Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

3,5,9,12-Tetra-*tert*-butyl-10,14-dicyclohexyl-2,8-dioxatetracyclo[5.4.0.$2^{1,9}$.$1^{3,7}$]-tetradeca-4,12-diene-6,11-dione

Kathrin Meindl,[a]* Lidiya A. Maslovskaya,[b] Mathias Noltemeyer[a] and Andrei I. Savchenko[c]

[a]Institute of Inorganic Chemistry, Tammannstrasse 4, D-37077 Göttingen, Germany, [b]Belarussian State University, pr. F. Skoriny 4, Minsk 220050, Belarus, and [c]Institute of Organic Chemistry, Tammannstrasse 2, D-37077 Göttingen, Germany

Correspondence e-mail:
meindl@shelx.uni-ac.gwdg.de

Key indicators

Single-crystal X-ray study
T = 200 K
Mean σ(C–C) = 0.003 Å
R factor = 0.052
wR factor = 0.143
Data-to-parameter ratio = 15.3

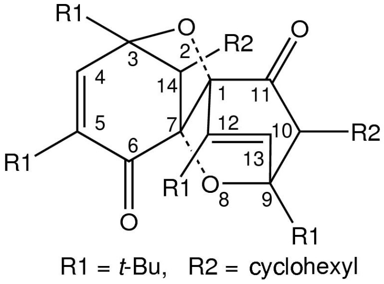
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 4 May 2005
Accepted 24 May 2005
Online 31 May 2005

The title compound, $C_{40}H_{62}O_4$, is formed by γ irradiation and contains a tetracyclo[5.4.0.$2^{1,9}$.$1^{3,7}$]tetradecane moiety. The cage consists of bicyclo[2.2.2]octane and bicyclo[3.2.1]octane rings, which are connected *via* a C—C single bond that is common to both rings. The title compound is formally a dimer of the adduct of a cyclohexyl radical and a 3,5-di-*tert*-butyl-*ortho*-quinone.

Comment

Sterically hindered *ortho*- and *para*-quinones formed from phenolic antioxidants may participate in further processes in a very complex manner. These compounds are well known trapping agents for alkyl radicals through the system of π bonds (Fendler & Fendler, 1974; Neta, 1988). As a part of our studies of the interaction of radiation-induced alkyl radicals with phenolic antioxidants (Maslovskaya *et al.*, 2002; Maslovskaya & Savchenko, 2003), we have investigated the transformation of 3,5-di-*tert*-butyl-*ortho*-quinone in cyclohexane solution under γ irradiation.



R1 = *t*-Bu, R2 = cyclohexyl
(I)

We present here the molecular structure (Fig. 1) of the title compound, (I), which is one of the products of the radiation-induced reaction of cyclohexyl radicals with 3,5-di-*tert*-butyl-*ortho*-quinone. This new substance has a tetracyclo[5.4.0.$2^{1,9}$.$1^{3,7}$]tetradecane framework. The main feature of the molecule is the C1–C7 bond [1.540 (2) Å], which is common to the bicyclo[2.2.2]- and the bicyclo[3.2.1]octene fragments. The dihedral angles in the bicyclo[3.2.1]octene system are 41.55 (13) (C3—C14—C6—C5), −2.26 (15) (C5—C6—C1—O2) and −17.23 (17)° (C1—O2—C3—C14), and are different from those described for a 6-oxabicyclo[3.2.1]oct-3-ene [refcode GOSLEF (Jotterand *et al.*, 1999) in the Cambridge Structural Database (CSD, Version 5.26; Allen, 2002)] (corresponding angles −29.1, 29.5 and 37.9°). The dihedral angles of the 2-oxabicyclo[2.2.2]octane fragment are −9.38 (13) (O8—C7—C12—C13), −0.31 (14) (C12—C13—C10—C11) and −1.06 (12)° (C10—C11—C7—O8), and do not

