JOURNAL OF CHEMICAL RESEARCH 2005 DECEMBER, 775–777 **RESEARCH PAPER** 775

The crystal structure and unclassical pyran conformation of 2-amino-7-methyl-4-(3-nitrophenyl)-5-oxo-4*H*,5*H*-pyran [4,3-*b*]pyran-3-carbonitrile

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The X-ray crystal structure of 2-amino-7-methyl-4-(3-nitrophenyl)-5-oxo-4*H*,5*H*-pyrano[4,3-*b*]pyrano-3- carbonitrile **1**, is determined. It is interesting that all the atoms of the pyran ring are coplanar, which is different from that of other similar compounds. The structure is stabilised by intermolecular hydrogen bonds. The structure of the product is also characterised by IR, NMR spectra and elemental analysis.

Keywords: crystal structure, pyran conformation, pyrano[4,3-*b*]pyran

The synthesis of pyran and their derivatives is of high interest in organic chemistry. In particular, 2-aminopyrans constitute the basic structure of natural products possessing biological and pharmacological activities,[1,2] such as antijuvenile hormones,[3] antiallergenics[4] and anticancer agents.[5] These promoted us to synthesise these compounds using a new method, the utility of fluoride salts as a potential base in a variety of synthetic reactions has been recognised in recent years. Especially alumina coated with potassium fluoride (KF-alumina) has been a versatile solid-supported reagent developed by Ando *et al.* for alkylation.[6] Over the years, the reagent has found application in a large number of organic reactions.[7] We now present the crystal structure of the 2-amino-7-methyl-4-(3-nitrophenyl)-5-oxo-4*H*,5*H*-pyrano[4,3-*b*]pyran-3-carbonitrile **1**.

Experimental

All chemicals were of analytical reagents grade and were used directly without further purification.

General procedure for synthesis of 2-amino-7-methyl-4-(3-nitrophenyl)-5-oxo-4H,5H-pyrano[4,3-b]pyran-3–carbonitrile: A dry 50 ml flask was charged with 3-nitrobenzaldehyde (2 mmol), malononitrile, 4-hydroxyl-6-methyl-2-pyrone (2 mmol), KF-alumina (250 mg) and ethyl alcohol (10 ml). The mixture was stirred at refluxing temperature for 5 h. The mixture was allowed to room temperature and poured into 200 ml water; the solid was filtered off and washed with water. The crude product was purified by recrystallisation from 95% EtOH to give pale yellow crystals in 82% yield, m.p. 238–240 °C, ^{1}H NMR (DMSO-d_6) δ: 2.24 (s, 3H, CH_3), 4.57 (s, 1H, CH), 6.32 (s, 1H, =CH), 7.35(s, 2H, NH_2), 7.64 (t, *J* = 8.0 Hz, 1H, ArH), 7.73(tt, *J* = 8.0 Hz, *J'* = 1.2 Hz, 1H, ArH), 8.05 (t, *J* = 2.0 Hz, 1H, ArH), 8.13(dd, dd, *J* = 8.0 Hz, *J'* = 2.0 Hz, *J''* = 1.2 Hz, 1H, ArH); IR (KBr, cm^{-1}): 3400, 3327, 3109, 2199, 1716, 1615, 1526, 1448, 1383, 1263, 1200, 1143, 1024, 977, 817, 759, 733 cm^{-1}. Anal.calcd for $C_{16}H_{11}N_3O_5$: C 59.08, H 3.41, N 12.92; found C 58.97, H 3.56, N 12.87.

