# Crystal structure of bis(*tert*-butyl) 2-(*tert*-butylamino)-5-acetyl-6-methyl-4*H*-pyran-3,4-dicarboxylate, $C_{22}H_{35}NO_6$

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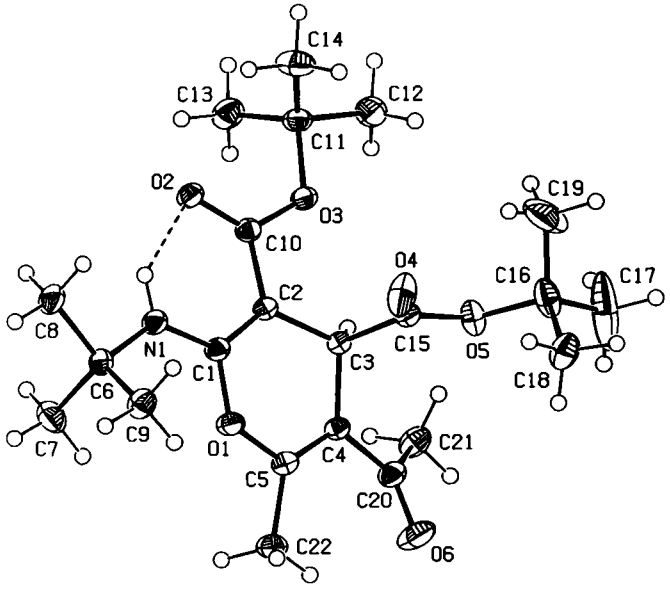
Received May 10, 2005, accepted and available on-line July 11, 2005; CCDC no. 1267/1547




**Abstract**

$C_{22}H_{35}NO_6$, monoclinic, *C*12/*c*1 (no. 15), $a = 21.727(4)$ Å, $b = 10.954(2)$ Å, $c = 22.073(4)$ Å, $\beta = 116.609(4)°$, $V = 4697.0$ Å$^3$, $Z = 8$, $R_{gt}(F) = 0.046$, $wR_{ref}(F^2) = 0.128$, $T = 120$ K.

**Source of material**

The title compound was synthesized by the reaction of *tert*-butyl isocyanide and bis(*tert*-butyl)-acetylene dicarboxylate with 1,3-pentanedione in the presence of triethylamine as a base in hot 1,4-xylene, then purified by column chromatography on silica-gel using a mixture of ethylacetate and hexane (*v*/*v* 30:70) as eluent. Recrystallization from acetone gave crystals suitable for X-ray structure analysis.

**Discussion**

Some of 2-amino-4*H*-pyran derivatives have fairly low stability, for example in the presence of little amounts of $H^+$ ions or NaOH the ring transformation process take place and furan and pyridine derivatives are produced [1,2]. Some substituted 2-amino-4*H*-pyrans contain electron withdrawing groups, and fused heterocyclic rings are stable and have been shown to exhibit biological activities [3]. There are some new reports on the crystal structures of 2-amino-4*H*-pyrans with electron withdrawing groups [4-8]. Recently we have reported the crystal structure of an 2-amino-4*H*-pyran derivative [9].

The crystal structure analysis of the title compound was performed in view of its good stability. The molecule is stabilized by one intramolecular N–H···O bond. Details of N1–H1A···O2 are: $d$(N1—H1A) = 0.86 Å; $d$(H1A···O2) = 2.01 Å, $d$(N1···O2) = 2.675 Å, ∠N1–H1A···O2 = 134°. The three-dimensional network is formed by Van der Waals forces as well as intermolecular hydrogen bonding.

