

Structural Aspects of the Solid-State Photochemistry of Tetrahydronaphthoquinones

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Abstract

Crystal structure and photochemical studies of a series of *cis*-4 α ,5,8,8 α -tetrahydro-1,4-naphthoquinone derivatives have revealed the detailed course of the photoreactions in the solid state and in solution. The most favourable reaction involves (2 + 2) intermolecular cycloaddition in the solid state for those crystals with parallel C=C bonds in adjacent molecules with separations of <4.1 Å. In the absence of such a molecular-packing arrangement unimolecular processes occur, the most favoured involving β -H abstraction by O or γ -H abstraction by C. The H...O or C abstraction distances are slightly smaller than normal van der Waals contacts, the orientations of the groups are favourable, and new bonds are formed with a minimum of atomic movement in the solid state. In solution the same photoproducts are formed, with additional products which require conformational changes which are topochemically forbidden in the crystal lattice. Reduction of the tetrahydronaphthoquinones yields 4 $\alpha\beta$,5,8,8 $\alpha\beta$ -tetrahydro-1-naphthoquin-4 α -ols and -4 β -ols. The two series have different molecular conformations, with the hydroxyl groups occupying more sterically favoured pseudo-equatorial positions. As a consequence, solid-state photochemical reaction in the 4 α -ol series proceeds *via* abstraction of a C(5) hydrogen atom by C(3) followed by C(2)–C(5) bonding, while in the 4 β -series a C(8) hydrogen atom is abstracted by C(3) followed by C(2)–C(8) bonding. Distances and orientations are again favourable for H abstraction and new bond formation with minimum atomic movement. In solution, reaction proceeds *via* a kinetically favourable (2 + 2) intramolecular cycloaddition, involving a higher-energy conformer which is topochemically forbidden in the solid state. Lattice control of the photochemical process (crystal engineering) has been exploited by designing a 4 α -methyl-4 β -ol derivative, in which the bulkier 4 α -methyl substituent constrains the molecule to adopt the conformation typical of the 4 α -ol series and to give the appropriate 4 α -ol photoproduct.

Introduction

Detailed investigations of solid-state photochemical reactions began with the elegant study of dimerization

of the *trans*-cinnamic acids (Cohen & Schmidt, 1964; Cohen, Schmidt & Sonntag, 1964; Schmidt, 1964). These materials crystallize in three polymorphic modifications. In the α -form molecules are arranged about centres of symmetry with antiparallel double bonds; irradiation of the crystals with sunlight induces a (2 + 2) intermolecular cycloaddition, yielding a four-membered-ring dimer whose centrosymmetric *trans* stereochemistry follows exactly from the arrangement of the reactant molecules in the crystal lattice (Fig. 1). In the β -form nearest-neighbour molecules have parallel double bonds and photoirradiation produces a *cis*-type dimer. Schmidt *et al.* used the term 'topochemistry' to describe these types of reaction, the course of the reaction being controlled by topochemical factors. The principle was also formulated that reaction in the solid state occurred with a minimum of atomic or molecular movement. Finally the distances between the reacting double bonds were found to be 3.6–4.1 Å (in the γ -form, which is stable to irradiation, these distances are greater than 4.1 Å). The present paper reviews the photochemistry of a series of tetrahydronaphthoquinone derivatives, the detailed course of the photoreactions being deduced from crystal structure studies and application of topochemical principles.

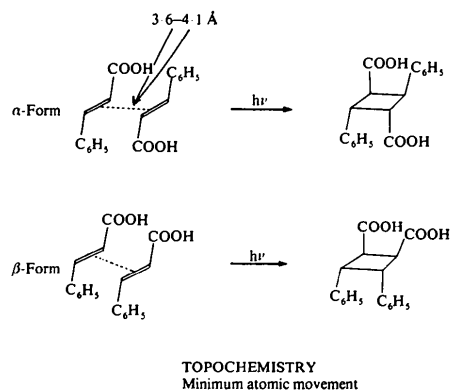


Fig. 1. Photodimerization of *trans*-cinnamic acids.

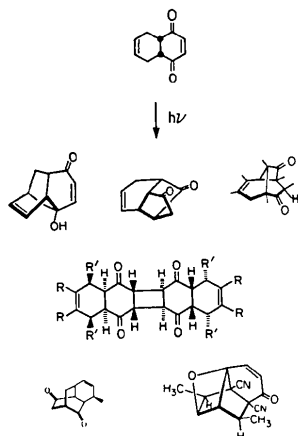


Fig. 2. Photoproducts from irradiation of *cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinones.

Tetrahydronaphthoquinones

Photoirradiation of a series of *cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone derivatives, in solution or in the solid state, produces a bewildering variety of condensed ring systems (Fig. 2)* (Scheffer, Bhandari, Gayler & Wostradowski, 1975; Scheffer, Jennings & Louwerens, 1976; Scheffer & Dzakpasu, 1978).† An understanding of the mechanisms by which these various photoproducts are formed has been obtained from crystal structure studies of the reactants (and where necessary of the photoproducts) (Phillips & Trotter, 1977*a,b*) and by correlation of the observed molecular conformations with changes which occur as the reactions proceed (Scheffer & Dzakpasu, 1978).