X-ray analysis

A summary of the crystallographic data is given in Table 1. A single crystal **1** with dimensions of 0.28 mm × 0.14 mm × 0.14 mm was mounted on a Siemens P4 diffractmeter. The data were collected at the temperature of 289(2) K with graphite monochromated Mo*K*α (λ = 0.71073 Å) radiation, using the ω scan technique. 2810 independent reflections were collected, of which 1825 reflections with $I > 2\sigma(I)$ were observed. The structure was solved by direct methods using the SHELXTL[8] program and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, the hydrogen atoms were positioned geometrically and refined as riding [C–H = 0.93–0.98 Å, and $U_{iso}(H) = 1.2U_{eq}(C)$], except for H1A and H1B on the atom N. A full-matrix least-squares refinement gave final $R = 0.0423$ and $\omega R = 0.0961$ with $\omega = 1/[\sigma^2(F_o^2) + (0.0510P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 1 Crystallographic data for **1**

Empirical formula	$C_{16} H_{11} N_3 O_5$
Color/shape	Pale yellow/Block
Formula weight	325.28
Temperature	289(2) K
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	*a* = 5.709(1) Å, α = 90°. *b* = 14.616(2) Å, β = 94.219(3)° *c* = 18.228(3) Å, γ = 90°
Volume	1516.8(8) Å^3
Z	4
Density (calculated), Mg/m^3	1.424
Absorption coefficient, mm^{-1}	0.109
Diffractometer/scan	Siemens P4/ω
F(000)	672
Crystal size	0.28 × 0.14 × 0.14 mm
Theta range for data collection	1.79 to 25.49°
Limiting indices	$-6 \le h \le 6$, $-13 \le k \le 17$, $-20 \le l \le 22$
Reflections collected	8123
Independent reflections	2810 [R(int) = 0.0339]
Data / restraints / parameters	2810 / 2 / 227
Goodness-of-fit on F^2	0.952
Final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0423, wR2 = 0.0961
R indices (all data)	R1 = 0.0686, wR2 = 0.1049
Extinction coefficient	0.0006(10)
Largest diff. peak and hole	0.153 and -0.181 e. Å^{-3}

Analysis

Melting point was determined in open capillaries and is uncorrected. IR spectrum was recorded on a Tensor 27 spectrometer in KBr. ^{1}H NMR spectrum was obtained for solution in DMSO-d_6 with Me_4Si as internal standard using a Bruker-400 spectrometer. Elemental analysis was carried out using Carlo Erba 1110 analyser. X-ray diffraction was measured on a Siemens P4 diffractometer.

Results and discussion

The selected bond lengths and bond angles are given in Table 2. The structure of **1** and packing arrangement in a unit cell of **1** are shown in Figs. 1 and 2. The X-ray crystal structure determination indicates that the atoms C(1), C(2), C(3), C(4), C(5) and O(1) form a six-membered ring, with the interatomic distances 1.356(2) Å for C(1)–C(2) and 1.350(2) Å for C(4)–C(5), which are near to that of the typical C=C double bond (1.34 Å), The bond angles of C(1)–C(2)–O(1), C(1)–C(2)–C(3), C(3)–C(4)–C(5) and C(4)–C(5)–O(1) are 122.48(15), 123.78(15), 123.91(16) and 122.72(15)° respectively, which also illustrate that C(1), C(2), C(4) and C(5) all adopt *sp*^{2} hybridisation and form C–C double bonds. Obviously, they are longer than that of the typical C=C double bond because of the existence of the conjugate system and there are corresponding shortening of the C–O single bond (1.3618

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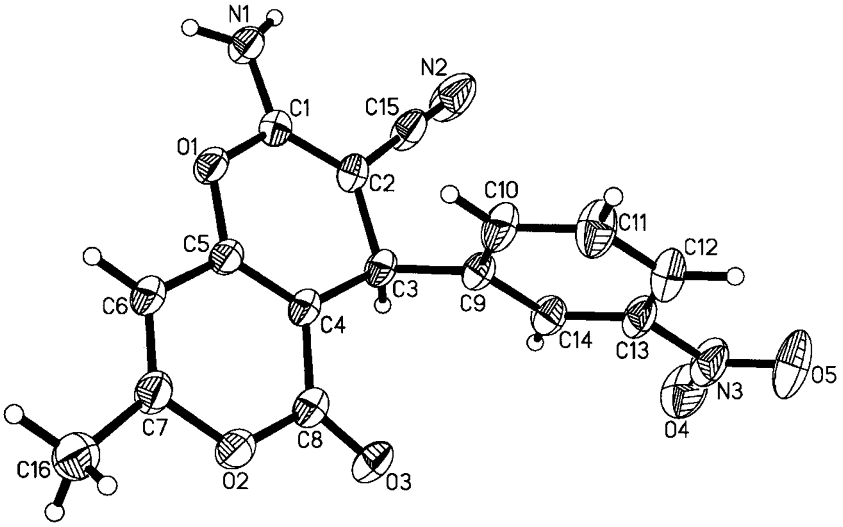

