Conformational Control of Photochemical Reactions of Tetrahydro-1,4-naphthoquinones

By Sara Ariel and James Trotter

*Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Y6*

Abstract

The crystal structures of two asymmetrically substituted tetrahydro-1,4-naphthoquinones have been determined and correlated with their photochemical behaviour. $T = 295$ K, Mo $K\alpha_1$, $\lambda = 0.70930$ Å. (I): 6,7-Benzo-2,4a-dimethyl-*cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (2,4a-dimethyl-*cis*-4a,9a,9,-10-tetrahydro-1,4-anthracenedione), $C_{16}H_{16}O_2$, $M_r = 240.30$, triclinic, $P\bar{1}$, $a = 6.834$ (3), $b = 9.817$ (4), $c = 10.071$ (4) Å, $\alpha = 85.46$ (2), $\beta = 73.48$ (3), $\gamma = 76.71$ (3)°, $V = 630.4$ (5) Å^3, $Z = 2$, $D_x = 1.266$ g cm^{-3}, $F(000) = 256$, $\mu = 0.73$ cm^{-1}, $R = 0.042$ for 2130 observed reflections. (II): 6,7-Benzo-2,3,4a-trimethyl-*cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (2,3,4a-trimethyl-*cis*-4a,9a,9,10-tetrahydro-1,4-anthracenedione), $C_{17}H_{18}O_2$, $M_r = 254.33$, monoclinic, $P2_1/a$, $a = 9.8329(17)$, $b = 8.0652(8)$, $c = 17.3772$ (32) Å, $\beta = 102.69$ (1)°, $V = 1344.4$ (4) Å^3, $Z = 4$, $D_x = 1.256$ g cm^{-3}, $F(000) = 544$, $\mu = 0.75$ cm^{-1}, $R = 0.052$ for 1330 observed reflections. Bond lengths and angles are close to normal values for both molecules (I) and (II). In each structure the two fused non-aromatic six-membered rings are twisted with respect to each other; however, while the solid-state conformation of compound (I) is such that the bridgehead methyl group is pseudo-axial to the cyclohexenone moiety, in compound (II) the methyl group is pseudo-equatorial. Molecular-energy calculations are used to determine the energy difference between the two molecular conformations for each compound, and the different photochemical behaviour of (I) and (II) in the solid state and in solution is interpreted; the solid-state reactions are topochemically controlled, while reactions in solution are governed by the amounts and reactivities of the two conformers.

Introduction

As part of a study of the photochemistry of asymmetrically substituted 1,4-naphthoquinone systems (Ariel, Evans, Hwang, Jay, Scheffer, Trotter & Wong, 1985) it was found that irradiation of compound (I) gives the same cyclobutanone-type photoproduct (III) in solution as it does in the solid state. Ene-dione (II) undergoes photolysis in solution to give two isomeric cyclobutanones, (IV) and (V), in the ratio of 57 to 43; in the solid state only cyclobutanone (V)

is formed. The crystal structures of compounds (I) and (II) have been determined in an attempt to understand their photochemical behaviour in the two media.

| Solution | 57 | : | 43 |
| Solid | 0 | : | 100 |
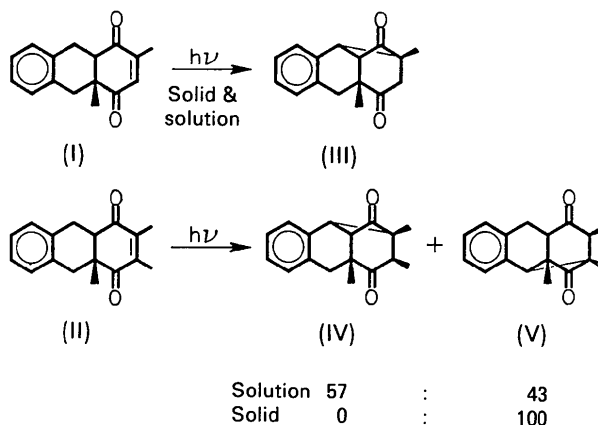
Experimental

