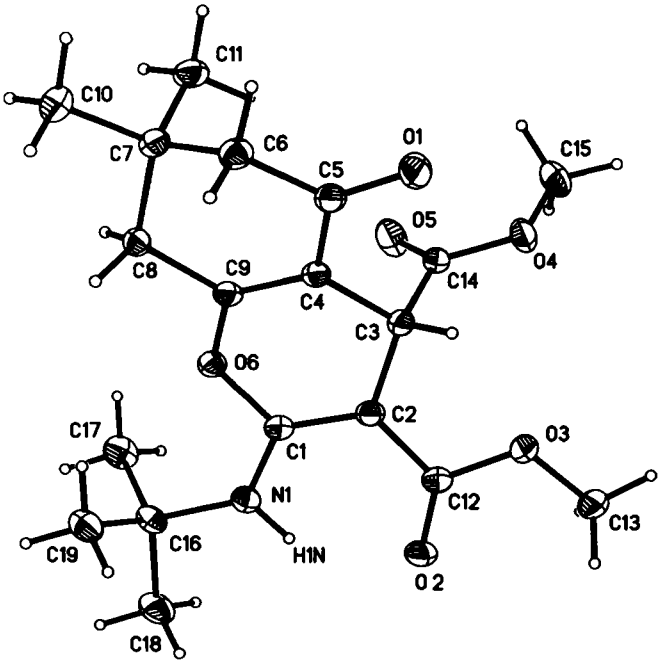
Crystal structure of dimethyl 2-(*tert*-butylamino)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3,4-dicarboxylate, $C_{19}H_{27}NO_6$

A. Zonouzi*[I], H. Rahmani[II], H. Samareh Afsari[I] and M. Nezamabadi[I]

[I] University of Tehran, Department of Chemistry, P.O. Box 14155-6455, Tehran, Iran
[II] Iranian Research Organization for Science and Technology (IROST), Institute of Chemical Technologies, P.O. Box 15815-3538, Tehran, Iran

Received August 23, 2005, accepted and available on-line December 5, 2005; CCDC no. 1267/1632



Abstract

$C_{19}H_{27}NO_6$, monoclinic, $P12_1/c1$ (no. 14), a = 13.457(3) Å, b = 8.978(2) Å, c = 15.790(4) Å, β = 90.32(2)°, V = 1907.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.043, $wR_{ref}(F^2)$ = 0.112, T = 193 K.

Source of material

The title compound was synthesized by the reaction of *tert*-butyl isocyanide and dimethyl acetylene dicarboxylate with 1,1-dimethyl-3,5-diketocyclohexane in cold dichloromethane, then purified by column chromatography on silica-gel using a mixture of ethyl acetate and hexane (*v*/*v* 30:70) as eluent. Recrystallization from acetone gave crystals suitable for X-ray structure analysis.

Discussion

Some of substituted 4*H*-chromenes have been shown to exhibit biological activity as anti-cancer, antihypertensive and coronary dilating agents [1,2]. There are some reports on the crystal structures of 2-amino-4*H*-chromenes [3-7]. Recently we reported the crystal structure of a 2-amino-4*H*-chromene derivative [8].

The crystal structure determination of the title compound was performed in view of its good stability. The molecule is stabilized by one intramolecular hydrogen bond, N1–H1N···O2 with d(N1—H1A) = 0.90 Å, d(H1N···O2) = 1.985 Å, d(N1···O2) = 2.710 Å, ∠N1–H1A···O2 = 136.2°. The conformation of the pyran ring in the title compound is a distorted boat.

Table 1. Data collection and handling.

Crystal:	colorless plate, size 0.25 × 0.40 × 0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.94 cm^{-1}
Diffractometer, scan mode:	Rebuild Syntex $P2_1$/Siemens P3, $\theta/2\theta$
$2\theta_{max}$:	54.12°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4410, 4142
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3240
$N(param)_{refined}$:	235
Program:	SHELXTL [9]