Fig. 1 The molecular structure of **1** showing 50% probability displacement ellipsoids.

Table 2 Selected bond lengths (Å) and selected bond angles (°) for **1**

Bond distances for Compound **1**			
O(1)–C(1)	1.3618(19)	C(1)–C(2)	1.356(2)
O(1)–C(5)	1.3720(19)	C(2)–C(15)	1.406(3)
O(2)–C(7)	1.3763(19)	C(2)–C(3)	1.519(2)
O(2)–C(8)	1.388(2)	C(3)–C(4)	1.505(2)
O(3)–C(8)	1.2104(18)	C(3)–C(9)	1.521(2)
O(4)–N(3)	1.215(2)	C(4)–C(5)	1.350(2)
O(5)–N(3)	1.229(2)	C(4)–C(8)	1.433(2)
N(1)–C(1)	1.340(2)	C(5)–C(6)	1.420(2)
N(2)–C(15)	1.143(2)	C(6)–C(7)	1.328(2)
N(3)–C(13)	1.478(2)	C(7)–C(16)	1.471(3)
Bond angles for compound **1**			
C(1)–O(1)–C(5)	118.77(12)	C(8)–C(4)–C(3)	118.20(14)
C(7)–O(2)–C(8)	122.37(14)	C(4)–C(5)–O(1)	122.72(15)
O(4)–N(3)–O(5)	123.65(19)	C(4)–C(5)–C(6)	123.02(16)
O(4)–N(3)–C(13)	118.94(19)	O(1)–C(5)–C(6)	114.24(14)
O(5)–N(3)–C(13)	117.4(2)	C(7)–C(6)–C(5)	118.49(16)
N(1)–C(1)–C(2)	127.80(17)	C(6)–C(7)–O(2)	120.61(16)
N(1)–C(1)–O(1)	109.71(14)	C(6)–C(7)–C(16)	128.13(17)
C(2)–C(1)–O(1)	122.48(15)	O(2)–C(7)–C(16)	111.27(16)
C(1)–C(2)–C(15)	118.16(16)	O(3)–C(8)–O(2)	116.08(17)
C(1)–C(2)–C(3)	123.78(15)	O(3)–C(8)–C(4)	126.38(17)
C(15)–C(2)–C(3)	118.06(14)	O(2)–C(8)–C(4)	117.55(14)
C(4)–C(3)–C(2)	108.09(13)	C(10)–C(9)–C(3)	121.02(14)
C(4)–C(3)–C(9)	112.47(14)	C(14)–C(9)–C(3)	120.21(16)
C(2)–C(3)–C(9)	112.44(15)	C(12)–C(13)–N(3)	119.07(18)
C(5)–C(4)–C(8)	117.89(16)	C(14)–C(13)–N(3)	118.33(19)
C(5)–C(4)–C(3)	123.91(16)	N(2)–C(15)–C(2)	179.0(2)