Crystal size $0.4 \times 0.5 \times 0.5$ mm for (I) $[0.2 \times 0.5 \times 0.5$ mm for (II)], m.p. 353–354 K [380–381 K], Enraf-Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, lattice parameters from setting of 25 reflections with $19 \leq \theta \leq 24°$ [$15 \leq \theta \leq 19°$]. 2489 unique reflections with $\theta \leq 27°$ for (I) [1915 with $\theta \leq 25°$ for (II)], $h = -8 \rightarrow 8$, $k = -12 \rightarrow 12$, $l = 0 \rightarrow 12$ [$h = -11 \rightarrow 11$, $k = 0 \rightarrow 9$, $l = 0 \rightarrow 20$]; $\omega - (1/3)\theta$ [$\omega - (5/3)\theta$] scan, ω-scan width $(1.1 + 0.3 \tan \theta)°$ [$(0.9 + 0.3 \tan \theta)°$] extended 25% on each side for background measurement, horizontal aperture $(2.0 + \tan \theta)$ mm, vertical aperture 4 mm, Lp corrections, absorption ignored. Three standard reflections [303, 241, 235 for (I), 207, 222, 033 for (II)] were monitored every hour of exposure time for random intensity fluctuations [$\pm 2\%$ for (I), $\pm 0.5\%$ for (II)], and were recentered every 150 reflections for orientation control. Two intense low-order reflections omitted from final refinement of compound (II) because of suspected extinction errors. Both structures were solved by direct methods using *SHELX*76 (Sheldrick, 1976) and were refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$. All H atoms were located in difference syntheses and their temperature factors were refined isotropically. 227 parameters for

Table 1. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^3$)

$$U_{eq} = \tfrac{1}{3} \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

	Compound (I)				Compound (II)			
	x	y	z	U_{eq}	x	y	z	U_{eq}
O(1)	−158 (2)	8737 (1)	6513 (1)	71	5114 (2)	−2732 (2)	8570 (1)	72
O(2)	2612 (2)	5030 (1)	10010 (1)	57	2841 (2)	3183 (2)	7982 (1)	71
C(1)	491 (2)	7892 (1)	7319 (1)	44	4544 (3)	−1382 (3)	8466 (2)	44
C(2)	−370 (2)	8097 (1)	8844 (2)	48	5256 (3)	104 (4)	8870 (1)	46
C(21)	−2158 (3)	9318 (2)	9325 (3)	79	6575 (4)	−222 (6)	9466 (2)	71
C(3)	428 (2)	7181 (2)	9707 (1)	49	4706 (3)	1620 (3)	8697 (1)	44
C(4)	2227 (2)	6004 (1)	9235 (1)	40	3449 (3)	1851 (3)	8055 (1)	43
C(4a)	3574 (2)	6119 (1)	7760 (1)	37	2968 (2)	441 (3)	7489 (1)	40
C(4a1)	4832 (3)	7240 (2)	7730 (2)	52	1470 (3)	730 (5)	7037 (2)	59
C(5)	5102 (2)	4742 (1)	7265 (2)	46	3945 (3)	320 (4)	6912 (2)	45
C(6)	4141 (2)	3620 (1)	6935 (1)	43	3777 (3)	−1279 (3)	6441 (1)	46
C(7)	2193 (2)	3949 (1)	6664 (1)	41	3172 (3)	−2680 (3)	6690 (2)	48
C(8)	874 (2)	5420 (1)	6817 (2)	43	2619 (4)	−2675 (4)	7434 (2)	56
C(8a)	2083 (2)	6559 (1)	6832 (1)	39	3091 (3)	−1192 (3)	7965 (2)	41
C(9)	5242 (3)	2228 (1)	6845 (2)	55	4258 (3)	−1346 (5)	5752 (2)	64
C(10)	4446 (3)	1195 (2)	6488 (2)	67	4126 (4)	−2777 (6)	5303 (2)	80
C(11)	2523 (3)	1509 (2)	6222 (2)	64	3509 (4)	−4144 (6)	5537 (2)	80
C(12)	1409 (3)	2880 (2)	6306 (1)	53	3043 (3)	−4096 (4)	6225 (2)	66
C(31)					5317 (5)	3176 (5)	9117 (3)	71

