Table 1. *Selected torsion angles (°)*

N9—C1′—C2′—O2′	−87.8 (4)	C3′—C4′—O4′—C1′	−7.7 (4)
O4′—C1′—C2′—C3′	35.4 (3)	O4′—C4′—C5′—O5′	−80.9 (3)
C3′—C2′—O2′—S	−172.0 (2)	C3′—C4′—C5′—O5′	38.5 (4)
C1′—C2′—O2′—S	72.8 (3)	C2′—O2′—S—OS2	−69.4 (3)
C1′—C2′—C3′—C4′	−38.8 (3)	C2′—O2′—S—OS1	162.8 (3)
C2′—C3′—C4′—O4′	29.1 (3)	C2′—O2′—S—C10	46.4 (3)
C2′—C1′—O4′—C4′	−17.4 (3)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H61···N7^{i}	0.86	2.14	2.990 (5)	170
N6—H62···N1^{ii}	0.86	2.16	2.952 (5)	154
O3′—HO3′···O5′^{iii}	0.92 (5)	1.87 (5)	2.778 (4)	171 (5)
O5′—HO5′···N3	0.68 (6)	2.10 (6)	2.780 (4)	176 (7)

Symmetry codes: (i) $2-x, \frac{1}{2}+y, 1-z$; (ii) $2-x, y-\frac{1}{2}, 1-z$; (iii) $1-x, y-\frac{1}{2}, -z$.

All H atoms were located riding on their parent atoms, and their occupancies and U values were refined.

Data collection: *CAD*-4 (Enraf–Nonius, 1985). Cell refinement: *CAD*-4 (Enraf–Nonius, 1985). Data reduction: *Structure Determination Package* (Frenz, 1982). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *Xtal_GX* (Hall & du Boulay, 1995). Software used to prepare material for publication: *SHELXL*93.

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References

Altona, C. & Sundaralingam, M. (1972). *J. Am. Chem. Soc.* **94**, 8205–8212.

Enraf–Nonius (1985). *CAD-4 Diffractometer Control Program*. Enraf–Nonius, Delft, The Netherlands.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Frenz, B. A. (1982). *Enraf–Nonius Structure Determination Package*. Version 4.2. Enraf–Nonius, Delft, The Netherlands.

Gautham, N., Seshadri, T. P., Viswamitra, M. A. & Salisbury, S. A. (1983). *Acta Cryst.* C**39**, 459–461.

Hall, S. R. & du Boulay, D. (1995). *Xtal_GX*. University of Western Australia, Australia.

Krishnan, R. & Seshadri, T. P. (1993). *J. Biomol. Struct. Dyn.* **10**, 727–745.

Mande, S. S., Seshadri, T. P. & Viswamitra, M. A. (1988). *Acta Cryst.* C**44**, 912–914.

Mande, S. S., Seshadri, T. P. & Viswamitra, M. A. (1989). *Acta Cryst.* C**45**, 92–94.

Neidle, S., Chattopadhyaya, J. P., Hossain, N. & Papchikhin, A. (1996). *Acta Cryst.* C**52**, 3173–3177.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–357.

Padiyar, G. S. & Seshadri, T. P. (1998). *J. Biomol. Struct. Dyn.* **15**, 793–821.

Saenger, W. & Suck, D. (1973). *Nature*, **242**, 610–612.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Suhadolnik, R. J. (1970). *Nucleoside Antibiotics*. New York: Wiley.

