Cannadine, J. C., Corden, J. P., Errington, W., Moore P. & Wallbridge, M. G. H. (1996). *Acta Cryst.* **C52**, 1014–1017.
Corden, J. P., Errington, W., Moore P. & Wallbridge, M. G. H. (1995). Unpublished results.
Corden, J. P., Errington, W., Moore P. & Wallbridge, M. G. H. (1996). *Acta Cryst.* **C52**, 125–127.
Deng L. & Jacobsen, E. N. (1992). *J. Org. Chem.* **57**, 4320–4323.
Dow, J. A., Drake, S. R., Hursthouse, M. B. & Malik, K. M. A. (1993). *Inorg. Chem.* **32**, 5704–5708.
Pflugrath, J. W. & Messerschmidt, A. (1992). *Munich Area Detector Systems*. Enraf–Nonius, Delft, The Netherlands.
Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1996). **C52**, 3202-3204

3-Methoxy-1,4-benzoquinone 4-Oxime

Nicola Sardone,[a] Oliviero Carugo,[b]† John Charalambous[c] and Dinesh V. Raghvani[c]

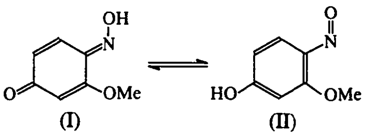
[a]*Centro Grandi Strumenti, Università degli Studi di Pavia, I-27100 Pavia, Italy,* [b]*Dipartimento di Chimica Generale, Università degli Studi di Pavia, I-27100 Pavia, Italy, and* [c]*Department of Applied Chemistry and Life Science, University of North London, London, England. E-mail: nicola@elicona.unipv.it*

(*Received 13 May 1996; accepted 5 July 1996*)

Abstract

The crystal structure of the title compound, $C_7H_7NO_3$, shows a strong quinoid character. The oximic function is *anti* with respect to the methoxy group so that no intramolecular hydrogen bonds involving the acidic H atom are formed, instead a strong intermolecular interaction is favoured. Two molecules are present in the asymmetric unit and they show no significant differences in their bond lengths and angles, but they do have different packing interactions.

Comment



(I) (II)

The asymmetric unit of the title compound, (I), contains two molecules which do not differ significantly from one another in terms of bond lengths and angles, but their packing contacts are quite different (see Figs. 1 and 2). It is well known that 1,4-quinone 4-oximes can present a tautomeric equilibrium between the quinone monooximic (I) and the nitrosophenolic (II) forms (see Scheme). In the structure presented here, both the experimental location of the H atoms and the alternation of short and long bonds within the hexaatomic ring clearly indicate that the quinoid structure (I) prevails. In addition, the bond lengths of the carbonyl and oxime groups compare well with expected values for a quinone monooxime structure (Carugo, Charalambous, Raghvani & Sardone, 1996). No charge delocalization involving the methoxy group is observed since the O2—C2 (O2′—C2′) bond length is within the expected range for single O—C_{sp^2} bonds (Allen *et al.*, 1987).

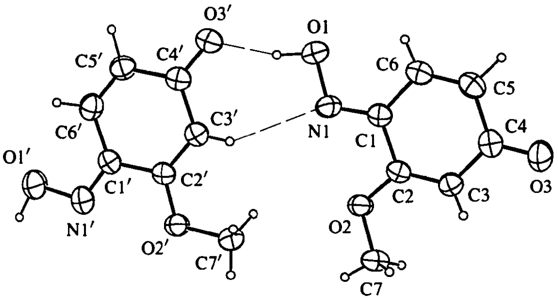


Fig. 1. Perspective view of the asymmetric unit of the title compound shown with 50% probability ellipsoids.

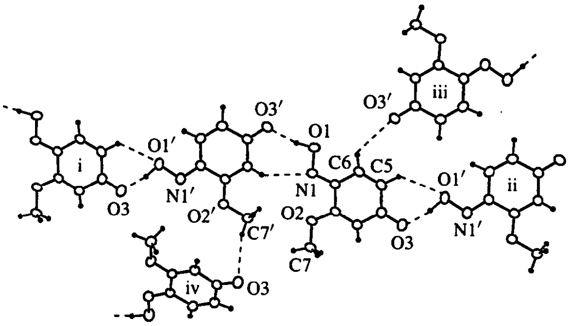


Fig. 2. The hydrogen-bonding interactions in the title compound. Symmetry codes: (i) $1+x, y, z-1$; (ii) $x-1, y, 1+z$; (iii) $-x, -y, 2-z$; (iv) $1+x, \frac{1}{2}-y, z-\frac{1}{2}$.