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

Atom	Site	x	y	z	U_{iso}
H(1N)	4*e*	0.8923	0.1089	0.6980	0.039
H(3A)	4*e*	0.6602	−0.2196	0.6066	0.032
H(6A)	4*e*	0.4201	−0.3395	0.8102	0.039
H(6B)	4*e*	0.4375	−0.1673	0.8030	0.039
H(8A)	4*e*	0.5822	−0.0492	0.8978	0.033
H(8B)	4*e*	0.6594	−0.1647	0.9331	0.033
H(10A)	4*e*	0.4965	−0.2297	1.0180	0.057
H(10B)	4*e*	0.4074	−0.3004	0.9678	0.057
H(10C)	4*e*	0.4320	−0.1308	0.9571	0.057
H(11A)	4*e*	0.6116	−0.4219	0.9577	0.056
H(11B)	4*e*	0.6183	−0.4426	0.8593	0.056
H(11C)	4*e*	0.5226	−0.4930	0.9076	0.056
H(13A)	4*e*	0.8488	−0.2092	0.4047	0.062
H(13B)	4*e*	0.9367	−0.1436	0.4585	0.062
H(13C)	4*e*	0.8547	−0.0374	0.4217	0.062
H(15A)	4*e*	0.7669	−0.6566	0.5445	0.066
H(15B)	4*e*	0.7631	−0.6588	0.6437	0.066
H(15C)	4*e*	0.8552	−0.5900	0.5976	0.066
H(17A)	4*e*	0.8799	−0.0016	0.9086	0.069
H(17B)	4*e*	0.9468	0.1308	0.9395	0.069
H(17C)	4*e*	0.9852	0.0227	0.8689	0.069
H(18A)	4*e*	1.0168	0.2389	0.7759	0.067
H(18B)	4*e*	0.9760	0.3495	0.8442	0.067
H(18C)	4*e*	0.9308	0.3494	0.7525	0.067
H(19A)	4*e*	0.7409	0.1775	0.8733	0.062
H(19B)	4*e*	0.7614	0.3120	0.8126	0.062
H(19C)	4*e*	0.8064	0.3114	0.9043	0.062

* Correspondence author (e-mail: zonouzi@khayam.ut.ac.ir)

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)	4*e*	0.8592(1)	0.0863(1)	0.74588(8)	0.0344(7)	0.0292(6)	0.0339(7)	−0.0088(5)	0.0025(5)	−0.0023(5)
O(1)	4*e*	0.51002(9)	−0.3615(2)	0.67228(7)	0.0496(7)	0.0585(8)	0.0357(6)	−0.0273(6)	0.0027(5)	−0.0105(6)
O(2)	4*e*	0.88441(9)	0.0494(1)	0.57705(7)	0.0433(6)	0.0291(6)	0.0416(6)	−0.0091(5)	0.0096(5)	0.0018(5)
O(3)	4*e*	0.80986(8)	−0.1532(1)	0.52109(6)	0.0426(6)	0.0359(6)	0.0288(5)	−0.0096(5)	0.0076(4)	−0.0007(5)
O(4)	4*e*	0.73635(9)	−0.4593(1)	0.59458(7)	0.0465(7)	0.0335(6)	0.0339(6)	−0.0003(5)	−0.0030(5)	−0.0103(5)
O(5)	4*e*	0.8080(1)	−0.4115(1)	0.71923(8)	0.0637(8)	0.0360(6)	0.0430(7)	0.0103(6)	−0.0179(6)	−0.0064(5)
O(6)	4*e*	0.75001(8)	−0.0652(1)	0.80922(6)	0.0323(5)	0.0295(5)	0.0263(5)	−0.0088(4)	−0.0026(4)	0.0004(4)
C(1)	4*e*	0.7947(1)	−0.0245(2)	0.73491(9)	0.0269(7)	0.0238(7)	0.0304(7)	−0.0009(6)	−0.0007(6)	0.0033(5)
C(2)	4*e*	0.7729(1)	−0.0957(2)	0.65993(9)	0.0289(7)	0.0251(7)	0.0285(7)	−0.0036(6)	−0.0002(6)	0.0027(5)
C(3)	4*e*	0.7006(1)	−0.2246(2)	0.65835(9)	0.0304(7)	0.0271(7)	0.0225(6)	−0.0046(6)	−0.0013(5)	0.0011(5)
C(4)	4*e*	0.6338(1)	−0.2148(2)	0.73456(9)	0.0287(7)	0.0234(7)	0.0252(7)	−0.0024(6)	−0.0003(5)	0.0026(5)
C(5)	4*e*	0.5364(1)	−0.2875(2)	0.73318(9)	0.0335(8)	0.0294(7)	0.0274(7)	−0.0062(6)	−0.0032(6)	0.0029(6)
C(6)	4*e*	0.4707(1)	−0.2627(2)	0.80881(9)	0.0290(7)	0.0360(8)	0.0319(8)	−0.0059(6)	−0.0010(6)	0.0025(6)
C(7)	4*e*	0.5294(1)	−0.2652(2)	0.89256(9)	0.0302(7)	0.0289(7)	0.0266(7)	−0.0006(6)	0.0023(5)	0.0034(6)
C(8)	4*e*	0.6114(1)	−0.1466(2)	0.88823(8)	0.0318(7)	0.0255(7)	0.0243(7)	0.0007(6)	−0.0013(5)	0.0001(5)
C(9)	4*e*	0.6634(1)	−0.1462(2)	0.80530(9)	0.0276(7)	0.0212(6)	0.0277(7)	−0.0018(5)	−0.0022(5)	0.0031(5)
C(10)	4*e*	0.4599(1)	−0.2281(2)	0.9656(1)	0.0361(8)	0.0460(9)	0.0327(8)	0.0008(7)	0.0057(6)	0.0014(7)
C(11)	4*e*	0.5747(1)	−0.4202(2)	0.9055(1)	0.0446(9)	0.0288(8)	0.0390(8)	−0.0002(7)	0.0039(7)	0.0080(7)
C(12)	4*e*	0.8273(1)	−0.0559(2)	0.58483(9)	0.0296(7)	0.0258(7)	0.0321(7)	0.0005(6)	−0.0003(6)	0.0041(6)
C(13)	4*e*	0.8673(1)	−0.1343(2)	0.4452(1)	0.052(1)	0.0372(9)	0.0347(8)	−0.0049(8)	0.0152(7)	0.0006(7)
C(14)	4*e*	0.7548(1)	−0.3741(2)	0.66190(9)	0.0326(7)	0.0279(7)	0.0272(7)	−0.0072(6)	0.0031(6)	−0.0014(6)
C(15)	4*e*	0.7844(1)	−0.6033(2)	0.5951(1)	0.042(1)	0.0370(9)	0.053(1)	0.0020(7)	0.0024(8)	−0.0167(8)
C(16)	4*e*	0.8819(1)	0.1721(2)	0.8237(1)	0.0319(8)	0.0262(7)	0.0388(8)	−0.0043(6)	−0.0033(6)	−0.0048(6)
C(17)	4*e*	0.9277(1)	0.0717(2)	0.8914(1)	0.045(1)	0.043(1)	0.048(1)	−0.0021(8)	−0.0146(8)	−0.0004(8)
C(18)	4*e*	0.9585(1)	0.2883(2)	0.7965(1)	0.0396(9)	0.0365(9)	0.058(1)	−0.0134(7)	−0.0002(8)	−0.0076(8)
C(19)	4*e*	0.7890(1)	0.2506(2)	0.8565(1)	0.0415(9)	0.0313(8)	0.051(1)	0.0002(7)	0.0034(7)	−0.0059(7)

