

Claudio Barrientos, Antonio Galdámez and Silvana Moris*

The crystal structure of 5-nitronaphthoquinone, $C_{10}H_5NO_4$

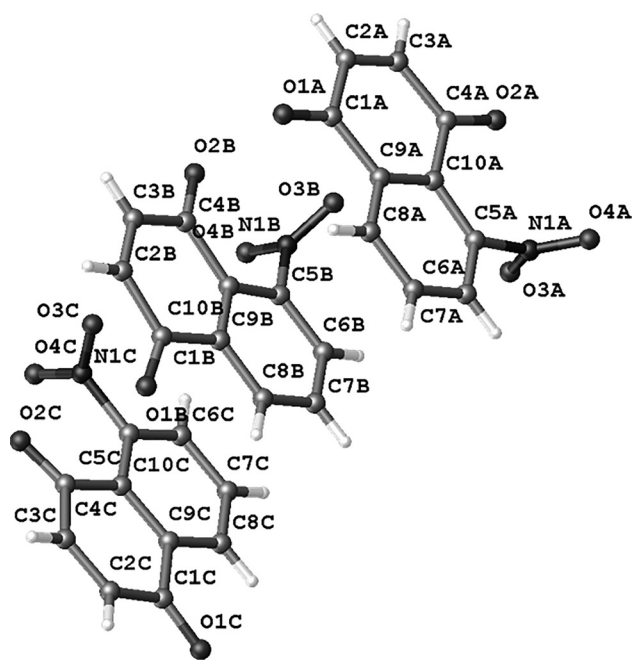


Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.10 × 0.09 × 0.06 mm
Wavelength:	Mo α radiation (0.71073 Å)
μ :	0.12 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II,
θ_{\max} , completeness:	26.4°, >99 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	33,183, 5487, 0.055
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 3217
$N(\text{param})_{\text{refined}}$:	406
Programs:	Bruker [1], Olex2 [2, 3], SHELX [4], PLATON [5]

1 Source of materials

The 5-nitronaphthoquinone was prepared following the reported methodology [6] starting from naphthoquinone in H_2SO_4 in presence of $NaNO_3$, the crude was precipitated in crushed ice to then vacuum filtered and washed with saturated $NaHCO_3$ dissolution. The solid obtained was recrystallized in acetone and yellow block-like crystals were obtained. The structure was confirmed by melting point [7] and, 1H NMR (400 MHz, Acetone- d_6) δ 8.32 (dd, $J = 7.8, 1.2$ Hz, 1H), 8.13 (t, $J = 7.8$ Hz, 1H), 8.05 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.18 (d, $J = 10.4$ Hz, 1H), 7.12 (d, $J = 10.4$ Hz, 1H) ^{13}C NMR (101 MHz, Acetone) δ 182.76, 181.78, 138.97, 138.41, 135.25, 133.04, 128.46, 127.56, 122.65.

2 Experimental details

Using Olex2 [2], with the olex2.solve [3] using Charge Flipping and refined with the SHELXL [4] the structure was solved. SADABS-2016/2 (Bruker, 2016/2) was used for absorption correction. Interactions were calculated using Platon [5]. Reflections were merged by SHELXL according to the crystal class for the calculation of statistics and refinement. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters as $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$, the constraint distances of C–H was 0.93 Å.

3 Comment

Quinones are organic compounds that consist in two-carbonyl keto with two carbon–carbon double bonds in a six membered

<https://doi.org/10.1515/ncrs-2023-0211>

Received May 4, 2023; accepted May 15, 2023;

published online May 31, 2023

Abstract

$C_{10}H_5NO_4$, triclinic, $P\bar{1}$ (no. 2), $a = 9.2564(8)$ Å, $b = 11.0464(9)$ Å, $c = 14.8016(12)$ Å, $\alpha = 110.132(2)^\circ$, $\beta = 106.157(3)^\circ$, $\gamma = 94.770(3)^\circ$, $V = 1337.7(2)$ Å³, $Z = 6$, $R_{\text{gt}}(F) = 0.0567$, $wR_{\text{ref}}(F^2) = 0.1797$, $T = 296.15$ K

CCDC no.: 2262885

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

*Corresponding author: Silvana Moris, Centro de Investigación de Estudios Avanzados del Maule (CIEAM), Vicerrectoría de Investigación y Postgrado, Universidad Católica del Maule, Talca, Chile, E-mail: smoris@ucm.cl