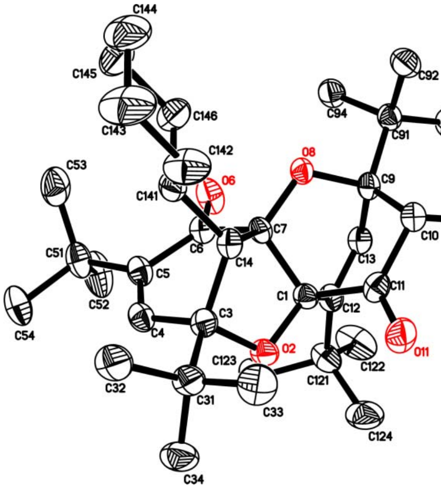


Figure 1
The molecular structure of compound (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

deviate much from the corresponding angles of eucalyptol (2-oxabicyclo[2.2.2]octane; Bond & Davies, 2001; CSD refcode MOFPAY), where the respective angles are 2.7, 0 and −2.7°. The three-atom bridge of the bicyclo[3.2.1]octene moiety is fixed in an almost planar conformation by the enone system C4—C5—C6—O6, with a torsion angle of 169.67 (18)°. The torsion angle O2—C1—C7—O8 [165.32 (13)°] describes the position of the bicyclic systems relative to one another.

Such a tetracyclic system (Fig. 1) has not been reported so far, but several compounds contain tricyclic fragments that can be formally derived from the title structure [CSD refcodes PACFOL01 (Fronczek & Caccamese, 1986), WANMAZ (Huipe-Nava *et al.*, 1993), PACFOL (Sims *et al.*, 1971), EGIVAR (Soriano-Garcia *et al.*, 2002) and LAUNIP (Kurata *et al.*, 1981)].

Experimental

The title compound, (I), was formed under γ irradiation (^{137}Cs source) of a deaerated cyclohexane solution containing 3,5-di-*tert*-butyl-*ortho*-quinone. The entire description of the results of the γ-radiolysis experiments will be published elsewhere (Maslovskaya & Savchenko, 2005). The compound was isolated as a minor product by preparative thin-layer chromatography on silica. Single crystals of (I) (m.p. 418–420 K) suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution in $Et_2O/CDCl_3/MeOH$ (1/1/1).

Crystal data

$C_{40}H_{62}O_4$
$M_r = 606.90$
Triclinic, $P\overline{1}$
$a = 10.006$ (2) Å
$b = 10.801$ (2) Å
$c = 17.705$ (4) Å
$\alpha = 89.63$ (3)°
$\beta = 83.97$ (3)°
$\gamma = 69.75$ (3)°
$V = 1784.4$ (7) Å^3

$Z = 2$
$D_x = 1.130$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 34 reflections
$\theta = 10$–12.5°
$\mu = 0.07$ mm^{-1}
$T = 200$ (2) K
Block, colourless
0.50 × 0.50 × 0.20 mm

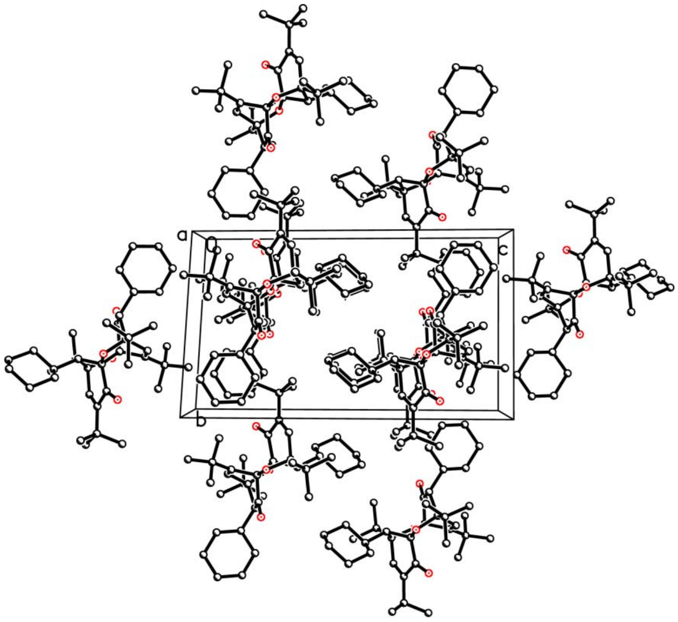


Figure 2
The crystal packing of (I); view along the *a* axis. H atoms have been omitted for clarity.