Acknowledgment. The support of this study by the Research Council at the University of Tehran through grant no. 514/3/634 is gratefully acknowledged.

References

1. Al-Haiz, M. A.; Mostafa, M. S.; El-Kady, M. Y.: Synthesis and Biological Evaluation of some new coumarin derivatives. Molecules **8** (2003) 275-286.
2. Yu, N.; Aramini, J. M.; Germann, M. W.; Huang, Z.: Reactions of salicylaldehydes with alkyl cyanoacetates on the surface of solid catalysts: syntheses of 4*H*-chromene derivatives. Tetrahedron Lett. **41** (2000) 6993-6996.
3. Guo, C.; Gu, P.; Zhang, L. D.; Li, Y.: Ethyl 2-amino-4-(3-fluorophenyl)-4*H*-benzo[*h*]chromene-3-carboxylate. Acta. Crystallogr. E**61** (2005) o2125-o2127.
4. Yu, C. X.; Shi, D. Q.; Wang, X. S.; Zhuang, Q. Y.: 3-Amino-1-(3,4-methylene dioxyphenyl)-9-methoxy-5,6-dihydro-1*H*-benzo[*f*]chromene-2-carbonitrile. Acta. Crystallogr. E**61** (2005) o84-o86.
5. Shi, D.-Q.; Wu, N.; Zhuang, Q.-Y.; Zhang, Y.: Methyl 2-amino-4-(4-chlorophenyl)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carboxylate *N*,*N*-dimethylformamide solvate. Acta Crystallogr. E**61** (2005) o87-o89.
6. Shi, D.-Q.; Wu, N.; Zhuang, Q.; Zhang, Y.: 2-Amino-4-(3,4-dichlorophenyl)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carbonitrile *N*,*N*-dimethylformamide solvate. Acta Crystallogr. E**60** (2004) o2339-o2341.
7. Malecka, M.; Massa, W.; Budzisz, E.: (+/−)-(4-oxo-4*H*-chromene 2-yl)-(phenyl)methyl acetate. Acta Crystallogr. C**60** (2004) o762-o764.
8. Zonouzi, A.; Rahmani, H.; Samareh Afsari, H.; Nezamabadi, M.: Crystal structure of dimethyl 2-(*tert*-butylamino)-5,7,7-trimethyl-5,6,7,8-tetrahydro-4*H*-chromene-3,4-dicarboxylate, $C_{20}H_{30}NO_5$. Z. Kristallogr. NCS **220** (2005) 267-268.
9. Sheldrick, G. M.: SHELXTL. Structure Determination Software Suite. Version 5.10. Bruker AXS, Madison, Wisconsin, USA 1998.