Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.705$, $T_{\max} = 0.799$
7043 measured reflections
3093 independent reflections
2668 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.043$
$\theta_{\max} = 74.86°$
$h = -1 \rightarrow 14$
$k = -16 \rightarrow 16$
$l = -1 \rightarrow 25$
3 standard reflections
frequency: 120 min
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.125$
$S = 1.057$
3093 reflections
264 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0587P)^2 + 0.4861P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.005$
$\Delta\rho_{\max} = 0.213$ e Å^{-3}
$\Delta\rho_{\min} = -0.270$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0031 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

N1—C2	1.294 (2)	C11—O11	1.197 (2)
C6—O6	1.234 (2)	C16—O16	1.191 (2)
N1—C2—N3	126.74 (14)	C8—N7—C5	106.27 (11)
C2—N3—C4	115.75 (11)	C8—N9—C4	102.80 (11)
N1—C6—C5	114.06 (11)		
C8—N7—C10—C11	106.8 (2)	C2—N3—C15—C16	−68.9 (2)
N7—C10—C11—O12	172.02 (13)	N3—C15—C16—O16	−6.5 (3)
O11—C11—O12—C13	1.8 (2)	C15—C16—O17—C18	−179.5 (2)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *DATREDXL* (Brookhaven National Laboratory & University of Birmingham, 1986). Program(s) used to solve structure: *MULTAN*84 (Main, Germain & Woolfson, 1984). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

We thank the Engineering and Physical Sciences Research Council (EPSRC), for a total technology studentship (GS), the EPSRC Mass Spectrometry Service (Swansea), Celltech Therapeutics (Slough), for continuous support of the DNA molecular recognition project, and Mike Eaton and Jim Turner for helpful discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1236). Services for accessing these data are described at the back of the journal.

References

Brookhaven National Laboratory & University of Birmingham (1986). *DATREDXL. Program for Data Reduction.* University of Birmingham, England.
Chan, D. M. C., Sood, G., Schwalbe, C. H. & Fraser, W. (1995). *Acta Cryst.* C**51**, 2383–2386.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Flensburg, C. & Egholm, M. (1994). *Acta Cryst.* C**50**, 1480–1482.
Green, G. R., Grinter, T. J., Kincey, P. M. & Jarvest, R. L. (1990). *Tetrahedron*, **46**, 6903–6914.
Johnson. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Main, P., Germain, G. & Woolfson, M. M. (1984). *MULTAN*84. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Universities of York, England, and Louvain, Belgium.
Munns, A. R. I. & Tollin, P. (1970). *Acta Cryst.* B**26**, 1101–1113.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Robins, M. J., Zou, R. M., Guo, Z. & Wnuk, S. F. (1996). *J. Org. Chem.* **61**, 9207-9212.
Rosenstein, R. D., Oberding, M., Hyde, J. R., Zubieta, J., Karlin, K. D. & Seeman, N. C. (1982). *Cryst. Struct. Commun.* **11**, 1507–1513.
Schmalle, H. W., Hänggi, G. & Dubler, E. (1988). *Acta Cryst.* C**44**, 732–736.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Sletten, J. & Jensen, L. H. (1969). *Acta Cryst.* B**25**, 1608–1614.
Sood, G., Schwalbe, C. H. & Fraser, W. (1997). *Acta Cryst.* C**53**, 1624–1626.
Thewalt, U., Bugg, C. E. & Marsh, R. E. (1970). *Acta Cryst.* B**26**, 1089–1101.