Data collection

Stoe AED2 diffractometer
$\omega/2\theta$ scans
6351 measured reflections
6254 independent reflections
5087 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.154$
$\theta_{\rm max} = 25.0°$

$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -9 \rightarrow 21$
3 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.143$
$S = 1.03$
6254 reflections
410 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0722P)^2 + 0.8303P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.28$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.23$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0076 (19)

Table 1
Selected geometric parameters (Å, °).

C1—C7	1.540 (2)		
C4—C5—C6—O6	169.67 (18)	C1—O2—C3—C14	−17.23 (17)
O2—C1—C7—O8	165.32 (13)	O8—C7—C12—C13	−9.38 (13)
C3—C14—C6—C5	41.55 (13)	C12—C13—C10—C11	−0.31 (14)
O2—C1—C6—C5	−2.26 (15)	C10—C11—C7—O8	−1.06 (12)

H atoms bonded to C atoms were placed at calculated positions and refined using a riding model. The constrained C—H distances were 0.95, 0.98, 0.99 and 1.00 Å for aryl, methyl, methylene and ethylene H atoms, respectively. The $U_{\rm iso}$(H) values were set at $1.5U_{\rm eq}$(C) for methyl H atoms and $1.2U_{\rm eq}$(C) for all other H atoms. Only a very small number of equivalent reflections was measured, which leads to a very high value of $R_{\rm int}$. As there are only weak van der Waals interactions between the molecules, the cyclohexyl and

Acta Cryst. (2005). E**61**, o1950–o1952 Meindl *et al.* • $C_{40}H_{62}O_4$ **o1951**

tert-butyl substituents are very flexible in the crystal structure (Fig. 2) and thus have larger U_{eq}, as would be expected for non-solvent C atoms.

Data collection: *DIF4* (Langhoff, 1986); cell refinement: *DIF4*; data reduction: *REDU4* (Langhoff, 1986); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2001); software used to prepare material for publication: *SHELXTL*.

LAM and AIS are grateful to Professor A. de Meijere for support during this work. KM is grateful to Dr S. Rühl, Göttingen, for his careful proofreading of the final manuscript.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Bond, A. D. & Davies, J. E. (2001). *Aust. J. Chem.* **54**, 683–684.

Fendler, J. H. & Fendler, E. J. (1974). *The Chemistry of the Quinoid Compounds*, Vol. 1, Part 2, edited by S. Patai & Z. Rappoport, pp. 539–578. New York: Wiley.

Fronczek, F. R. & Caccamese, S. (1986). *Acta Cryst.* C**42**, 1649–1651.

Huipe-Nava, E., Igonin, V. A., Lindeman, S. V., Struchkov, Y. T., Mendoza, V., Garcia, G, E. & Guzman, J. A. (1993). *Acta Cryst.* C**49**, 1207–1209.

Jotterand, N., Vogel, P. & Schenk, K. (1999). *Helv. Chim. Acta*, **82**, 821–847.

Kurata, K., Furusaki, A., Katayama, C., Kikuchi, H. & Suzuki, T. (1981). *Chem. Lett.* pp. 773–776.

Langhoff, H. (1986). *DIF4* (Revision 6.2) and *REDU4*. Stoe & Cie, Darmstadt, Germany.

Maslovskaya, L. A., Polyakov, Y. S. & Savchenko, A. I. (2002). *High Energy Chem.* **36**, 213–216.

Maslovskaya, L. A. & Savchenko, A. I. (2003). *Russ. J. Gen. Chem.* **73**, 394–400.

Maslovskaya, L. A. & Savchenko, A. I. (2005). *Russ. J. Gen. Chem.* In the press.

Neta, P. (1988). *The Chemistry of the Quinoid Compounds*, Vol. 2, Part 2, edited by S. Patai & Z. Rappoport, pp. 879–898. New York:Wiley.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (2001). *SHELXTL*. Release 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.

Sims, J. J., Fenical, W., Wing, R. M. & Radlick, P. (1971). *J. Am. Chem. Soc.* **93**, 3774–3775.

Soriano-Garcia, M., Huipe-Nava, E., Gonzalez, V. M., Garibay, E. G. & Guzman, J. A. (2002). *Anal. Sci.* **18**, 857–858.

o1952 Meindl *et al.* • $C_{40}H_{62}O_4$ *Acta Cryst.* (2005). E**61**, o1950–o1952