Crystal structure of 1-benzylthymine, $C_{12}H_{12}N_2O_2$

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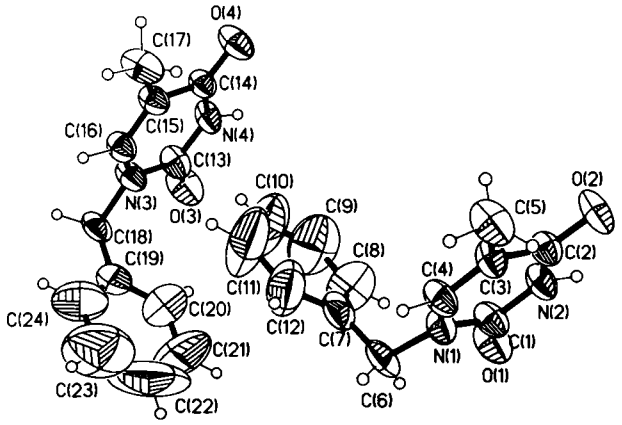

Abstract

$C_{12}H_{12}N_2O_2$, monoclinic, $P12_1/n1$ (No. 14), a = 13.868(7) Å, b = 12.143(6) Å, c = 14.476(7) Å, β = 109.960(8)°, V = 2291.3 Å^3, Z = 8, $R_{gt}(F)$ = 0.065, $wR_{ref}(F^2)$ = 0.200, T = 293 K.

Source of material

The title compound was synthesized through the benzylation of thymine with benzyl bromide by neutralization of potassium carbonate in National NN-S568WFS 900W Microwave Oven, and then the single crystals were grown by recrystallization from dichloromethane. The title compound is very unstable in air.

Experimental details

It is very difficult to obtain single crystals of good quality for X-ray diffraction experiments. This might explain the very low ratio $N(hkl)_{gt}/N(param)$ and the extremely high displacement parameters for C20 – C24. Furthermore, it was not possible to perform a low temperature experiment.

Discussion

A great deal of attention has been devoted to the role of nucleobases, since they are responsible for a wide range of biochemical processes, such as complementary base pairings in genetic information storage and transfer and some enzymatic reactions [1]. Consequently, much interest has been focused on thymine and its derivatives [2,3]. However, to our knowledge, 1-benzylthymine has not been reported so far. In order to better understand the benzylation of thymine, the synthesis and crystal structure of the title compound has been investigated. The title compound consists of two different rings (upper figure), the phenyl ring and the heterocyclic ring. The atoms of C7, C8, C9, C10, C11 and C12 have a good coplanarity and they form a conjugated plane with average deviation of 0.0134 Å. the bond lengths of C7—C8, C8—C9, C9—C10, C10—C11, C11—C12 and C12—C7 are 1.351(8) Å, 1.386(9) Å, 1.259(9) Å, 1.39(1) Å, 1.43(1) Å, 1.370(7) Å, respectively, which are between single bond and double bond and agree with that in benzene [4]. Moreover, the atoms of C1, C2, C3, C4, N1 and N2 have also a good coplanarity and they form an other conjugated plane with average deviation of 0.0101 Å. Furthermore, the distances of C6—C7, C6—N1, [1.501(7) Å, 1.482(5) Å], clearly indicate two single bonds. Therefore, there is not conjugated role between the phenyl ring and the heterocyclic ring. It is interesting that hydrogen-bonding interactions and π-π interactions play an important role in the crystal structure of the title compound. The oxygen atoms of carbonyl groups in one molecule form hydrogen bonds with hydrogen atoms, which are combined with nitrogen atoms of heterocyclic rings in other molecules. This can be seen from the relatively short intermolecular distances in this structure, such as N2···O4 (–x+1, –y+2, -z) of 2.872 Å and N4···O2 (–x+1, –y+2, –z) of 2.834 Å. In addition, there are π-π stacking between the adjacent phenyl rings along the [01 1] (face to face separation is 3.46 Å) [5]. Therefore, these hydrogen-bonds and π-π stacking interactions interweave an interesting three-dimensional network.

Table 1. Data collection and handling.