Both six-membered rings deviate slightly from planarity leading to a pseudo-boat conformation in which the quinoid C1 and C4 atoms (C1′ and C4′) lie up (and down) with respect to the mean plane. The least-squares planes of the two rings in the asymmetric unit form a dihedral angle of 3.1 (7)°.

The oximic group is *anti* with respect to the methoxy moiety and therefore no intramolecular hydrogen bond involving the acidic H atom is formed, thus favouring a strong intermolecular interaction. The two molecules, which are not equivalent symmetrically, are connected through two hydrogen bonds, *i.e.* a strong O—H···O interaction [HO1···O3′ 1.73 (3),

---

† Present address: EMBL, Heidelberg, 69012 Heidelberg, Germany.

© 1996 International Union of Crystallography
Printed in Great Britain – all rights reserved

Acta Crystallographica Section C
ISSN 0108-2701 © 1996

O1···O3′ 2.667 (2) Å and O1—HO1···O3′ 165 (2)°] and a weaker C—H···N interaction [H3′···N1 2.63, C3′···N1 3.401 (3) Å and C3′—H3′···N1 149°]. The asymmetric unit interacts with two neighbouring units through a third strong hydrogen bond [HO1′···O3^{i} 1.67 (3), O1′···O3^{i} 2.657 (2) Å and O1′—HO1′···O3^{i} 166 (2)°; symmetry code: (i) $1+x$, y, $z-1$] forming strands roughly parallel to the **c** direction. The crystal packing is also stabilized by van der Waals and stacking interactions between the six-membered rings translated along the **a** direction. It is worth noting that there are three short C—H···O contacts that might also play a role in stabilizing the packing (Fig. 2); H5···O1′^{ii} 2.64, C5···O1′^{ii} 3.320 (3) Å and C5—H5···O1′^{ii} 127°; H6···O3′^{iii} 2.72, C6···O3′^{iii} 3.340 (3) Å and C6—H6···O3′^{iii} 128°; H7C′···O3^{iv} 2.56, C7′···O3^{iv} 3.459 (2) Å and C7′—H7C′···O3^{iv} 165° [symmetry codes: (ii) $x-1$, y, $1+z$; (iii) $-x$, $-y$, $2-z$; (iv) $1+x$, $\frac{1}{2}-y$, $z-\frac{1}{2}$].

Experimental

The title compound was prepared by reaction of 3-methoxyphenol with sodium nitrite and hydrochloric acid in aqueous ethanol. The resulting orange solid was chromatographed on silica to give 5-methoxy-1,2-benzoquinone 2-oxime with toluene and the title compound, 2-methoxy-1,4-benzoquinone 4-oxime, with diethyl ether. The crystal used for analysis was obtained from ethanol solution.

Crystal data

$C_7H_7NO_3$
$M_r = 153.14$
Monoclinic
$P2_1/c$
$a = 3.846\,(1)$ Å
$b = 25.673\,(2)$ Å
$c = 13.992\,(1)$ Å
$\beta = 96.36\,(1)°$
$V = 1372.9\,(4)$ Å^3
$Z = 8$
$D_x = 1.4817$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 30$–$35°$
$\mu = 0.955$ mm^{-1}
$T = 293\,(2)$ K
Plate
0.29 × 0.22 × 0.05 mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.917$, $T_{\max} = 0.999$
5246 measured reflections
2462 independent reflections

1983 observed reflections $[I < 2\sigma(I)]$
$R_{\text{int}} = 0.018$
$\theta_{\max} = 70°$
$h = -4 \rightarrow 4$
$k = -31 \rightarrow 31$
$l = 0 \rightarrow 17$
3 standard reflections monitored every 300 reflections intensity decay: 0.4%