Claudio Barrientos, Facultad de Ingeniería, Instituto de ciencias Químicas aplicada, Universidad Autónoma de Chile, Talca, Chile

Antonio Galdámez, Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C1C	0.8189 (3)	−0.0060 (3)	1.0218 (2)	0.0624 (7)
C1B	0.8013 (3)	0.4327 (3)	0.94615 (18)	0.0602 (7)
C1A	0.8264 (3)	0.5575 (3)	0.6313 (2)	0.0656 (7)
C2B	0.7121 (4)	0.5346 (3)	0.9383 (2)	0.0789 (9)
H2B	0.7202 (4)	0.6053 (3)	0.9975 (2)	0.0946 (11)*
C2A	0.7252 (3)	0.5477 (3)	0.5317 (2)	0.0739 (8)
H2A	0.6624 (3)	0.6088 (3)	0.5294 (2)	0.0887 (10)*
C2C	0.8341 (4)	0.1051 (3)	1.1149 (2)	0.0784 (9)
H2C	0.9111 (4)	0.1161 (3)	1.1746 (2)	0.0941 (11)*
C3B	0.6215 (4)	0.5295 (3)	0.8510 (2)	0.0754 (9)
H3B	0.5681 (4)	0.5971 (3)	0.8504 (2)	0.0905 (10)*
C3A	0.7208 (3)	0.4552 (3)	0.4456 (2)	0.0684 (8)
H3A	0.6536 (3)	0.4525 (3)	0.3848 (2)	0.0821 (9)*
C3C	0.7426 (4)	0.1904 (3)	1.1173 (2)	0.0736 (8)
H3C	0.7567 (4)	0.2594 (3)	1.1787 (2)	0.0883 (10)*
C4B	0.6010 (3)	0.4217 (2)	0.75449 (19)	0.0553 (6)
C4A	0.8172 (3)	0.3567 (2)	0.44194 (19)	0.0529 (6)
C4C	0.6198 (3)	0.1803 (3)	1.0269 (2)	0.0604 (7)
C5C	0.5001 (3)	0.0622 (2)	0.83660 (18)	0.0482 (6)
C5B	0.6817 (3)	0.2112 (2)	0.67086 (16)	0.0457 (5)
C5A	1.0114 (3)	0.2682 (2)	0.54634 (18)	0.0512 (6)
C6B	0.7745 (3)	0.1204 (2)	0.6723 (2)	0.0588 (7)
H6B	0.7668 (3)	0.0510 (2)	0.6126 (2)	0.0706 (8)*
C6A	1.1124 (3)	0.2755 (3)	0.6368 (2)	0.0655 (7)
H6A	1.1747 (3)	0.2138 (3)	0.6380 (2)	0.0787 (9)*
C6C	0.4883 (3)	−0.0350 (3)	0.7459 (2)	0.0652 (7)
H6C	0.4162 (3)	−0.0413 (3)	0.6856 (2)	0.0783 (9)*
C7B	0.8786 (3)	0.1342 (3)	0.7635 (2)	0.0626 (7)
H7B	0.9438 (3)	0.0747 (3)	0.7652 (2)	0.0751 (9)*
C7A	1.1198 (3)	0.3758 (3)	0.7256 (2)	0.0714 (8)
H7A	1.1880 (3)	0.3823 (3)	0.7873 (2)	0.0857 (10)*
C7C	0.5853 (4)	−0.1236 (3)	0.7454 (2)	0.0753 (8)
H7C	0.5790 (4)	−0.1899 (3)	0.6843 (2)	0.0903 (10)*
C8B	0.8878 (3)	0.2347 (3)	0.85228 (19)	0.0559 (6)
H8B	0.9558 (3)	0.2410 (3)	0.91400 (19)	0.0671 (8)*
C8C	0.6910 (3)	−0.1143 (3)	0.8346 (2)	0.0651 (7)
H8C	0.7549 (3)	−0.1750 (3)	0.8336 (2)	0.0781 (9)*
C8A	1.0273 (3)	0.4664 (3)	0.72374 (19)	0.0628 (7)
H8A	1.0316 (3)	0.5326 (3)	0.78432 (19)	0.0753 (9)*
C9B	0.7952 (3)	0.3270 (2)	0.84968 (16)	0.0454 (5)
C9C	0.7031 (3)	−0.0155 (2)	0.92578 (18)	0.0484 (6)
C9A	0.9275 (3)	0.4596 (2)	0.63195 (17)	0.0488 (6)
C10B	0.6922 (2)	0.3181 (2)	0.75754 (16)	0.0410 (5)
C10C	0.6068 (3)	0.0761 (2)	0.92869 (16)	0.0432 (5)
C10A	0.9188 (3)	0.3599 (2)	0.54060 (16)	0.0443 (5)
N1B	0.5625 (3)	0.1846 (2)	0.57292 (16)	0.0589 (6)
N1C	0.3932 (3)	0.1528 (2)	0.83158 (19)	0.0638 (6)
N1A	1.0014 (4)	0.1545 (3)	0.45486 (19)	0.0751 (7)
O1C	0.8964 (3)	−0.0899 (2)	1.02191 (19)	0.0946 (8)
O1B	0.8725 (3)	0.4325 (2)	1.02835 (14)	0.0947 (8)
O1A	0.8271 (3)	0.6412 (2)	0.70996 (18)	0.1060 (9)
O2A	0.8171 (3)	0.2777 (2)	0.36167 (14)	0.0792 (6)
O2B	0.5156 (3)	0.4185 (2)	0.67494 (16)	0.0938 (8)
O2C	0.5290 (4)	0.2516 (3)	1.0325 (2)	0.1314 (12)
O3A	0.8975 (4)	0.0609 (2)	0.42725 (19)	0.1095 (9)