Acta Cryst. (1998). C**54**, 116–119

Photochemistry of Triptycene-1,4-quinone

TAI Y. FU, JANET N. GAMLIN, GUNNAR OLOVSSON, JOHN R. SCHEFFER, JAMES TROTTER AND DEAN T. YOUNG

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1. E-mail: jtrt@xray4.chem.ubc.ca

(*Received 27 May 1997; accepted 15 September 1997*)

Abstract

Photolysis of 9,10-dihydro-9,10[1′,2′]benzenoanthracene-1′,4′-quinone, $C_{20}H_{12}O_2$, in oxygenated acetone gives the novel photoproduct 9,10-dihydro-9,10-ethanoanthracen-11-one-12-spiro-2′-cyclopent-4′-ene-1′, 3′-dione, $C_{20}H_{12}O_3$. The reactant quinone molecule has ideal *mm* symmetry and lies on a crystallographic mirror plane in *Pnma*; the photoproduct molecule has ideal *m* symmetry, which is not utilized in packing in $Pna2_1$. This product is formed only in the presence of oxygen and a mechanism for its formation is proposed. Unreactivity in attempted solid-state photolysis can be rationalized in terms of crystal packing.

Comment

Photolysis of triptycene-1,4-quinone (9,10-dihydro-9,10-[1′,2′]benzenoanthracene-1′,4′-quinone), (1) (Fig. 1), in deoxygenated acetonitrile, methanol, or ethanol, leads to a single di-π-methane type photoproduct, (3), whose structure was established from spectroscopic data (Fu *et al.*, 1995; Gamlin, 1996). The structure of (3) indicates that initial bond formation in the well established mechanism for the di-π-methane reaction (Zimmerman, 1991) is between quinone and benzo ring atoms (*e.g.* atoms C3 and C5 in Fig. 2*a*), which disrupts only one benzenoid ring, and results in a biradical which is stabilized by delocalization of an electron over the adjacent carbonyl group (Fig. 1); thus only one, of two possible, products is formed (the other would involve benzo–benzo bridging).

Photolysis of (1) in deoxygenated acetone also yields photoproduct (3), but when oxygen is present a different product is obtained, whose structure is established by X-ray crystal analysis as (2) (Figs. 1 and 2*b*); this structure is in accord with the spectroscopic data (see supplementary material). Photolysis in deoxygenated chloroform or carbon tetrachloride leads to chlorinated photoproducts (Fu *et al.*, 1995; Gamlin, 1996).

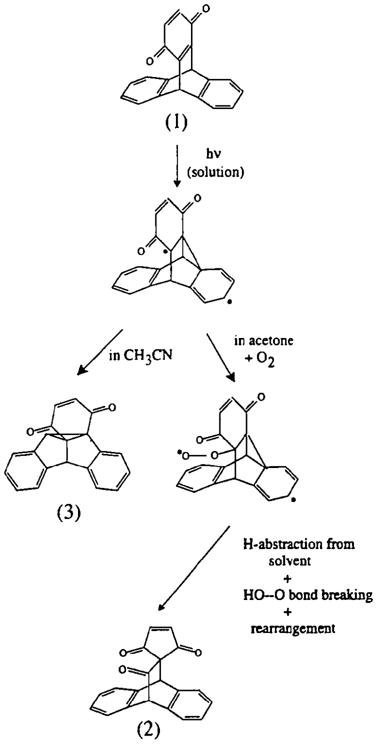


Fig. 1. Photochemistry of triptycene-1,4-quinone, (1).

