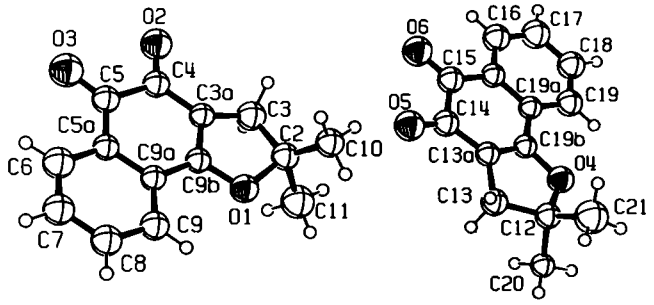
Crystal structure of 2,2-dimethyl-naphto[1,2*b*]1,2-dihydrofuran-4,5-dione, $C_{14}H_{12}O_3$

N. T. Do Valle[I], C. A. de Simone*[,I], M. A. Pereira[I], A. V. Pinto[II] and V. R. S. Malta[I]

[I] Universidade Federal de Alagoas, Depto. Química, 57072-970 - Maceió, AL, Brazil
[II] Núcleo de Pesquisas de Produtos Naturais - UFRJ, 21941-970 - Rio de Janeiro, RJ, Brazil

Received June 18, 2001, CCDC-No. 1267/686



Abstract

$C_{14}H_{12}O_3$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 6.958(2)$ Å, $b = 17.885(2)$ Å, $c = 18.008(2)$ Å, $V = 2241.0$ Å^3, $Z = 4$, $R_{gt}(F) = 0.073$, $wR_{ref}(F^2) = 0.207$, $T = 293$ K.

Source of material

The compound was cristallized from *N,N*-dimethylformamide at room temperature.

Experimental details

Due the easily deterioration of the crystal, which is strongly reflected in the quality of the collected data set ($R_{int} = 0.115$), it was shown to be inadequate to continue with the refinement of the anisotropic structure. Also, it was not possible to repeat all the data collection because we could not obtain new crystals for this sample.

Discussion

The naphthoquinonic compounds are easily found in the nature and theirs biological activity have been detected with various medicinal applications. Their action comes from antibiotics until antineoplasic, although some of them do not present defined function [1]. Among the naphthoquinonic compounds, the lapachol, lapachonas and theirs derivatives, are showing for more than one century, the interest of the scientific community of several countries due to the large range of biological activities presented for these compounds [2]. Among these activities we can mention: antiviral activity [3], antimalarial activity [4], antitumor activity [5], activity against the Trypanosoma cruzi, the protozoan of Chagas disease [6,7], etc. The title compound is a derivative of the β-lapachona and we have interest to find theirs particular biological activities. The majority of the structures of quinone found in the literature is a kind of pyran type while the related compound has a furan type structure. That is a new factor to be considered in the assessment of the structure-activity relationship in this class of compounds. There are two independent molecules in asymmetric unit. Bond lengths and angles are is good agreement, to within experimental accuracy, with the values found in the literature. The benzenic and quinonic rings are planar. The atoms C3a and C9b practically are located in the average plane of the quinonic ring with distances of 0.07(3) Å and –0.06(3) Å, respectively, of that plane. The atoms O2 and O3 practically accompany the plane of this ring with distances of –0.04(3) Å and 0.01(3) Å, respectively. The dihedral angles between the quinonic ring and benzenic ring is 1.7(1)°, showing that the naphtoquinonic bicycle is perfectly planar. The conformation of the five-membered ring is a twist (T), wherein C3 is 0.10(4) Å below and C3a is 0.10(3) Å above of the least squares plane respectively. The dihedral angles between the five-membered and quinonic ring and benzenic ring are 1.5(9)° and 1.1(9)°, respectively, indicating that the region formed for the same ones is almost planar.

Table 1. Data collection and handling.