Table 2: (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
O3B	0.5972 (3)	0.2115 (3)	0.50857 (16)	0.0967 (8)
O3C	0.4323 (3)	0.2530 (3)	0.8264 (3)	0.1441 (14)
O4B	0.4352 (2)	0.1297 (2)	0.56118 (16)	0.0890 (7)
O4A	1.0981 (3)	0.1581 (3)	0.4153 (2)	0.1204 (10)
O4C	0.2674 (3)	0.1210 (3)	0.8296 (3)	0.1398 (13)

ring and depending on the aromatic ring fused to the quinone we can find three types of quinones, benzoquinones, naphthoquinones and anthraquinones [6]. Quinones are natural occurring compounds which are found in plants, bacteria or insects [7, 8]. Quinones are interesting compounds due to multiple biological properties such as antibacterial, antifungal, antioxidant and anti-cancer [9–13]. Quinones are vastly studied due to redox properties which can be used for energy storage applications [14, 15].

In this structure, there are three crystallographically independent molecules in the asymmetric unit. (see the figure) Half-normal probability plot analysis was used to identify systematic geometrical differences. A comparison of the bond distances and angles of the fitted residues reveals that the molecules do not show any significant geometrical differences. The main difference lies in the conformations of the nitro-group, which are involved in intermolecular interactions and crystal-packing effects. The largest difference (0.0460 Å) is between the N1C–O3C bond in the first molecule and N1B–O4B in the second molecule (9.200 Δ/σ). The N–O bond lengths in the nitro group range from 1.170(3) to 1.220(4) Å. The angle between O–N–O in these structures range from 121.0(3) to 125.0(3)°, O–N–C range between 116.4(2) and 119.9(2)°, similar value to reported by us in Barrientos et al. [16, 17]. There are no classical hydrogen bonds in the crystal [5], only intermolecular C–H...O interactions with distances of 3.129(5)–3.273(4) Å between the donor and acceptor atoms are found [18]. The crystal structure exhibits C–O...p and N–O...p interactions [C(4A)–O(2A)...Cg(1) = 3.817(3) Å, C(4C)–O(2C)...Cg(7) = 3.939(4) Å, C(4C)–O(2C)...Cg(8) = 3.937(4) Å, N(1B)–O(3B)...Cg(1) = 3.101(3) Å, N(1C)–O(3C)...Cg(4) = 2.899(4) Å]. In crystal-packing the interaction between the quinone ring and the quinone oxygen of the next unit is observed (C(4A)–O(2A)...Cg(1)) [19–21], simultaneously in the next unit the interaction between the oxygen of the nitro group with the quinone ring is observed (N(1B)–O(3B)...Cg(1) and N(1C)–O(3C)...Cg(4)) generating a turn between the molecules that form the asymmetric unit.