(I), consisting of 102 positional parameters, 108 anisotropic temperature factors, 16 isotropic temperature factors and a scale factor; 244 parameters for (II), consisting of 111 positional parameters, 114 anisotropic temperature factors, 18 isotropic temperature factors and a scale factor. Convergence for (I) at $R = 0.042$, $wR = 0.046$ for 2130 observed reflections for which $F \geq 3\sigma(F)$. Convergence for (II) at $R = 0.052$, $wR = 0.042$ for 1330 observed reflections for which $F \geq 3\sigma(F)$, where $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$, $S = $ scan count and $B = $ time-averaged background count. $R = 0.055$, $wR = 0.050$ for all data of (I), $R = 0.093$, $wR = 0.053$ for all data of (II); $w = 1/\sigma^2(F)$, $(\Delta/\sigma)_{max} = 0.1$, ± 0.21 e Å^{-3} in final difference synthesis of (I), $(\Delta/\sigma)_{max} = 0.2$, ± 0.18 e Å^{-3} for (II), atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965).

Discussion

Final atomic coordinates are in Table 1, and bond distances, bond angles and selected torsion angles in Table 2.*

The conformations of compounds (I) (Fig. 1) and (II) (Fig. 2) are twisted about the C(4a)–C(8a) bond, as found for all the tetrahydro-1,4-naphthoquinones previously studied (Phillips & Trotter, 1976). The degree of 'twist' is shown by the torsion angles C(4)–C(4a)–C(8a)–C(8), −64.5 (1)° for (I), and C(5)–C(4a)–C(8a)–C(1), 64.4 (3)° for (II). Bond lengths

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond distances and angles involving H atoms, and stereodiagrams of the packing of compounds (I) and (II) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44223 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and bond angles have normal values. The C(sp^3)–C(sp^3) bond distances (Table 2) are in the range 1·526 (2)–1·540 (2) Å, mean 1·536 Å, for (I); range 1·519 (4)–1·545 (4) Å, mean 1·532 Å, for (II).

The tetrahydronaphthoquinone ring system can exist in two low-energy conformations, A and B (Fig. 3); both have fused six-membered rings with half-chair conformations and are folded and twisted about the C(4a)–C(8a) bond. A and B conformers can be interconverted by ring 'flipping' involving single-bond rotations, *via* a higher-energy conformer with eclipsed 4a/8a bridgehead substituents. The naphthoquinones studied previously (Phillips & Trotter, 1976) are all symmetrically substituted, so that conformers A and B are exactly equivalent. In the naphthoquin-4-ol series (Greenhough & Trotter, 1981), the two conformers are nonequivalent, and the conformation adopted in the solid state is invariably that which places the bulkier C(4) substituent (usually OH) in a pseudo-equatorial site of the half-chair six-membered ring.

(I) and (II) are also asymmetric, because of the C(4a)-Me substituent. For (I) only conformer A is found in the solid state (Figs. 1 and 3), with the C(4a)-Me substituent in a pseudo-axial site on the half-chair cyclohexenone ring (and in a pseudo-equatorial site of the central ring); for (II) only conformer B is present in the crystal, with a pseudo-equatorial C(4a)-Me substituent on the cyclohexenone ring (and pseudo-axial on the central ring) (Figs. 2 and 3). A qualitative study of the molecular structures of (I) and (II) suggests that conformation A, with the cyclohexenone pseudo-axial Me substituent, is slightly more stable, since conformation B exhibits unfavourable 1–3 diaxial steric interactions between the cyclohexenone pseudo-equatorial C(4a)-Me group and the pseudo-axial H atom on C(8) of the central ring. A more quantitative understanding