Crystal:	red, irregular, size 0.35 × 0.35 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.95 cm^{-1}
Diffractometer, scan mode:	Turbo CAD-4, ω/2θ
$2\theta_{max}$:	49.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3008, 2924
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 931
$N(param)_{refined}$:	143
Programs:	SHELXS-97 [8], SHELXL-97 [9], ORTEP3 [10]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
O(1)	1*a*	0.262(2)	0.8886(3)	0.3481(2)	0.048(2)
O(2)	1*a*	0.241(3)	0.9995(3)	0.5785(3)	0.065(2)
O(3)	1*a*	0.244(3)	1.1365(3)	0.5132(3)	0.070(2)
O(4)	1*a*	0.249(3)	0.3617(3)	0.4238(3)	0.053(1)
O(5)	1*a*	0.241(3)	0.6102(3)	0.4874(3)	0.066(2)
O(6)	1*a*	0.245(3)	0.5707(3)	0.6340(3)	0.068(2)
C(2)	1*a*	0.237(4)	0.8238(4)	0.4034(4)	0.051(2)
C(3)	1*a*	0.271(3)	0.8616(4)	0.4787(4)	0.056(3)
H(3A)	1*a*	0.1806	0.8440	0.5157	0.069(5)
H(3B)	1*a*	0.4010	0.8531	0.4963	0.069
C(3A)	1*a*	0.239(3)	0.9420(4)	0.4608(4)	0.039(2)
C(4)	1*a*	0.248(4)	1.0042(4)	0.5101(4)	0.046(2)

* Correspondence author (e-mail: cas@fapeal.br)

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
C(5)	1*a*	0.252(4)	1.0806(4)	0.4740(4)	0.048(2)
C(5A)	1*a*	0.249(4)	1.0869(4)	0.3912(3)	0.041(2)
C(6)	1*a*	0.254(5)	1.1560(4)	0.3573(4)	0.058(2)
H(6)	1*a*	0.2583	1.1993	0.3858	0.069
C(7)	1*a*	0.251(5)	1.1607(4)	0.2810(4)	0.057(2)
H(7)	1*a*	0.2496	1.2072	0.2578	0.069
C(8)	1*a*	0.252(5)	1.0969(4)	0.2399(4)	0.055(2)
H(8)	1*a*	0.2531	1.1007	0.1884	0.069
C(9)	1*a*	0.250(5)	1.0264(4)	0.2721(4)	0.049(2)
H(9)	1*a*	0.2498	0.9835	0.2430	0.069
C(9A)	1*a*	0.248(4)	1.0222(4)	0.3484(3)	0.039(2)
C(9B)	1*a*	0.251(4)	0.9525(4)	0.3875(3)	0.040(2)
C(10)	1*a*	0.063(3)	0.7815(9)	0.389(1)	0.052(5)
H(10A)	1*a*	0.0663	0.7359	0.4174	0.069
H(10B)	1*a*	0.0545	0.7701	0.3374	0.069
H(10C)	1*a*	-0.0465	0.8106	0.4041	0.069
C(11)	1*a*	0.422(3)	0.778(1)	0.380(1)	0.078(7)
H(11A)	1*a*	0.5330	0.8097	0.3839	0.069
H(11B)	1*a*	0.4080	0.7616	0.3293	0.069
H(11C)	1*a*	0.4362	0.7356	0.4118	0.069
C(12)	1*a*	0.238(4)	0.4022(4)	0.3512(4)	0.046(2)
C(13)	1*a*	0.250(5)	0.4851(4)	0.3717(4)	0.053(2)
H(13A)	1*a*	0.3695	0.5071	0.3545	0.069