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | colorless plate, size 0.60 × 0.45 × 0.35 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 0.83 cm$^{-1}$ |
| Diffractometer, scan mode: | Bruker SMART 1000 CCD, $\varphi/\omega$ |
| $2\theta_{max}$: | 56° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 21560, 5204 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 4181 |
| $N(param)_{refined}$: | 262 |
| Programs: | SHELXS-97 [10], SHELXL-97 [11] |

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

| Atom | Site | *x* | *y* | *z* | $U_{iso}$ |
|---|---|---|---|---|---|
| H(1A) | 8*f* | 0.1067 | 0.4277 | 0.2880 | 0.033 |
| H(3A) | 8*f* | 0.2682 | 0.2564 | 0.2376 | 0.027 |
| H(7A) | 8*f* | 0.1189 | 0.3184 | 0.4143 | 0.060 |
| H(7B) | 8*f* | 0.1420 | 0.4169 | 0.4719 | 0.060 |
| H(7C) | 8*f* | 0.1966 | 0.3558 | 0.4534 | 0.060 |
| H(8A) | 8*f* | 0.0332 | 0.4635 | 0.3347 | 0.052 |
| H(8B) | 8*f* | 0.0565 | 0.5921 | 0.3215 | 0.052 |
| H(8C) | 8*f* | 0.0563 | 0.5642 | 0.3911 | 0.052 |
| H(9A) | 8*f* | 0.1786 | 0.6546 | 0.3819 | 0.050 |
| H(9B) | 8*f* | 0.2339 | 0.5653 | 0.4330 | 0.050 |
| H(9C) | 8*f* | 0.1793 | 0.6257 | 0.4518 | 0.050 |
| H(12A) | 8*f* | 0.1627 | 0.1537 | 0.0677 | 0.062 |
| H(12B) | 8*f* | 0.1649 | 0.2887 | 0.0452 | 0.062 |
| H(12C) | 8*f* | 0.1032 | 0.2036 | 0.0003 | 0.062 |
| H(13A) | 8*f* | 0.0304 | 0.1873 | 0.1169 | 0.059 |
| H(13B) | 8*f* | 0.0857 | 0.0951 | 0.1170 | 0.059 |
| H(13C) | 8*f* | 0.0229 | 0.1316 | 0.0485 | 0.059 |
| H(14A) | 8*f* | 0.0281 | 0.4012 | 0.0766 | 0.067 |
| H(14B) | 8*f* | 0.0198 | 0.3564 | 0.0058 | 0.067 |
| H(14C) | 8*f* | 0.0812 | 0.4422 | 0.0505 | 0.067 |
| H(17A) | 8*f* | 0.4388 | 0.3756 | 0.1881 | 0.164 |
| H(17B) | 8*f* | 0.4207 | 0.4561 | 0.1236 | 0.164 |
| H(17C) | 8*f* | 0.3750 | 0.3427 | 0.1196 | 0.164 |
| H(18A) | 8*f* | 0.3701 | 0.6362 | 0.2276 | 0.063 |
| H(18B) | 8*f* | 0.4226 | 0.6323 | 0.1968 | 0.063 |
| H(18C) | 8*f* | 0.4326 | 0.5458 | 0.2571 | 0.063 |
| H(19A) | 8*f* | 0.2703 | 0.5952 | 0.1218 | 0.153 |
| H(19B) | 8*f* | 0.2684 | 0.4817 | 0.0777 | 0.153 |
| H(19C) | 8*f* | 0.3145 | 0.5946 | 0.0818 | 0.153 |

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**Table 2.** Continued.

| Atom | Site | x | y | z | $U_{iso}$ |
|---|---|---|---|---|---|
| H(21A) | 8*f* | 0.4350 | 0.1286 | 0.3087 | 0.054 |
| H(21B) | 8*f* | 0.3696 | 0.1896 | 0.2514 | 0.054 |
| H(21C) | 8*f* | 0.3617 | 0.0959 | 0.3011 | 0.054 |

**Table 2.** Continued.

| Atom | Site | x | y | z | $U_{iso}$ |
|---|---|---|---|---|---|
| H(22A) | 8*f* | 0.4131 | 0.3260 | 0.4655 | 0.051 |
| H(22B) | 8*f* | 0.3515 | 0.3121 | 0.4838 | 0.051 |
| H(22C) | 8*f* | 0.3779 | 0.4424 | 0.4774 | 0.051 |