Table 2. *Bond lengths* (Å), *bond angles* (°), *and selected torsion angles* (°)

	Compound (I)	Compound (II)
O(1)–C(1)	1·213 (2)	1·220 (3)
C(1)–C(2)	1·492 (2)	1·485 (4)
C(2)–C(21)	1·500 (2)	1·494 (4)
C(2)–C(3)	1·335 (2)	1·344 (4)
C(3)–C(4)	1·475 (2)	1·483 (3)
O(2)–C(4)	1·215 (2)	1·222 (3)
C(4)–C(4a)	1·519 (2)	1·510 (4)
C(4a)–C(4a1)	1·538 (3)	1·528 (4)
C(4a)–C(5)	1·526 (2)	1·537 (4)
C(5)–C(6)	1·507 (2)	1·516 (4)
C(6)–C(7)	1·395 (2)	1·389 (4)
C(7)–C(8)	1·510 (2)	1·510 (5)
C(8)–C(8a)	1·539 (2)	1·519 (4)
C(1)–C(8a)	1·510 (2)	1·509 (4)
C(4a)–C(8a)	1·540 (2)	1·545 (4)
C(6)–C(9)	1·396 (2)	1·383 (4)
C(9)–C(10)	1·371 (3)	1·383 (6)
C(10)–C(11)	1·376 (3)	1·363 (7)
C(11)–C(12)	1·381 (2)	1·373 (6)
C(7)–C(12)	1·395 (3)	1·388 (5)
C(3)–C(31)		1·508 (5)
C(2)–C(1)–O(1)	120·6(1)	119·8 (3)
C(8a)–C(1)–O(1)	121·9 (1)	121·5 (2)
C(8a)–C(1)–C(2)	117·4 (1)	118·6 (2)
C(1)–C(2)–C(3)	119·4 (1)	120·2 (2)
C(1)–C(2)–C(21)	117·2 (2)	115·7 (3)
C(21)–C(2)–C(3)	123·3 (2)	124·1 (3)
C(2)–C(3)–C(4)	123·3 (1)	120·7 (2)
C(3)–C(4)–O(2)	120·8 (1)	119·8 (2)
C(4a)–C(4)–C(3)	116·0 (1)	119·0 (2)
C(4a)–C(4)–O(2)	123·1 (1)	121·2 (2)
C(5)–C(4a)–C(4)	112·1 (1)	108·8 (2)
C(8a)–C(4a)–C(4)	107·2 (1)	108·5 (2)
C(4a1)–C(4a)–C(4)	107·8 (1)	110·4 (2)
C(4a1)–C(4a)–C(5)	108·6 (1)	110·1 (2)
C(4a1)–C(4a)–C(8a)	110·9 (1)	111·0 (2)
C(5)–C(4a)–C(8a)	110·2 (1)	108·0 (2)
C(4a)–C(5)–C(6)	115·3 (1)	113·4 (2)
C(5)–C(6)–C(7)	121·2 (1)	121·9 (2)
C(9)–C(6)–C(7)	118·9 (1)	119·3 (3)
C(9)–C(6)–C(5)	119·8 (1)	118·9 (3)
C(6)–C(7)–C(8)	121·5 (1)	121·6 (3)
C(12)–C(7)–C(8)	119·4 (1)	119·8 (3)
C(12)–C(7)–C(6)	119·0 (1)	118·7 (3)
C(7)–C(8)–C(8a)	114·5 (1)	113·8 (3)
C(4a)–C(8a)–C(1)	111·9 (1)	110·4 (2)
C(8)–C(8a)–C(1)	107·4 (1)	113·2 (2)
C(4a)–C(8a)–C(8)	111·3 (1)	111·6 (2)
C(10)–C(9)–C(6)	121·1 (2)	120·9 (3)
C(9)–C(10)–C(11)	120·4 (2)	120·0 (4)
C(10)–C(11)–C(12)	119·4 (2)	119·5 (4)
C(11)–C(12)–C(7)	121·2 (2)	121·6 (3)
C(2)–C(3)–C(31)		123·4 (3)
C(31)–C(3)–C(4)		115·9 (3)
C(4)–C(3)–C(2)–C(1)	3·8 (2)	−5·1 (4)
C(4a)–C(4)–C(3)–C(2)	18·5 (2)	−12·6 (4)
C(3)–C(4)–C(4a)–C(5)	−168·1 (1)	−75·3 (3)
C(3)–C(4)–C(4a)–C(8a)	−47·1 (2)	41·9 (3)
C(3)–C(4)–C(4a)–C(4a1)	72·4 (2)	163·8 (3)
C(3)–C(2)–C(1)–C(8a)	6·4 (2)	−10·0 (4)
C(2)–C(1)–C(8a)–C(4a)	−37·5 (2)	40·2 (3)
C(1)–C(8a)–C(4a)–C(4)	55·7 (1)	−53·3 (3)
C(1)–C(8a)–C(4a)–C(5)	177·9 (1)	64·4 (3)
C(1)–C(8a)–C(4a)–C(4a1)	−61·8 (2)	−174·8 (2)
C(8)–C(8a)–C(4a)–C(4a1)	178·0 (1)	58·3 (3)
C(8)–C(8a)–C(4a)–C(5)	57·7 (2)	−62·4 (3)
C(6)–C(5)–C(4a)–C(4a1)	−167·2 (1)	−72·3 (3)
C(7)–C(6)–C(5)–C(4a)	20·0 (2)	−20·1 (4)
C(9)–C(6)–C(5)–C(4a)	−162·5 (1)	160·7 (3)
C(8a)–C(8)–C(7)–C(6)	18·3 (2)	−13·8 (4)
C(4)–C(4a)–C(8a)–C(8)	−64·5 (1)	179·8 (2)