Acta Cryst. (1999). C**55**, 608–610

2-Bromo-2,3-diphenylmethano-2,3-dihydronaphthoquinone

TAKUMI OSHIMA,[a] KAZUAKI FUKUSHIMA[a] AND TATSUYA KAWAMOTO[b]

[a]*Department of Applied Chemistry, Faculty of Engineering, Osaka University, 1-16 Machikaneyama, Toyonaka, Osaka 560-0043, Japan, and* [b]*Department of Chemistry, Graduate School of Science, Osaka University, 1-16 Machikaneyama, Toyonaka, Osaka 560-0043, Japan. E-mail: oshima@ch.wani.osaka-u.ac.jp*

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Abstract

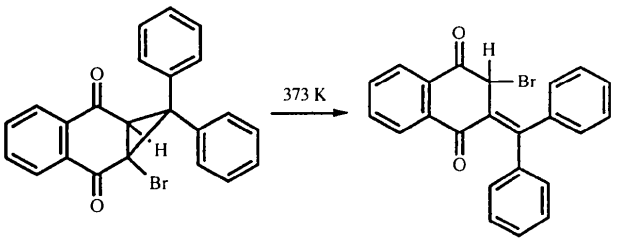
In the title compound, a diphenylhomonaphthoquinone, $C_{23}H_{15}BrO_2$, the quinone frame adopts a slightly boat-shaped conformation, with folding angles of 11 (3) and 14 (3)°. The severe steric congestion between the *endo*-phenyl group and the quinone moiety results in considerable freezing of the aromatic ring.

Comment

The thermal ring-opening of cyclopropanes is much influenced by the spatial arrangement of adjacent unsaturated substituents such as C=C, C=O and phenyl groups, because the cyclopropane σ-bond is recognized as being greatly analogous to a C=C double bond (Meijere, 1979; Wong *et al.*, 1989). The most favourable orbital interaction is geometrically attained in the bisected conformation between the cyclopropane ring and the planes of the unsaturated substituents (Tidwell, 1985; Crabb & Patel, 1992).

Thermolysis of the title compound, (I), at 373 K yields the diphenylmethylene-substituted dihydronaphthoquinone, (II), *via* cyclopropane ring-opening accompanied by a simultaneous bromide migration (Oshima *et al.*, 1994). A preliminary kinetic study of the thermolysis of (I) and of *p*-substituted homologues reveals that the *exo*-aromatic substituents affect the rates much more than the corresponding *endo*-ones. The logarithmic correlation of the rate constants (ks^{-1} at 373 K in toluene) with the Brown σ^+ (Brown & Okamoto, 1958) was $\log k = -0.79\sigma^+ - 4.39$ ($r = 0.999$) for the five *endo*-aromatic substituents (*p*-CH_3O, *p*-CH_3, *p*-H, *p*-Cl, *p*-NO_2), while the more pronounced substituent effects were observed for the corresponding *exo*-substituents, for which $\log k = -1.90\sigma^+ - 4.23$ ($r = 0.999$). The negative ρ values (−0.79 and −1.90) and the correlation with σ^+ imply that the electron-donating π-participation of the aromatic rings to the breaking cyclopropane bond plays an important role in the bromide-releasing ring-

opening of (I). The X-ray crystal analysis of (I) was undertaken in order to explore the structural features of this aromatic participation.



(I) (II)

The molecular structure of (I) is shown in Fig. 1. The two quinone carbonyl groups are slightly folded, as indicated by the torsion angles of 165.3 (13)° for O2—C9—C8—C3 and −163.9 (12)° for O1—C2—C3—C8. In the conformationally fixed homonaphthoquinone frame, the π-conjugation of the carbonyl groups seems to be considerable, because the torsion angle for O1—C2—C1—*m*1, where *m*1 is the midpoint of the distal C10—C11 bond, is −158.3° and the corresponding angle for O2—C9—C10—*m*2, where *m*2 is the midpoint of the C1—C11 bond, is 161.5°, both being almost in an effective range of ±30° about the ideal 180° (*trans*-bisected; Allen, 1980).

