_x = 1.334 g/cm^3
μ(Mo K$_\alpha$) = 0.098 mm^{-1}
T = 293 K
Yellow
Crystal size: 0.13 × 0.20 × 0.30 mm
λ(Mo K$_\alpha$) = 0.71073 Å
R = 0.0574 wR = 0.1457
No. of reflections measured = 4900
No. of reflections used = 2474
[$I > 2\sigma(I)$]
No. of parameters = 412
Goodness-of-fit = 0.998
$(\Delta/\sigma)_{max}$ = 0.001
$(\Delta\rho)_{max}$ = 0.482
$(\Delta\rho)_{min}$ = –0.301
$2\theta_{max}$ = 52.58°
Measurements: Enraf-Nonius CAD-4 diffractometer
Program system: CAD-4 EXPRESS Software
Structure determination: SHELXS97
Refinement: full matrix least-squares

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Table 2 Final atomic coordinates and equivalent isotropic thermal parameters

Atom	x	y	z	U_{eq}/Å^2
N1	1.4604(3)	1.1393(2)	1.3337(2)	0.0419(6)
N2	1.3847(3)	1.2252(2)	1.3799(2)	0.0434(7)
N3	1.0884(3)	1.0220(2)	1.1895(2)	0.0415(6)
O1	1.3942(2)	0.9534(2)	1.2051(2)	0.0522(6)
O2	0.8282(2)	1.0395(2)	1.1308(2)	0.0514(6)
O3	0.7236(2)	0.5844(2)	0.8525(2)	0.0477(6)
O4	0.4978(3)	0.3616(2)	0.7161(2)	0.0592(7)
O5	0.2184(4)	0.4132(3)	0.6359(3)	0.0976(10)
O6	0.2006(3)	0.5597(2)	0.8471(2)	0.0748(8)
O7	0.5009(2)	0.6963(2)	0.8823(2)	0.0507(6)
C1	1.6065(4)	1.1579(3)	1.5097(3)	0.0485(8)
C2	1.7294(4)	1.1386(3)	1.5684(3)	0.0566(10)
C3	1.8267(5)	1.0837(3)	1.5172(3)	0.0600(10)
C4	1.8029(4)	1.0468(4)	1.4066(3)	0.0586(10)
C5	1.6842(4)	1.0662(3)	1.3461(3)	0.0490(9)
C6	1.5845(3)	1.1213(3)	1.3975(2)	0.0395(7)
C7	1.4697(4)	1.3587(3)	1.4063(3)	0.0594(10)
C8	1.1398(5)	1.2718(4)	1.3441(4)	0.0549(10)
C9	1.2448(3)	1.1917(3)	1.3243(2)	0.0407(7)
C10	1.2246(3)	1.0829(3)	1.2516(2)	0.0387(7)
C11	1.3624(3)	1.0457(3)	1.2549(2)	0.0406(7)
C12	1.0651(3)	0.9179(3)	1.1208(2)	0.0411(7)
C13	0.9191(3)	0.8626(3)	1.0600(2)	0.0390(7)
C14	0.8861(4)	0.7460(3)	0.9868(3)	0.0428(8)
C15	0.7486(3)	0.6940(3)	0.9282(2)	0.0402(7)
C16	0.6345(3)	0.7550(3)	0.9424(2)	0.0384(7)
C17	0.6635(4)	0.8693(3)	1.0113(3)	0.0432(8)
C18	0.8044(3)	0.9241(3)	1.0682(2)	0.0402(7)
C19	0.6494(5)	0.4719(3)	0.8871(3)	0.0578(10)
C20	0.6163(5)	0.3633(3)	0.7949(4)	0.0650(11)
C21	0.3566(6)	0.3110(6)	0.7479(5)	0.0859(14)
C22	0.2367(5)	0.2985(4)	0.6591(4)	0.0841(13)
C23	0.0877(5)	0.4486(5)	0.6603(4)	0.1011(17)
C24	0.0734(5)	0.4774(4)	0.7808(4)	0.0867(14)
C25	0.2504(4)	0.6763(3)	0.8157(3)	0.0542(9)
C26	0.3808(4)	0.7553(3)	0.8935(3)	0.0480(8)
H2	0.941(7)	1.060(5)	1.169(4)	0.152

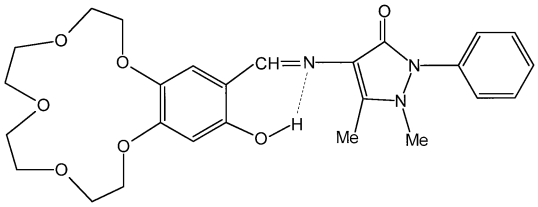

Fig. 1 Chemical diagram.

Table 3 Torsion angles (°)

C10-N3-C12-C13	-179.8(3)	N1-N2-C9-C8	-173.1(3)
C7-N2-N1-C11	-142.6(3)	C7-N2-C9-C8	-37.6(5)
C9-N2-N1-C6	-157.2(2)	C7-N2-N1-C6	65.2(4)

parameters of 22 hydrogen atoms (out of 31) also being refined.

The title molecule (Fig. 2) contains short intramolecular N··H–O hydrogen bonds [O2–H2 1.07(6), H2··N3 1.55(7), N3··O2 2.54(6)Å, N3··H2–O2 150.8(5)°], which means that the compound is in phenol-imine form as in 4-{[(1*E*)-(2-hydroxyphenyl)methylidene]amino}-1,5-dimethyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-one.[5] [O–H 0.97(3), H··N 1.71(3), O··N 2.607(3)Å, O–H··N 153(2)°]. The ligand cavity plays an important role in the complexation and metal-ion selectivity. The intramolecular distances, O3··O5 [5.016(5)Å], O3··O6 [4.820(5)], O4··O6 [4.231(4)], O4··O7 [3.965(4)], O5··O7 [4.248(5)Å] may indicate the hole size of the macrocycle. The relative macrocyclic inner-hole size, estimated as being twice the mean distance of the donor atoms from their centroid, is approximately 1.56 Å, using the modified covalent radius of the O_{sp^3} (0.76 Å) atoms as in the literature method.[6]

The ϕ_{CN} torsion angle (C13–C12–N3–C10) is –179.8(3)°,

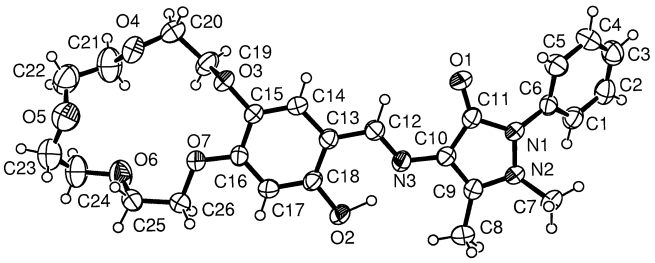

Fig. 2 Molecular structure of the title compound along with atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

which shows that the configuration about C12–N3 bond is *anti* (1*E*). The ϕ_{CN} (C8–C9–N2–C7) and ϕ_{NN} (C7–N2–N1–C6) torsion angles are –37.6(5) and 65.2(4)°, respectively showing that the conformations about C9–N2 and N1–N2 are *gauche*.

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