Refinement

Refinement on F
$R = 0.038$
$wR = 0.034$
$S = 0.627$
1983 reflections
208 parameters
Only the acidic H atoms were refined isotropically
Unit weights kept $\Sigma w(\Delta F)^2$ uniform over ranges of $\sin\theta/\lambda$ and $|F_o|$
$(\Delta/\sigma)_{\max} = 0.2$

$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.05$ e Å^{-3}
Extinction correction: Zachariasen (1963)
Extinction coefficient: 5.588×10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2A, 2.3.1 and 2.2C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.2175 (5)	0.04819 (6)	0.9708 (1)	0.0543 (5)
O2	0.4270 (4)	0.19849 (5)	1.0100 (1)	0.0381 (4)
O3	0.1534 (5)	0.17893 (6)	1.3295 (1)	0.0519 (5)
N1	0.2987 (4)	0.09987 (6)	0.9810 (1)	0.0366 (5)
C1	0.2347 (5)	0.11763 (7)	1.0640 (1)	0.0295 (5)
C2	0.3193 (5)	0.17266 (7)	1.0846 (1)	0.0293 (5)
C3	0.2894 (5)	0.19247 (8)	1.1722 (1)	0.0334 (6)
C4	0.1682 (5)	0.16110 (8)	1.2474 (1)	0.0348 (6)
C5	0.0626 (5)	0.10747 (8)	1.2242 (2)	0.0380 (7)
C6	0.0945 (5)	0.08733 (8)	1.1380 (2)	0.0365 (6)
C7	0.5188 (6)	0.25273 (8)	1.0240 (2)	0.0406 (6)
O1′	0.9605 (5)	0.11090 (7)	0.4566 (1)	0.0558 (6)
O2′	0.8680 (4)	0.17365 (5)	0.71357 (9)	0.0370 (4)
O3′	0.3839 (4)	0.01367 (6)	0.8019 (1)	0.0456 (5)
N1′	0.9286 (5)	0.13460 (7)	0.5432 (1)	0.0403 (5)
C1′	0.8139 (5)	0.10286 (8)	0.6046 (1)	0.0318 (5)
C2′	0.7655 (5)	0.12372 (7)	0.6998 (1)	0.0294 (5)
C3′	0.6287 (5)	0.09392 (8)	0.7656 (1)	0.0328 (5)
C4′	0.5265 (5)	0.04084 (8)	0.7442 (1)	0.0329 (5)
C5′	0.5921 (6)	0.01916 (8)	0.6513 (2)	0.0381 (6)
C6′	0.7252 (5)	0.04843 (8)	0.5858 (1)	0.0379 (5)
C7′	0.8232 (6)	0.19582 (8)	0.8063 (2)	0.0405 (6)

Table 2. *Geometric parameters (Å, °)*

O1—N1	1.367 (2)	O1′—N1′	1.373 (2)
O2—C2	1.340 (2)	O2′—C2′	1.349 (2)
O2—C7	1.444 (2)	O2′—C7′	1.444 (3)
O3—C4	1.243 (3)	O3′—C4′	1.241 (3)
N1—C1	1.297 (3)	N1′—C1′	1.296 (3)
C1—C2	1.471 (3)	C1′—C2′	1.466 (3)
C1—C6	1.446 (3)	C1′—C6′	1.455 (3)
C2—C3	1.344 (3)	C2′—C3′	1.348 (3)
C3—C4	1.444 (3)	C3′—C4′	1.441 (3)
C4—C5	1.462 (3)	C4′—C5′	1.462 (3)
C5—C6	1.331 (3)	C5′—C6′	1.330 (3)
C2—O2—C7	117.6 (2)	C2′—O2′—C7′	116.2 (2)
O1—N1—C1	111.8 (2)	O1′—N1′—C1′	112.1 (2)
N1—C1—C6	125.1 (2)	N1′—C1′—C6′	125.0 (2)
N1—C1—C2	116.9 (2)	N1′—C1′—C2′	117.3 (2)
C2—C1—C6	118.0 (2)	C2′—C1′—C6′	117.6 (2)
O2—C2—C1	113.8 (2)	O2′—C2′—C1′	114.4 (2)
C1—C2—C3	120.1 (2)	C1′—C2′—C3′	120.8 (2)
O2—C2—C3	126.0 (2)	O2′—C2′—C3′	124.9 (2)
C2—C3—C4	121.4 (2)	C2′—C3′—C4′	120.9 (2)
O3—C4—C3	121.3 (2)	O3′—C4′—C3′	121.8 (2)
C3—C4—C5	117.9 (2)	C3′—C4′—C5′	118.4 (2)
O3—C4—C5	120.8 (2)	O3′—C4′—C5′	119.9 (2)
C4—C5—C6	121.1 (2)	C4′—C5′—C6′	121.0 (2)
C1—C6—C5	121.3 (2)	C1′—C6′—C5′	121.3 (2)