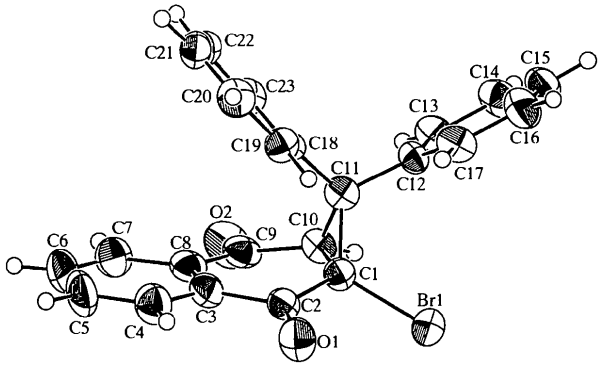


Fig. 1. A view of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level, and H atoms are drawn as spheres of an arbitrary radius.

The two phenyl groups in (I) adopt nearly perpendicular conformations for the π-orbital interaction with cyclopropane, as indicated by the torsion angles of 88.6° for C19—C18—C11—*m*3 and 75.3° for C13—C12—C11—*m*3, where *m*3 represents the midpoint of the distal C1—C10 bond. However, in solution, the *exo*-phenyl ring is allowed to adopt an ideal bisected conformation associated with free rotation around the C11—C12 axis, whereas the *endo*-phenyl is far from such a favourable alignment, due to the steric repulsion with the facing quinone plane. Based on the X-ray crystal data, the computationally attempted aromatic rotation (on the C11—C18 axis) to a bisected conformation (CAChe Scientific, 1995) leads to unendurable intramolecular contacts between C23 (*o*-C atom of the *endo*-aromatic) and the fused quinone C atoms C3 and C8, of 2.285 and 2.332 Å, respectively. These values are well below the sum of the van der Waals radii for two C atoms (3.54 Å). These stereochemical situations are responsible for the kinetic substituent effects described above.

Experimental

The title compound was prepared according to the procedure described by Oshima *et al.* (1994) and recrystallized from hexane–benzene solution at room temperature.

Crystal data

$C_{23}H_{15}BrO_2$
M_r = 403.274
Monoclinic
$C2/c$
a = 18.62 (1) Å
b = 12.691 (8) Å
c = 17.42 (1) Å
β = 121.17 (5)°
V = 3522 (4) Å^3
Z = 8
D_x = 1.52 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 22 reflections
θ = 10.7–12.4°
μ = 2.348 mm^{-1}
T = 298 K
Plate
0.7 × 0.5 × 0.3 mm
Colourless

Data collection

MacScience *MXC*3 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical *via* ψ scans (*CRYSTAN*; Edwards *et al.*, 1995)
T_{min} = 0.335, T_{max} = 0.494
4592 measured reflections
3455 independent reflections

2641 reflections with $I > 2.5\sigma(I)$
R_{int} = 0.054
θ_{max} = 26.43°
$h = 0 \rightarrow 24$
$k = -16 \rightarrow 0$
$l = -22 \rightarrow 19$
3 standard reflections every 100 reflections
intensity decay: none

Refinement

Refinement on F
R = 0.054
wR = 0.067
S = 2.296
2641 reflections
250 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o) + 0.005F_o^2]$

$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 1.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.73 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Br1—C1	1.910 (8)	C10—C11	1.524 (11)
O1—C2	1.201 (10)	C11—C12	1.510 (11)
O2—C9	1.209 (11)	C11—C18	1.515 (11)
C1—C2	1.498 (11)	C12—C13	1.375 (11)
C1—C10	1.524 (11)	C12—C17	1.379 (12)
C1—C11	1.540 (11)	C13—C14	1.383 (13)