Crystal:	colorless fragment, size 0.29 × 0.52 × 0.60 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.87 cm^{-1}
Diffractometer, scan mode:	Siemens CCD, 600 frames, $\Delta\omega$ = 2°
$2\theta_{max}$:	54.56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11837, 4854
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1234
$N(param)_{refined}$:	349
Programs:	SHELX-97 [6], ORTEP-II [7]

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

Atom	Site	x	y	z	U_{iso}
H(9)	4e	0.71	0.9771	0.1863	0.172
H(10)	4e	0.782	0.8245	0.1664	0.204
H(11)	4e	0.729	0.6551	0.2057	0.217
H(12)	4e	0.6072	0.6534	0.2881	0.145
H(20)	4e	0.9899	0.9499	0.3568	0.226
H(21)	4e	0.9034	0.9136	0.4652	0.359
H(22)	4e	0.9037	0.7436	0.5304	0.336
H(23)	4e	0.9945	0.6142	0.4885	0.253
H(24)	4e	1.0812	0.6421	0.3849	0.154
H(1)	4e	0.241(3)	1.003(3)	0.134(3)	0.05(1)
H(2)	4e	0.382(2)	0.663(2)	0.237(2)	0.018(9)
H(3)	4e	0.215(4)	0.627(5)	0.023(4)	0.11(3)
H(4)	4e	0.149(2)	0.638(5)	0.093(4)	0.13(3)
H(5)	4e	0.250(3)	0.572(4)	0.117(3)	0.07(2)
H(6)	4e	0.515(3)	0.886(4)	0.369(3)	0.09(2)

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(7)	4e	0.497(3)	0.736(4)	0.362(3)	0.09(2)
H(8)	4e	0.593(4)	0.978(4)	0.268(4)	0.09(2)
H(13)	4e	0.899(3)	0.992(3)	0.039(3)	0.05(1)
H(14)	4e	1.004(2)	0.661(3)	0.169(2)	0.04(1)
H(15)	4e	0.845(3)	0.621(3)	-0.068(1)	0.10(2)
H(16)	4e	0.869(3)	0.560(2)	0.025(2)	0.10(2)
H(17)	4e	0.780(2)	0.632(4)	-0.006(4)	0.26(5)
H(18)	4e	1.141(3)	0.753(4)	0.283(3)	0.08(2)
H(19)	4e	1.149(3)	0.884(3)	0.306(3)	0.08(1)