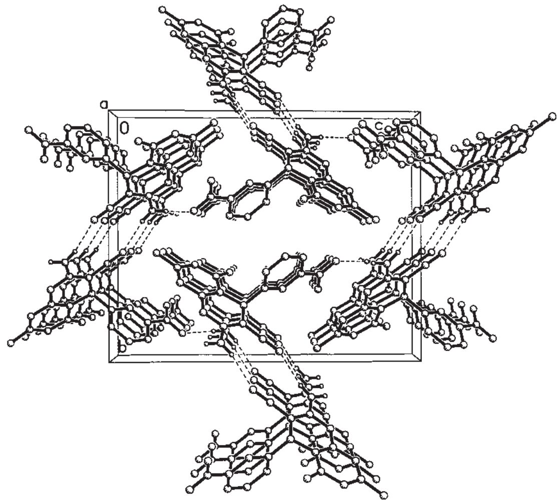

Fig. 2 The packing arrangement in a unit cell of **1** along *a*.

(19) Å for O(1)–C(1) and 1.3720(19) Å for O(1)–C(5). There is a little difference from the other similar pyran derivatives (Figure 3). The comparison of bond distances and bond angles in pyran rings is listed in Table 3. It is interesting that all the atoms of the pyran ring are coplanar, with atoms C(1), C(2), C(3), C(4), C(5) and O(1) deviating from the mean plane by –0.0171, –0.0094, 0.0304, –0.0298, 0.0041 and 0.0218 Å,

Table 3 Comparison of bond distances (Å) and angles (°) in the pyran rings

Compound	a	b	c	d	e	f	Ref.
1	1.3618(19)	1.356(2)	1.519(2)	1.505(2)	1.350(2)	1.3720(19)	This work
2	1.361(4)	1.337(5)	1.513(5)	1.505(4)	1.368(5)	1.384(4)	9
3	1.350(2)	1.327(2)	1.513(2)	1.512(2)	1.352(2)	1.401(2)	
4	1.370(2)	1.348(2)	1.496(3)	1.528(3)	1.355(3)	1.379(2)	10
5	1.372(3)	1.332(3)	1.517(3)	1.505(3)	1.357(3)	1.375(3)	11
6	1.3560(17)	1.324(2)	1.514(2)	1.501(2)	1.350(2)	1.3985(17)	12
Compound	ab	bc	cd	de	ef	fa	Ref.
1	122.48(15)	123.78(15)	108.09(13)	123.91(16)	122.72(15)	118.77(12)	This work
2	122.5 (3)	123.8(3)	109.7(3)	121.7(3)	122.9(3)	118.9(3)	9
3	122.53(17)	122.15(16)	109.47(14)	122.43(16)	122.20(16)	118.6(3)	
4	128.10(17)	122.27(17)	106.70(15)	125.53(17)	123.14(17)	113.91(14)	10
5	122.52(19)	121.4(2)	109.71(18)	122.5(2)	122.8(2)	118.69(17)	11
6	122.40(14)	123.15(13)	109.26(12)	122.54(14)	123.56(14)	118.04(12)	12

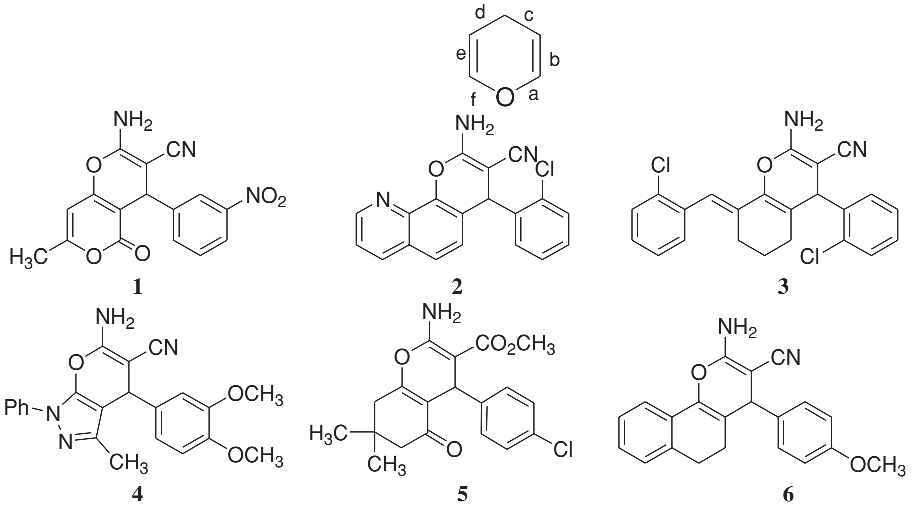

Fig. 3 The chemical structure diagrams of the compounds **1**, **2**, **3**, **4**, **5** and **6**.