C2—C3	1.490 (12)	C14—C15	1.363 (15)
C3—C4	1.398 (13)	C15—C16	1.375 (15)
C3—C8	1.406 (12)	C16—C17	1.396 (13)
C4—C5	1.374 (15)	C18—C19	1.388 (11)
C5—C6	1.378 (17)	C18—C23	1.390 (11)
C6—C7	1.376 (18)	C19—C20	1.382 (12)
C7—C8	1.399 (12)	C20—C21	1.374 (12)
C8—C9	1.476 (13)	C21—C22	1.377 (14)
C9—C10	1.473 (12)	C22—C23	1.389 (13)
Br1—C1—C2	112.7 (5)	C8—C9—C10	118.3 (8)
Br1—C1—C10	117.7 (6)	C1—C10—C9	119.1 (7)
Br1—C1—C11	119.0 (5)	C1—C10—C11	60.7 (5)
C2—C1—C10	118.8 (7)	C9—C10—C11	122.0 (7)
C2—C1—C11	119.4 (7)	C1—C11—C10	59.6 (5)
C10—C1—C11	59.6 (5)	C1—C11—C12	118.9 (7)
O1—C2—C1	122.0 (7)	C1—C11—C18	118.4 (6)
O1—C2—C3	120.8 (8)	C10—C11—C12	116.6 (7)
C1—C2—C3	117.2 (7)	C10—C11—C18	121.1 (7)
C2—C3—C4	118.0 (8)	C12—C11—C18	112.6 (7)
C2—C3—C8	121.8 (8)	C11—C12—C13	120.9 (8)
C3—C8—C9	121.5 (8)	C11—C12—C17	119.5 (7)
C7—C8—C9	120.4 (9)	C11—C18—C19	121.1 (7)
O2—C9—C8	122.5 (8)	C11—C18—C23	119.7 (7)
O2—C9—C10	119.3 (8)		
Br1—C1—C2—O1	23.3 (7)	C3—C8—C9—O2	165.3 (13)
Br1—C1—C2—C3	−155.5 (9)	C3—C8—C9—C10	−14.3 (8)
Br1—C1—C10—C9	138.4 (9)	C7—C8—C9—O2	−13.6 (9)
Br1—C1—C10—C11	−109.2 (7)	C7—C8—C9—C10	166.8 (12)
Br1—C1—C11—C10	106.9 (7)	O2—C9—C10—C1	−163.2 (12)
Br1—C1—C11—C12	1.2 (6)	O2—C9—C10—C11	125.0 (12)
Br1—C1—C11—C18	−141.8 (9)	C8—C9—C10—C1	16.4 (7)
C10—C1—C2—O1	166.8 (11)	C8—C9—C10—C11	−55.4 (9)
C10—C1—C2—C3	−12.0 (7)	C1—C10—C11—C1	0.0 (5)
C2—C1—C10—C9	−3.4 (7)	C1—C10—C11—C12	109.5 (8)
C2—C1—C10—C11	109.1 (8)	C1—C10—C11—C18	−106.9 (8)
C11—C1—C2—O1	−123.8 (11)	C9—C10—C11—C1	107.9 (9)
C11—C1—C2—C3	57.4 (8)	C9—C10—C11—C12	−142.6 (11)
C2—C1—C11—C10	−108.1 (8)	C9—C10—C11—C18	1.0 (7)
C2—C1—C11—C12	146.3 (10)	C1—C11—C12—C13	109.6 (10)
C2—C1—C11—C18	3.2 (7)	C1—C11—C12—C17	−74.9 (9)
C11—C1—C10—C9	−112.5 (8)	C1—C11—C18—C19	54.5 (8)
C10—C1—C11—C10	0.0 (5)	C1—C11—C18—C23	−130.5 (10)
C11—C1—C10—C11	0.0 (5)	C10—C11—C12—C13	41.3 (8)
C10—C1—C11—C12	−105.6 (8)	C10—C11—C12—C17	−143.3 (11)
C10—C1—C11—C18	111.3 (8)	C10—C11—C18—C19	124.3 (10)
O1—C2—C3—C4	13.5 (8)	C10—C11—C18—C23	−60.7 (8)
O1—C2—C3—C8	−163.9 (12)	C18—C11—C12—C13	−105.4 (10)
C1—C2—C3—C4	−167.6 (11)	C18—C11—C12—C17	70.1 (9)
C1—C2—C3—C8	14.9 (8)	C12—C11—C18—C19	−90.8 (9)
C2—C3—C4—C5	−178.2 (13)	C12—C11—C18—C23	84.3 (9)
C2—C3—C8—C7	177.2 (13)	C11—C12—C13—C14	177.5 (13)
C2—C3—C8—C9	−1.8 (8)	C11—C12—C17—C16	−177.2 (12)
C4—C3—C8—C9	−179.1 (13)	C11—C18—C19—C20	176.0 (12)
C6—C7—C8—C9	179.3 (14)	C11—C18—C23—C22	−176.5 (12)

The highest residual electron-density peak is located near Br1.