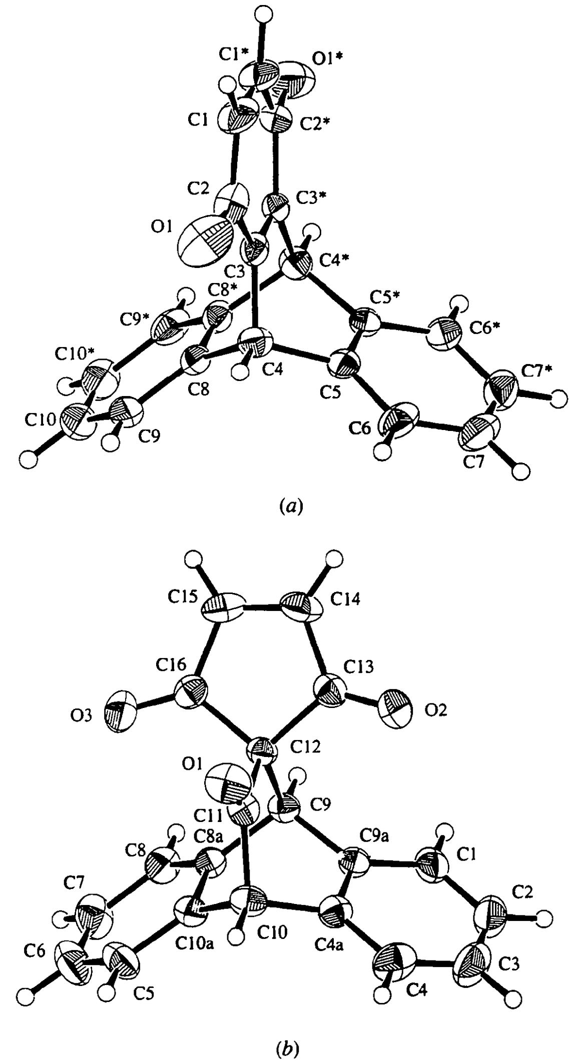


Fig. 2. Views of the molecules of (*a*) quinone (1), and (*b*) photoproduct (2) [33% ellipsoids; convenient crystallographic numbering system for (1) and dibenzobarrelene numbering system for (2)].

In the crystal structure of (1) (*Pnma*, $Z = 4$), the molecule lies on a crystallographic mirror plane, which is perpendicular to the plane of the quinone ring; the molecule has ideal *mm* symmetry (Fig. 2*a*). The molecule of photoproduct (2) has ideal symmetry *m* (Fig. 2*b*), which is not utilized in the crystal structure ($Pna2_1$, $Z = 4$). Both molecules have normal geometries and dimensions.

The reaction pathway for the formation of (2) probably proceeds through the same intermediate biradical as in the di-π-methane reaction (Fig. 1); this biradical could then undergo the di-π-methane rearrangement in the absence of oxygen to yield (3), or react with dissolved oxygen in the air-saturated acetone solvent. The O_2-containing intermediate could then abstract hydrogen from the solvent, and breaking of the HO—O bond and rearrangement would lead to photoproduct (2) (Fig. 1).

Irradiation of quinone (1) in the solid state leads to no photochemical reaction. This is unexpected, since photochemical reactivity in the solid state is found for a wide variety of 9,10-ethenoanthracene derivatives (*e.g.* Chen, Scheffer & Trotter, 1992), and the primary incentive for studying triptycene-1,4-quinone was to investigate its solid-state photochemistry. A likely reason for this lack of solid-state reactivity is the effect of intermolecular interactions. The molecules of (1) pack in layers on the mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$. Within each layer (Fig. 3), the molecules are interlocked so that the space between each ring in the molecule is partly filled by a ring from a neighbouring molecule. Photochemical reaction involves quinone–benzo bond formation, with a change in dihedral angle between the quinone and benzo rings from an ideal 120 to *ca* 60°. In the crystal, the atomic movements required are resisted by the interleaving rings of the neighbouring molecules.

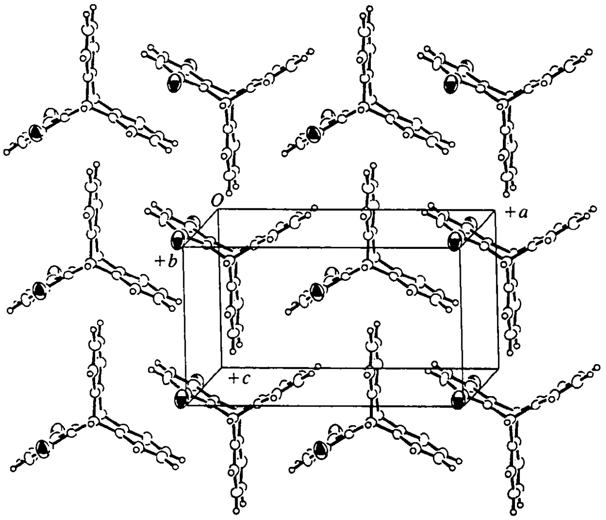


Fig. 3. View of the unit cell of quinone (1) showing one layer at $y = \frac{1}{4}$ (positive direction of the y axis towards the viewer).