**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) | 8*f* | 0.14468(5) | 0.43515(9) | 0.32445(5) | 0.0226(4) | 0.0359(5) | 0.0247(5) | 0.0022(4) | 0.0103(4) | −0.0053(4) |
| O(1) | 8*f* | 0.25980(4) | 0.41369(8) | 0.37922(4) | 0.0232(4) | 0.0354(4) | 0.0239(4) | 0.0039(3) | 0.0078(3) | −0.0038(3) |
| O(2) | 8*f* | 0.08182(4) | 0.35364(7) | 0.19678(4) | 0.0208(4) | 0.0328(4) | 0.0285(4) | 0.0017(3) | 0.0091(3) | −0.0009(3) |
| O(3) | 8*f* | 0.15262(4) | 0.29795(7) | 0.15094(4) | 0.0212(4) | 0.0349(4) | 0.0230(4) | 0.0007(3) | 0.0074(3) | −0.0024(3) |
| O(4) | 8*f* | 0.26739(6) | 0.54038(9) | 0.22395(7) | 0.0468(6) | 0.0326(5) | 0.0894(8) | 0.0110(4) | 0.0456(6) | 0.0186(5) |
| O(5) | 8*f* | 0.32970(5) | 0.40139(8) | 0.20066(5) | 0.0476(5) | 0.0305(4) | 0.0411(5) | −0.0073(4) | 0.0315(5) | −0.0049(3) |
| O(6) | 8*f* | 0.44991(5) | 0.2920(1) | 0.38997(5) | 0.0230(4) | 0.0673(7) | 0.0457(6) | 0.0059(4) | 0.0052(4) | −0.0143(5) |
| C(1) | 8*f* | 0.20143(5) | 0.39999(9) | 0.32000(5) | 0.0215(5) | 0.0239(4) | 0.0243(5) | 0.0019(4) | 0.0086(4) | 0.0018(4) |
| C(2) | 8*f* | 0.20341(5) | 0.35434(9) | 0.26324(5) | 0.0198(5) | 0.0249(5) | 0.0233(5) | 0.0021(4) | 0.0084(4) | 0.0014(4) |
| C(3) | 8*f* | 0.27100(5) | 0.33235(9) | 0.26217(5) | 0.0197(5) | 0.0242(4) | 0.0225(5) | 0.0006(4) | 0.0086(4) | 0.0006(4) |
| C(4) | 8*f* | 0.32899(5) | 0.32206(9) | 0.33331(5) | 0.0197(5) | 0.0256(5) | 0.0246(5) | 0.0024(4) | 0.0081(4) | 0.0009(4) |
| C(5) | 8*f* | 0.32078(5) | 0.3632(1) | 0.38629(5) | 0.0218(5) | 0.0272(5) | 0.0255(5) | 0.0011(4) | 0.0074(4) | 0.0002(4) |
| C(6) | 8*f* | 0.13846(6) | 0.4850(1) | 0.38352(6) | 0.0253(5) | 0.0305(5) | 0.0268(5) | 0.0015(4) | 0.0140(4) | −0.0012(4) |
| C(7) | 8*f* | 0.15009(8) | 0.3847(1) | 0.43561(7) | 0.0474(8) | 0.0421(7) | 0.0365(7) | 0.0030(6) | 0.0233(6) | 0.0088(5) |
| C(8) | 8*f* | 0.06421(6) | 0.5304(1) | 0.35506(7) | 0.0265(6) | 0.0439(6) | 0.0375(6) | 0.0024(5) | 0.0174(5) | −0.0032(5) |
| C(9) | 8*f* | 0.18709(6) | 0.5927(1) | 0.41556(7) | 0.0300(6) | 0.0346(6) | 0.0374(6) | −0.0014(5) | 0.0162(5) | −0.0074(5) |
| C(10) | 8*f* | 0.14002(6) | 0.33673(9) | 0.20234(5) | 0.0237(5) | 0.0226(4) | 0.0246(5) | 0.0009(4) | 0.0092(4) | 0.0011(4) |
| C(11) | 8*f* | 0.09636(6) | 0.2657(1) | 0.08475(6) | 0.0259(5) | 0.0373(6) | 0.0222(5) | 0.0025(4) | 0.0065(4) | −0.0024(4) |
| C(12) | 8*f* | 0.13538(7) | 0.2241(1) | 0.04592(7) | 0.0388(7) | 0.0545(8) | 0.0315(6) | −0.0006(6) | 0.0164(6) | −0.0087(5) |
| C(13) | 8*f* | 0.05504(7) | 0.1602(1) | 0.09250(7) | 0.0330(6) | 0.0408(6) | 0.0403(7) | −0.0058(5) | 0.0136(6) | −0.0075(5) |
| C(14) | 8*f* | 0.05232(8) | 0.3766(1) | 0.05136(7) | 0.0442(8) | 0.0472(7) | 0.0296(6) | 0.0140(6) | 0.0057(6) | 0.0030(5) |
| C(15) | 8*f* | 0.28792(6) | 0.4383(1) | 0.22642(6) | 0.0223(5) | 0.0290(5) | 0.0265(5) | 0.0017(4) | 0.0097(4) | 0.0033(4) |
| C(16) | 8*f* | 0.35659(9) | 0.4887(1) | 0.16733(8) | 0.0633(9) | 0.0412(7) | 0.0447(8) | −0.0228(6) | 0.0380(7) | −0.0117(6) |
| C(17) | 8*f* | 0.4020(2) | 0.4084(2) | 0.1479(2) | 0.187(3) | 0.057(1) | 0.184(3) | −0.054(1) | 0.173(3) | −0.056(1) |
| C(18) | 8*f* | 0.39932(7) | 0.5843(1) | 0.21664(8) | 0.0361(7) | 0.0380(6) | 0.0560(8) | −0.0088(5) | 0.0252(6) | −0.0104(6) |
| C(19) | 8*f* | 0.2970(1) | 0.5453(3) | 0.10656(9) | 0.101(2) | 0.143(2) | 0.0361(9) | −0.071(2) | 0.006(1) | 0.029(1) |
| C(20) | 8*f* | 0.39492(6) | 0.2621(1) | 0.34433(6) | 0.0232(5) | 0.0332(5) | 0.0315(6) | 0.0049(4) | 0.0104(5) | 0.0017(4) |
| C(21) | 8*f* | 0.38986(6) | 0.1598(1) | 0.29714(7) | 0.0269(6) | 0.0341(6) | 0.0460(7) | 0.0074(5) | 0.0153(5) | −0.0029(5) |
| C(22) | 8*f* | 0.37022(6) | 0.3607(1) | 0.45981(6) | 0.0286(6) | 0.0414(6) | 0.0255(6) | 0.0058(5) | 0.0072(5) | 0.0013(5) |