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}
N(1)	4e	0.4019(3)	0.8267(3)	0.2581(2)	0.047(2)	0.041(2)	0.050(2)	0.007(2)	0.005(2)	0.002(2)
N(2)	4e	0.2723(3)	0.9332(3)	0.1546(3)	0.052(3)	0.028(2)	0.048(2)	0.005(2)	-0.002(2)	0.001(2)
N(3)	4e	1.0248(3)	0.8256(3)	0.1862(2)	0.060(3)	0.041(2)	0.041(2)	0.000(2)	-0.003(2)	0.001(2)
N(4)	4e	0.9249(3)	0.9302(3)	0.0558(3)	0.052(3)	0.025(2)	0.055(3)	0.002(2)	-0.004(2)	-0.002(2)
O(1)	4e	0.4030(2)	1.0137(2)	0.2735(2)	0.074(2)	0.040(2)	0.069(2)	-0.007(2)	-0.009(2)	-0.014(2)
O(2)	4e	0.1415(2)	0.8605(2)	0.0286(2)	0.050(2)	0.043(2)	0.059(2)	0.003(2)	-0.016(2)	0.003(2)
O(3)	4e	1.0392(3)	1.0126(2)	0.1873(2)	0.087(3)	0.038(2)	0.078(3)	-0.016(2)	-0.011(2)	-0.006(2)
O(4)	4e	0.8085(2)	0.8548(2)	-0.0788(2)	0.071(2)	0.047(2)	0.051(2)	-0.006(2)	-0.010(2)	0.003(2)
C(1)	4e	0.3629(4)	0.9293(4)	0.2332(3)	0.055(3)	0.039(3)	0.046(3)	-0.004(3)	-0.002(3)	-0.003(2)
C(2)	4e	0.2212(3)	0.8448(3)	0.1003(3)	0.042(3)	0.038(3)	0.044(3)	-0.001(2)	0.004(2)	-0.003(2)
C(3)	4e	0.2650(3)	0.7384(3)	0.1323(3)	0.044(3)	0.030(3)	0.054(3)	0.002(2)	0.004(2)	-0.002(2)
C(4)	4e	0.3528(4)	0.7346(4)	0.2096(3)	0.061(4)	0.033(3)	0.048(3)	0.008(3)	0.004(3)	0.011(2)
C(5)	4e	0.2120(5)	0.6373(4)	0.0789(5)	0.075(5)	0.035(3)	0.066(4)	-0.007(3)	-0.003(4)	-0.008(3)
C(6)	4e	0.5058(4)	0.8161(6)	0.3327(4)	0.044(3)	0.081(5)	0.044(3)	0.005(3)	-0.011(3)	0.010(3)
C(7)	4e	0.5875(4)	0.8170(5)	0.2864(3)	0.044(3)	0.072(4)	0.054(3)	0.007(3)	-0.010(3)	-0.005(3)
C(8)	4e	0.6183(6)	0.9103(7)	0.2538(6)	0.105(6)	0.086(6)	0.142(7)	-0.021(5)	0.061(5)	-0.018(5)
C(9)	4e	0.6909(7)	0.9110(8)	0.2075(7)	0.121(7)	0.133(9)	0.201(9)	-0.016(6)	0.088(7)	0.010(7)
C(10)	4e	0.7308(7)	0.822(1)	0.1943(8)	0.135(8)	0.18(1)	0.23(1)	0.044(9)	0.114(7)	0.01(1)
C(11)	4e	0.7016(7)	0.7202(9)	0.2198(8)	0.166(9)	0.151(9)	0.26(1)	0.076(8)	0.115(9)	0.006(9)
C(12)	4e	0.6278(5)	0.7196(6)	0.2685(5)	0.115(6)	0.109(6)	0.152(7)	0.048(5)	0.061(5)	0.018(5)
C(13)	4e	0.9989(3)	0.9280(4)	0.1473(3)	0.047(3)	0.044(3)	0.056(3)	-0.008(3)	0.002(3)	0.002(3)
C(14)	4e	0.8739(3)	0.8407(3)	0.0028(3)	0.042(3)	0.038(3)	0.039(3)	0.000(2)	0.002(2)	-0.001(2)
C(15)	4e	0.9043(3)	0.7358(3)	0.0485(3)	0.061(3)	0.032(3)	0.041(3)	0.000(2)	0.007(3)	0.003(2)
C(16)	4e	0.9757(3)	0.7340(4)	0.1380(3)	0.060(3)	0.032(3)	0.045(3)	0.003(2)	0.007(3)	0.003(2)
C(17)	4e	0.8514(5)	0.6334(4)	-0.0007(4)	0.112(5)	0.024(3)	0.051(4)	-0.011(3)	0.002(3)	-0.002(2)
C(18)	4e	1.0979(4)	0.8163(5)	0.2874(3)	0.046(3)	0.066(4)	0.039(3)	0.002(3)	-0.008(3)	0.001(3)
C(19)	4e	1.0456(4)	0.7998(6)	0.3598(4)	0.072(4)	0.106(5)	0.046(3)	0.017(4)	0.008(3)	-0.001(4)
C(20)	4e	0.9922(7)	0.8798(9)	0.3834(6)	0.202(9)	0.26(1)	0.119(7)	0.116(9)	0.077(7)	0.012(7)
C(21)	4e	0.940(1)	0.857(2)	0.449(1)	0.25(1)	0.53(3)	0.19(2)	0.17(2)	0.17(1)	0.04(1)
C(22)	4e	0.939(2)	0.758(2)	0.488(1)	0.23(2)	0.55(4)	0.089(9)	-0.00(2)	0.092(9)	0.05(1)
C(23)	4e	0.9925(9)	0.684(1)	0.4620(9)	0.21(1)	0.28(2)	0.17(1)	-0.03(1)	0.109(9)	0.04(1)
C(24)	4e	1.0453(6)	0.7001(7)	0.3999(5)	0.158(7)	0.151(8)	0.099(6)	-0.019(6)	0.073(5)	0.018(5)

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