Experimental

Quinone (1) was synthesized by Diels–Alder reaction of *p*-benzoquinone and anthracene, followed by aromatization and oxidation (details in supplementary material). Photolysis in acetone in the presence of oxygen gave photoproduct (2).

Compound (1)

Crystal data

$C_{20}H_{12}O_2$
$M_r = 284.31$
Orthorhombic
Pnma
$a = 13.979 (2)$ Å
$b = 12.608 (7)$ Å
$c = 8.024 (2)$ Å
$V = 1414 (1)$ Å^3
$Z = 4$
$D_x = 1.335$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 15 reflections
$\theta = 10.2$–$17.8°$
$\mu = 0.080$ mm^{-1}
$T = 294$ K
Plate
0.30 × 0.20 × 0.08 mm
Yellow

Data collection

Rigaku AFC-6*S* diffractometer
ω–2θ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.93$, $T_{\max} = 0.99$
2657 measured reflections
2657 independent reflections

506 reflections with $I > 3\sigma(I)$
$\theta_{\max} = 32.52°$
$h = 0 \rightarrow 21$
$k = 0 \rightarrow 19$
$l = -12 \rightarrow 0$
3 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.058$
$wR(F^2) = 0.177$
$S = 1.087$
2657 reflections
100 parameters
H atoms in calculated positions, C—H = 0.95 Å, $U = 1.2U(\mathrm{C})$

$w = 1/[\sigma^2(F_o^2) + 0.0004(F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.032$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (2)

Crystal data

$C_{20}H_{12}O_3$
$M_r = 300.31$
Orthorhombic
$Pna2_1$
$a = 12.274 (3)$ Å
$b = 7.957 (3)$ Å
$c = 15.444 (3)$ Å
$V = 1508 (1)$ Å^3
$Z = 4$
$D_x = 1.322$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 23 reflections
$\theta = 10.0$–$17.7°$
$\mu = 0.083$ mm^{-1}
$T = 294$ K
Prism
0.40 × 0.20 × 0.20 mm
Yellow

Data collection

Rigaku AFC-6*S* diffractometer
ω–2θ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.96$, $T_{\max} = 0.98$
2278 measured reflections
2278 independent reflections

1100 reflections with $I > 3\sigma(I)$
$\theta_{\max} = 29.99°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 11$
$l = -21 \rightarrow 0$
3 standard reflections every 200 reflections intensity decay: 0.1%

Refinement

Refinement on F^2
$R(F) = 0.037$
$wR(F^2) = 0.103$
$S = 1.078$
2278 reflections
207 parameters
H atoms in calculated positions, C—H = 0.95 Å, $U = 1.2U(\mathrm{C})$

$w = 1/[\sigma^2(F_o^2) + 0.0004(F_o)^2]$
$(\Delta/\sigma)_{\max} = 0.07$
$\Delta\rho_{\max} = 0.46$ e Å^{-3}
$\Delta\rho_{\min} = -0.48$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

X-ray intensity data for (1) are rather weak, with only 19% greater than 3σ. For (2), the opposite polarity gave identical R factors to the reported structure.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994); cell refinement: *MSC/AFC Diffractometer Control Soft-*

ware; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structures: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1071). Services for accessing these data are described at the back of the journal. Details of the synthesis and photochemistry are also available.

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.

Chen, J., Scheffer, J. R. & Trotter, J. (1992). *Tetrahedron*, **48**, 3251–3274.

Fu, T. Y, Gamlin, J. N., Olovsson, G., Scheffer, J. R., Trotter, J. & Young, D. T. (1995). *Tetrahedron Lett.* **36**, 2025–2028.

Gamlin, J. N. (1996). PhD thesis, University of British Columbia, Vancouver, Canada.