Acknowledgements: We gratefully acknowledge support by FONDEQUIP EQM200138 for D8 Venture diffractometer.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: FONDEQUIP EQM200138.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. BRUKER. *SAINTE, APEX2 and SADABS*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2009.
2. Bourhis L. J., Dolomanov O. V., Gildea R. J., Howard J. A. K., Puschmann H. The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment-Olex2 dissected. *Acta Crystallogr.* 2015, *A71*, 59–75.
3. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, *42*, 339–341.
4. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
5. Spek A. L. Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* 2003, *36*, 7–13.
6. Shvartsberg M. S., Kolodina E. A., Lebedeva N. I., Fedenok L. G. Vicinal acetylenic derivatives of 2-amino-1,4-naphthoquinone as a key precursors of heterocyclic quinones. *Russ. Chem. Bull.* 2012, *61*, 582–588.
7. Ivashkina N. V., Romanov V. S., Moroz A. A., Shvartsberg M. S. 5-Arylethynyl-1,4-naphthoquinones. *Russ. Chem. Bull.* 1984, *33*, 2345–2348.
8. Dulo B., Phan K., Githaiga J., Raes K., De Meester S. Natural quinone dyes: a review on structure, extraction techniques, analysis and application potential. *Waste Biomass. Valorization* 2021, *12*, 6339–6374.
9. Abaham I., Joshi R., Pardasani P., Pardasani R. T. Recent advances in 1,4-benzoquinone chemistry. *J. Braz. Chem. Soc.* 2011, *22*, 385–421.
10. Borges M. E., Tejera R. L., Diaz L., Esparza P., Ibanez E. Natural dyes extraction from cochineal (*Dactylopius coccus*). New extraction methods. *Food Chem.* 2012, *132*, 1855–1860.
11. Srivastava S., Chowdhury A. R., Maurya S. Antimicrobial efficacy of methylated lac dye, an anthraquinone derivative. *Indian J. Microbiol.* 2017, *57*, 470–476.
12. Khan S. A., Ahmad A., Khan M. I., Yusuf M., Shahid M., Manzoor N., Mohammad F. Antimicrobial activity of wool yarn dyed with *Rheum emodi* L. (Indian Rhubarb). *Dyes Pigments* 2012, *95*, 206–214.
13. Tsao Y.-C., Chang Y.-J., Wang C.-H., Chen L. Discovery of isoplumbagin as a novel NQO1 substrate and anti-cancer quinone. *Int. J. Mol. Sci.* 2020, *21*, 4378.
14. Jones A., Ejigu A., Wang B., Adams R., Bissett M., Dryfe R. Quinone voltammetry for redox-flow battery applications. *J. Electroanal. Chem.* 2022, *920*, 116572.
15. Sedenho G., De Porcellinis D., Jing Y., Kerr E., Mejia-Mendoza L. M., Vazquez-Mayagoitia A., Aspuru-Guzik A., Gordon R. G., Crespilho F., Aziz M. J. Effect of molecular structure of quinones and carbon electrode surfaces on the interfacial electron transfer process. *ACS Appl. Energy Mater.* 2020, *3*, 1933–1943.
16. Barrientos C., Barahona P., Guevara J. L., Squella J. A., Moris S. The crystal structure of 4-(pyren-1-yl)butyl-3-nitrobenzoate, C₂₇H₂₁NO₄. *Z. Kristallogr. N. Cryst. Struct.* 2019, *234*, 1213–1214.
17. Barrientos C., Squella J. A., Moris S. The crystal structure of 4-(pyren-1-yl)butyl-4-nitrobenzoate, C₂₇H₂₁NO₄. *Z. Kristallogr. N. Cryst. Struct.* 2023, *238*, 459–461.
18. Moris S., Galdamez A., Jara P., Saitz-Barria C. Synthesis of novel *p*-tert-butylcalix[4]arene derivative: structural characterization of a methanol inclusion compound. *Crystals* 2016, *6*, 114.
19. Steed K. M., Steed J. W. Packing problems: high Z' crystal structures and their relationship to cocrystals, inclusion compounds, and polymorphism. *Chem. Rev.* 2015, *115*, 2895–2933.
20. Desiraju G. R. On the presence of multiple molecules in the crystal asymmetric unit (Z' > 1). *Cryst. Eng. Comm.* 2007, *9*, 91–92.
21. Nichol G. S., Clegg W. The importance of weak C–H...O bonds and π...π stacking interactions in the formation of organic 1,8-bis(dimethylamino)naphthalene complexes with Z' > 1. *Cryst. Growth Des.* 2006, *6*, 451–460.