of the situation was obtained from molecular-mechanics calculations, using the *MMP2* computer program (Allinger & Flanagan, 1983) to evaluate the conformational-energy difference between the *A* and *B* conformations of both compounds.

The starting points for the calculations for (I) were the observed conformation *A* (Fig. 1) and a conformation *B* based on the observed structure of (II) [and *vice versa* for compound (II)]. Although the energy differences are small (Table 3), they are in accord with conformation *A* being slightly more stable than *B*, by 0·4 and 1·2 kJ mol^{-1} for (I) and (II), respectively. The fact that compound (II) crystallizes in its less stable *B* conformation is presumably the result of intermolecular packing interactions, although no interaction can be pinpointed as being particularly important.

The proposed mechanism in the photochemical reactions of 1,4-tetrahydronaphthoquinone systems (Scheffer, 1980; Trotter, 1983) involves γ-H abstraction by enone carbon, followed by C–C bond formation. For (I) in the solid state (conformation *A*), this involves abstraction of H(82) by C(3), followed by C(2)–C(8) bonding to form (III); for (II) (conformation *B* in the crystal), abstraction of H(51) by C(2) followed by C(3)–C(5) bonding to form (V). Ideal geometry should involve short H$_\gamma \cdots$C [H(82)$\cdots$C(3) for (I); H(51)$\cdots$C(2) for (II)] and C$\cdots$C [C(2)$\cdots$C(8)
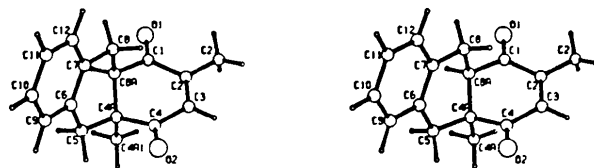

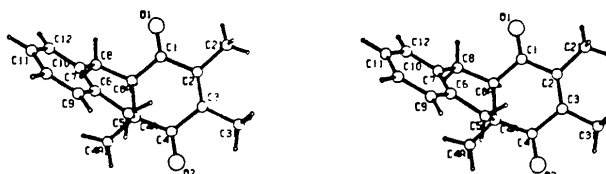Fig. 1. Stereoview of compound (I) with crystallographic atom labelling.