Molecular Structure Corporation (1994). *MSC/AFC Diffractometer Control Software*. Version 4.3.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1995). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Zimmerman, H. E. (1991). *Organic Photochemistry*, Vol. 11, edited by A. Padwa, ch. 1. New York: Marcel Dekker.

Acta Cryst. (1998). C**54**, 119–120

N-Benzyl-3-benzylideneisoindolin-1-one

M. Wahab Khan,[a] Subhadra Guha,[b] Alok K. Mukherjee[b] and Nitya G. Kundu[a]

[a]*Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India, and* [b]*Department of Physics, Jadavpur University, Calcutta 700 032, India. E-mail: sspmm@iacs.ernet.in*

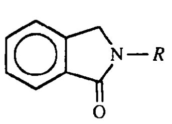
(*Received 23 June 1997; accepted 9 September 1997*)

Abstract

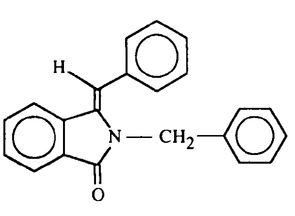
The title compound, $C_{22}H_{17}NO$, is formed by the palladium-catalyzed reaction between *N*-benzyl-*o*-iodobenzamide and phenylacetylene. The molecules contain three planar parts, namely the isoindolinone moiety (*A*) and the phenyl rings of the benzyl and benzylidene groups (*B* and *C*, respectively), and display the *Z* configuration. Rings *B* and *C* are inclined by 14.9 (1)° with respect to each other and are approximately orthogonal to the isoindolinone moiety *A*; the dihedral angles *A*/*B* and *A*/*C* are 98.23 (4) and 111.08 (3)°, respectively.

Comment

Palladium-catalyzed heteroannulation has been found to be a useful synthetic tool for the formation of a variety of heterocyclic compounds (Chowdhury & Kundu, 1996; Spencer *et al.*, 1995; Kundu & Pal, 1993). However, efforts towards the synthesis of compounds containing the isoindolinone moiety, (1), through palladium-catalyzed reactions have been limited in nature (Cho *et al.*, 1996). Recently, we synthesized *N*-benzyl-3-benzylidene-1-isoindolinone, (2), by the palladium-catalyzed reaction between *N*-benzyl-*o*-iodobenzamide and phenylacetylene. The X-ray structural study of (2) was undertaken in order to establish the regio- and stereospecificities of the reaction.



(1)



(2)

The results of the present X-ray analysis are in agreement with those of analyses of corresponding substituted isoindolinone structures (Feeder & Jones, 1996; Barrett *et al.*, 1995; Barrett, Kahwa & Williams, 1996). The *Z* configuration of the molecule, which contains three essentially planar parts, is established by the torsion angles N—C15—C16—C17 −3.1 (2) and C15—N—C7—C6 −69.4 (2)°. The isoindolinone moiety (*A*: atoms N, C8–C15) is planar to within 0.012 (1) Å. The two phenyl rings (*B*: atoms C1–C6; *C*: atoms C17–C22), with a maximum deviation of 0.016 (2) Å for an in-plane atom (C20) from the corresponding least-squares plane

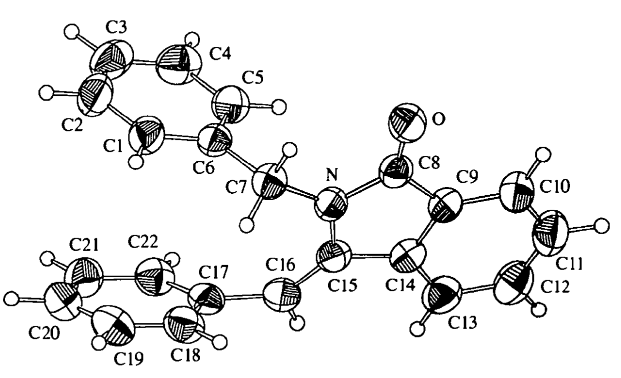


Fig. 1. *ZORTEP* (Johnson, 1976; Zsolnai, 1995) view (50% probability level) of the title molecule.