*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. Meyers, P. L.; Lewis, J. W.: The reaction of 1,1-diethylaminoprop-1-yne with benzylidene ketones. J. Heterocyclic. Chem. **10** (1973) 165-166.
2. Zhou, J.-F.: One-step synthesis of pyridine and 4*H*-pyran derivatives from bisarylidenecyclohexanone and malononitrile under microwave irradiation. Synth. Commun. **33** (2003) 99-103.
3. 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.
4. Yu, C.-X.; Shi, D.-Q.; Wang, X.-S.; Zhuang, Q.-Y.: 3-Amino-1-(3,4-methylenedioxyphenyl)-9-methoxy-5,6-dihydro-1*H*-benzo[*f*]chromene-2-carbonitrile. Acta Crystallogr. C**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. C**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. C**60** (2004) o2339-o2341.
7. Shi, D.-Q.; Niu, L.; Wang, X.; Zhuang, Q.; Zhang, Y.: 2-Amino-3-cyano-4-(2,4-dichlorophenyl)-8-methyl-pyrano[3,2-*c*]-pyran-5(4*H*)-one ethanol solvate. Acta. Crystallogr. C**60** (2004) o1995-o1997.
8. Wang, X.-S.; Zeng, Z.-S.; Shi, D.-Q.; Chen, H.; Wei, X.-Y.; Zong, Z.-M.: Methyl 2-amino-4-(4-nitrophenyl)-5-oxo-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carboxylate dimethylformamide solvate. Acta. Crystallogr. C**60** (2004) o1745-o1747.
9. 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.
10. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
11. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.