Data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988). Cell refinement: *CELDIM* (Enraf–Nonius, 1988). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1253). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.
Carugo, O., Charalambous, J., Raghvani, D. V. & Sardone, N. (1996). *Acta Cryst.* **C52**, 153–155.
Enraf–Nonius (1988). *CAD*-4 *Manual*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Universities of York, England, and Louvain, Belgium.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1996). **C52**, 3204–3207

cis- and *trans*-4-*tert*-Butylcyclohexyl *p*-Nitrobenzenesulfonate at 130 K

JONATHAN M. WHITE, JOSY GIORDANO AND ALISON J. GREEN

School of Chemistry, University of Melbourne, Parkville, Vic 3052, Australia. E-mail: jonathan_white@muwayf.unimelb.edu.au

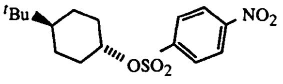
(*Received 19 April 1996; accepted 24 July 1996*)

Abstract

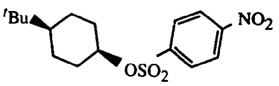
The structures of the title axial and equatorial cyclohexyl *p*-nitrobenzenesulfonate esters, $C_{16}H_{23}NO_5S$, determined at 130 K are reported. The $C_{alkyl}—O_{ester}$ bond distances of 1.487 (2) and 1.492 (2) Å are not significantly different from one another. The geometry of the sulfonate function with respect to both the phenyl and cyclohexane rings is essentially identical in both structures.

Comment

As part of our structural studies on the factors influencing C—O bond distances (White & Robertson, 1992; White, Green & Kuan, 1995), we required accurate C—O bond distances for axial and equatorial cyclohexyl *p*-nitrobenzenesulphonate esters for comparison purposes. The conformationally constrained cyclohexyl nosylates, *trans*-4-*tert*-butylcyclohexyl *p*-nitrobenzenesulfonate, (1), and *cis*-4-*tert*-butylcyclohexyl *p*-nitrobenzenesulfonate, (2), were chosen for this low-temperature study.

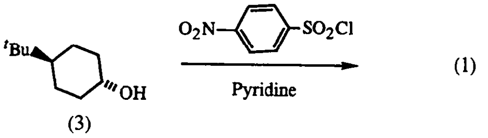


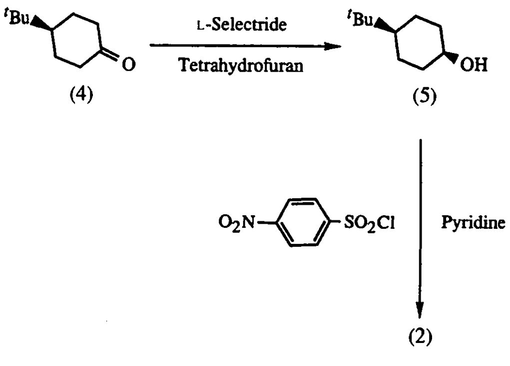
(1)



(2)

Compound (1) was prepared by esterification of commercially available *trans*-4-*tert*-butylcyclohexanol, (3), with *p*-nitrobenzenesulfonyl chloride in pyridine, and (2) was prepared by selective reduction of 4-*tert*-butylcyclohexanone, (4), with L-selectride giving *cis*-4-*tert*-butylcyclohexanol, (5), as the major product, which was similarly esterified using *p*-nitrobenzenesulfonyl chloride in pyridine.





The C1—O1 distances of 1.487 (2) and 1.492 (2) Å for (1) and (2), respectively, do not differ significantly

© 1996 International Union of Crystallography
Printed in Great Britain – all rights reserved

Acta Crystallographica Section C
ISSN 0108-2701 © 1996