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(13B)	1*a*	0.1429	0.513	0.3512	0.069
C(13A)	1*a*	0.242(4)	0.4828(4)	0.4546(4)	0.042(2)
C(14)	1*a*	0.252(4)	0.5431(4)	0.5054(4)	0.051(2)
C(15)	1*a*	0.249(5)	0.5218(4)	0.5863(4)	0.053(2)
C(15A)	1*a*	0.253(4)	0.4421(4)	0.6083(3)	0.044(2)
C(16)	1*a*	0.249(5)	0.4225(4)	0.6826(4)	0.059(2)
H(16)	1*a*	0.2473	0.4590	0.7194	0.069
C(17)	1*a*	0.248(5)	0.3481(4)	0.7006(5)	0.068(3)
H(17)	1*a*	0.2442	0.3345	0.7504	0.069
C(18)	1*a*	0.251(5)	0.2935(4)	0.6481(4)	0.061(2)
H(18)	1*a*	0.2519	0.2435	0.6622	0.069
C(19)	1*a*	0.254(4)	0.3125(4)	0.5733(4)	0.054(2)
H(19)	1*a*	0.2568	0.2757	0.5369	0.069
C(19A)	1*a*	0.254(4)	0.3866(4)	0.5547(3)	0.041(2)
C(19B)	1*a*	0.245(4)	0.4119(4)	0.4785(4)	0.041(2)
C(20)	1*a*	0.431(2)	0.3828(8)	0.3106(9)	0.047(5)
H(20A)	1*a*	0.5363	0.4049	0.3371	0.069
H(20B)	1*a*	0.4274	0.4022	0.2609	0.069
H(20C)	1*a*	0.4469	0.3296	0.3091	0.069
C(21)	1*a*	0.073(3)	0.3708(9)	0.313(1)	0.069(6)
H(21A)	1*a*	0.0566	0.3955	0.2661	0.069
H(21B)	1*a*	-0.0399	0.3776	0.3427	0.069
H(21C)	1*a*	0.0939	0.3183	0.3048	0.069

Acknowledgments. This work has received partial support from CNPq, CAPES, FAPEAL and FINEP.

References

1. Pinto, A.V.; Ferreira, V.F.; Coutada, L. C. M.: Síntese de Análogos de Xiloidonas e Lapachonas. An. Acad. brasil. Ciênc. **52** (1980) 477-479.
2. Subramanian, S.: Estudo da Relação Estrutura-Atividade Biológica do Lapachol, das Lapachonas e de Alguns de seus Derivados. São Carlos. Tese Doutorado. Instituto de Química de São Carlos. USP 1996.
3. Pinto, A. V.; Pinto M. do C.; Lagrota, M. H.; Wigg, M. D.; Aguiar, M. A.: Antiviral activity of naphthoquinones. I. Lapachol derivatives against enteroviruses. A. N. Rev. Latinoam. Microbiol. **29** (1987) 15-20.
4. Fieser, L. F.; Schirmer J. P.; Archer S.; Lorenz, R. R. and Pfaffenb, P. I.: Naphthoquinone antimalarials. 29. 2-hydroxy-3-(ω-cyclohexylalkyl)-1,4-naphthoquinones. J. Med. Chem. **10** (1967) 513-517.
5. Li, C. J.; Li, Y. Z.; Pinto, A. V.; Pardee, A. B.: Potent inhibition of tumor survival in vivo by β-lapachone plus taxol: combining drugs imposes different artificial checkpoints. Proc. Natl. Acad. Sci. USA, Nov. 9, 1999; 96(23): 13369-74.
6. Gonçalves, A. M.; Vasconcellos, M. E.; Do Campo, R; de Cruz, F. S.; de Souza W.; Leon,W.: Evaluation of the toxicity of 3-allyl-β-lapachone against Trypanosoma cruzi bloodstream forms. Mol. Biochem. Parasit. **1** (1980) 167-176.
7. Pinto, A.V.; Ferreira, V.F.; Capella, R. S.; Gilbert, B.; Pinto, M. do C.; da Silva, J. S.: Activity of some naphthoquinones on blood stream forms of Trypanosoma cruzi. Trans. R. Soc. Trop. Med. Hyg. **81** (1987) 609-610.
8. Sheldrick, G. M.: SHELXS-97. Program for Crystal Structure Resolution. University of Göttingen: Göttingen, Germany 1997.
9. Sheldrick, G. M.: SHELXL-97. Program for Crystal Structures Analysis. University of Göttingen: Göttingen, Germany 1997.
10. Farrugia, L. J.: ORTEP3 for Windows. J. Appl. Cryst. **30** (1997) 565.