Data collection: *CRYSTAN* (Edwards *et al.*, 1995). Cell refinement: *CRYSTAN*. Data reduction: *CRYSTAN*. Program(s) used to solve structure: *CRYSTAN*. Program(s) used to refine structure: *CRYSTAN*. Molecular graphics: *CRYSTAN*. Software used to prepare material for publication: *CRYSTAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1073). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (1980). *Acta Cryst.* B**36**, 81–96.

Brown, H. C. & Okamoto, Y. (1958). *J. Am. Chem. Soc.* **80**, 4979–4987.

CAChe Scientific (1995). *CAChe Work-System*. Version 3.8. CAChe Scientific, Inc., Beaverton, Oregon, USA.

Crabb, T. A. & Patel, A. V. (1992). *Rodd's Chemistry of Carbon Compounds*, 2nd Suppl. to the 2nd ed., edited by M. Sainsbury, Vol. II*A/B*, ch. 1, pp. 1–80. Amsterdam: Elsevier.

Edwards, C., Gilmore, C. J., Mackay, S. & Stewart, N. (1995). *CRYSTAN. A Computer Program for the Solution and Refinement of Crystal Structures*. MacScience, Yokohama, Japan.

Meijere, A. (1979). *Angew. Chem. Int. Ed. Engl.* **18**, 809–826.

Oshima, T., Tamada, K. & Nagai, T. (1994). *J. Chem. Soc. Perkin Trans.* 1, pp. 3325–3333.

Tidwell, T. T. (1985). *The Chemistry of the Cyclopropyl Group*, edited by Z. Rappoport, pp. 565–632. New York: John Wiley & Sons.

Wong, H. N. C., Hon, M.-Y., Tse, C.-W. & Yip, Y.-C. (1989). *Chem. Rev.* **89**, 165–198.

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Absolute structure of an *N*-pentenoyl benzisothiazole

ANDREW B. HUGHES, MAUREEN F. MACKAY AND NARELLE L. MCCAFFREY

Department of Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia. E-mail: xraymm2@lure.latrobe.edu.au

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Abstract

The title compound, (+)-(3a*R*,6*S*,7a*S*)-1-(8,8-dimethyl-2,2-dioxo-1,3,3a,4,5,6,7,7a-octahydro-3a,6-methano-2,1-benzisothiazol-1-yl)-3,4-dimethyl-4-penten-1-one, $C_{17}H_{27}NO_3S$, was isolated as the major product from a copper-mediated conjugate addition reaction. The absolute stereochemistry of the *N*-pentenoyl side chain was established. The latter is extended and the cyclohexane ring adopts a boat conformation, whilst the benzisothiazole ring is between a half-chair and envelope.

Comment

As part of a project on the synthesis of a marine natural product, a diastereoselective conjugate addition was performed which resulted in the isolation of the title compound, (1), as a mixture of diastereoisomers (yield 53%). The conjugate addition was between the cuprate, generated *in situ* from 2-propenyl magnesium bromide and cuprous iodide, and the crotonyl sultam, (2). The major diastereoisomer of the title compound, $[\alpha]_D^{24}$ + 64° (c = 0.06 in $CHCl_3$), crystallised from a hexane solution of the product mixture. The minor diastereoisomer was easily removed as it remained dissolved in the mother liquors. The diastereoisomeric excess was approximately 50% (based on ^{1}H NMR integral ratios). An X-ray analysis of crystals of (1) was