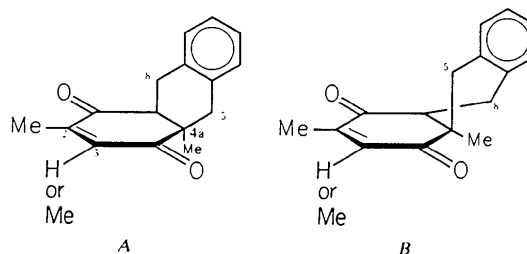Fig. 2. Stereoview of compound (II) with crystallographic atom labelling.

Fig. 3. Compounds (I) and (II) exhibiting conformations *A* and *B*.

Table 3. *Minimized MMP2 steric energy* (kJ mol^{-1})

	Conformation			
Compound	A	B	A:B at 298 K = exp $(-\Delta E/RT)$	
(I)	40·3	40·7	54:46	
(II)	47·5	48·7	62:38	

for (I); C(3)···C(5) for (II)], with τ_C [angle subtended by the C···H$_\gamma$ vector and its projection on the plane of the C(2)=C(3) double bond] and Δ_C [C(2)=C(3)···H(82) for (I); C(3)=C(2)···H(51) for (II)] angles of 90°, since abstraction is *via* the *p* orbital. The H$_\gamma$···C [2·94 (2); 2·87 (3) Å] and C···C [3·260 (2); 3·204 (4) Å] distances are close to the van der Waals distances of 2·90 and 3·40 Å, and τ_C [47 (1); 50 (1)°] and Δ_C [75 (2); 74 (2)°] are not far from ideal values. The conformations are thus quite favourable for the formation of the cyclobutanones (III) and (V) as the sole photoproducts in the solid state, *via* topochemically controlled reactions.

In solution, both conformers *A* and *B* are likely present for both (I) and (II). The *A*:*B* ratios can be estimated from the conformational energy differences (Table 3), as 54:46 for (I) and 62:38 for (II). In the photoreaction of (I) in solution, conformation *A* gives rise to a biradical intermediate with a tertiary radical centre at C(2), and this results in the formation of (III) as the sole photoproduct in solution (as in the solid state). Conformation *B* for (I) gives a secondary radical centre, at C(3), which is a much less favourable process, so that no photoproduct is formed *via* this route. For (II), both conformers give tertiary radical centres, since both C(2) and C(3) carry Me substituents, so that two photoproducts are formed, (IV) and (V), derived from conformers *A* and *B*, respectively; the observed (IV):(V) ratio of 57:43 is close to the calculated *A*:*B* ratio for (II) of 62:38.

Finally, a second reaction pathway in the photolysis of tetrahydronaphthoquinones involves β-H abstraction from C(5) [or C(8)] by carbonyl oxygen O(2) [or O(1)]. The parameters in (I) and (II) are favourable for such a process, H···O = 2·57 (2), 2·48 (3) Å, τ_O = 1 (1), 1 (2)°, C–O···H = 80 (1), 83 (2)° (Trotter, 1983). However, the next step in the reaction involves C(4)···C(7) [or C(1)···C(6)] bonding, and these processes are precluded, since they would disrupt the aromatic ring systems. Hence no such photoproducts are obtained from (I) and (II).

References

ALLINGER, N. L. & FLANAGAN, H. L. (1983). *J. Comput. Chem.* **4**, 399.

ARIEL, S., EVANS, S., HWANG, C., JAY, J., SCHEFFER, J. R., TROTTER, J. & WONG, Y.-F. (1985). *Tetrahedron Lett.* **26**, 965–968.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

GREENHOUGH, T. J. & TROTTER, J. (1981). *Acta Cryst.* B**37**, 126–132.

PHILLIPS, S. E. V. & TROTTER, J. (1976). *Acta Cryst.* B**32**, 3088–3106.

SCHEFFER, J. R. (1980). *Acc. Chem. Res.* **13**, 283–290.

SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

TROTTER, J. (1983). *Acta Cryst.* B**39**, 373–381.