Table 4 Comparison of conformation in the pyran rings

Compound	1	2	3	4	5	6
Conformation	Coplanar	Half-chair	Boat	Half-chair	Boat	Half-chair
Ref.	This work	9		10	11	12

Table 5 Hydrogen bonds geometry for **1**

(*D*–H · · · *A*)	*D*–H (Å)	H · · · *A* (Å)	*D* · · · *A*(Å)	*D*–H · · · *A*(°)	Symmetry codes
N(1)–H(1B) · · · N(2)	0.870(9)	2.204(10)	3.062(3)	169.2(17)	*−x, −y, 1−z*
N(1)–H(1A) · · · O(5)	0.861(9)	2.248(10)	3.103(2)	172.0(18)	*x-1, −y+1/2, z+1/2*

respectively, which is different from other similar pyran rings. A comparison of the conformation in pyran rings is shown in Table 4. The plane is nearly parallel to another pyran ring, forming a dihedral angle of 4.07°, and nearly perpendicular to phenyl ring [C(9)–C(14)], forming a dihedral angle of 86.87°.

Intermolecular N(1)–H(1B)···N(2) and N(1)–H(1A)···O(5) hydrogen bonds (Table 5) are formed between the amine and cyano group or nitro group (Figure 2).

We are grateful to the Foundation (04KJB150139) of the Education Committee of Jiangsu Province for financial support.

Received 15 June 2005; accepted 8 August 2005
Paper 05/3311

References

1 Fisons Ltd., *Jpn Kokai Tokkyo Koho JP* 5804722, 1983; *Chem. Abstr.*, **98**(1983), 137619b.
2 J.B. Montandon, F.J. Zijlstra, J.H.P. Wilson, *Int. J. Tissue React.*, 1989, **11**, 107.
3 G.T. Brooks, A.P. Ottridge, R.C. Jennings, D.W. Mace, B.A. Alexander, *Pestic. Sci.* 1985, **16**, 571; *Chem. Abstr.*, **106**(1986), 202243h.
4 E.C. Witte, P. Neubert, A. Roesch, *DE* 3427985, 1986; *Chem. Abstr.*, **104**(1986), 224915f.
5 T. Hyana, H. Saimoto, *Jpn Kokai Tokkyo Koho JP* 62181276, 1987; *Chem. Abstr.*, **108**(1988), 37645p.
6 T. Ando, J. Yamawaki, T. Kawate, S. Sumi, T. Hanafusa, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2504.
7 J.H. Clark, *Chem. Rev.*, 1980, **80**, 429.
8 G.M. Sheldrick, *SHELXTL*, *Structure Determination Software Program*. Version 5.10; Bruker Analytical X-ray Systems. Inc.: Madison, WI, 1997.
9 X.S. Wang, D.Q. Shi, S.J. Tu and C.S. Yao, *J. Chem. Cryst.*, 2004, **34**, 159.
10 X.S. Wang, D.Q. Shi, L.C. Rong, C.S. Yao and G.Y. Dai, *Chin. J. Struct. Chem.*, 2003, **22**, 331.
11 X.S. Wang, D.Q. Shi, S.J. Tu and C.S. Yao, *Chinese J. Struct. Chem.*, 2002, **21**, 597.
12 X.S. Wang, Y.L. Li, D.Q. Shi, S.J. Tu, *Acta Cryst.,* 2003, E**59**, o1210.