The tetrahydronaphthoquinones are readily synthesized by Diels–Alder addition of appropriate 1,3-dienes and *p*-quinones. Irradiation with a mercury lamp and filter ($\lambda > 340$ nm) for solids (usually powders, but single crystals have also been used) and for solutions in various solvents. In the solid samples care was taken to prevent melting or breakdown of the crystal lattice (by cooling and keeping conversions below 25%) (Scheffer, 1980), so that true solid-state reactions are observed.

β -H abstraction by O

For tetrahydronaphthoquinones (1), (2) and (3) (Fig. 3) irradiation produces enone-alcohols in the solid state and in solution, and for (1) an additional photoproduct is isolated from the solution photolysis. The formation of these photoproducts can be rationalized by a mechanism involving β -H abstraction by carbonyl O

[i.e. abstraction of a C(8) hydrogen atom by O(1)] to form a biradical, which can then form tricyclic products (Fig. 4). The 1,8-bonding photoproduct has not been observed, but the 1,6- and 3,8-bonding products are those in Fig. 3, and the 3,6-bonding product has been found in solution studies of other derivatives.

X-ray crystal structure studies of compounds (1), (2) and (3) indicate that all three have similar 'twist' conformations with staggered bridgehead substituents (Fig. 5). H_β is in a favourable position to be abstracted by the carbonyl O bonded to C(1); the ideal geometry would have a short $H_\beta \cdots O$ distance, with the C(8)–H bond in the plane of the carbonyl group, with $C(1)=O \cdots H = 90^\circ$, since abstraction probably involves an $(n, \pi^*)^1$ excited state in which the new O–H bond is formed using the half-occupied O n orbital. Deviations from this ideal geometry can be indicated by angles τ_o and Δ_o (Fig. 6). Table 1 shows that the $H_\beta \cdots O$ distances for (1), (2) and (3) are 2.46, 2.57, and 2.58 Å, respectively, all shorter than the van der Waals distance of 2.72 Å, τ_o angles are 3–8° and Δ_o angles 80.7–83.6°, close to the ideal values of 0 and 90°, respectively.†

The biradical intermediate (Fig. 4) is likely to have a conformation very similar to that of the ground-state precursor (Fig. 5), which is favourable for formation of a C(1)–C(6) bond to yield the enone-alcohol. The C(1)–C(6) distances (Table 1) are 3.51, 3.46, and 3.38 Å for (1), (2), and (3), respectively, of the order of the van der Waals distance of 3.40 Å. In the photoproduct this distance is reduced to a bonding distance of about 1.5 Å, which involves movement of each of C(1) and C(6) by about 1 Å, with smaller movements of other atoms. Hence the solid-state

† For all the crystals studied, standard deviations are of the order of 0.002–0.008 Å, 0.1–0.6° for non-hydrogen distances and angles, and 0.02–0.06 Å, 2–3° for distances and angles involving H atoms.

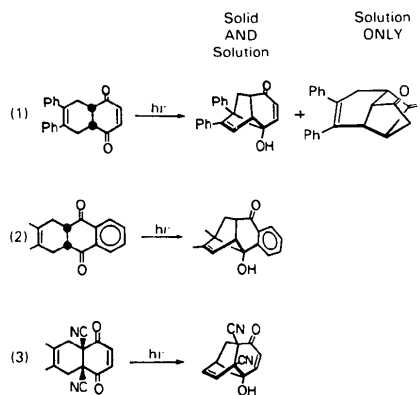


Fig. 3. Photolysis of tetrahydronaphthoquinone derivatives (1), (2), (3).

* In this and other figures, specific structures are often given as representative of the series.

† Extensive references to related photochemical work are given in these papers.

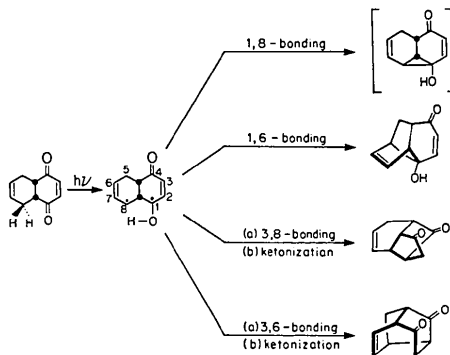


Fig. 4. β -H abstraction by O, and subsequent photoproduct formation.

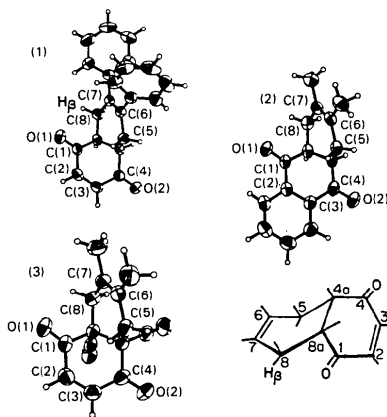
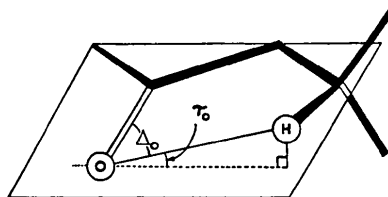


Fig. 5. Views of the molecules of (1), (2), (3).



Sum of van der Waals radii: O + H = 2.72 Å
C + C = 3.40 Å

Ideal $\tau_0 = 0^\circ$
Ideal $\Delta_0 = 90^\circ$

Fig. 6. Parameters relevant to β -H abstraction by carbonyl O.

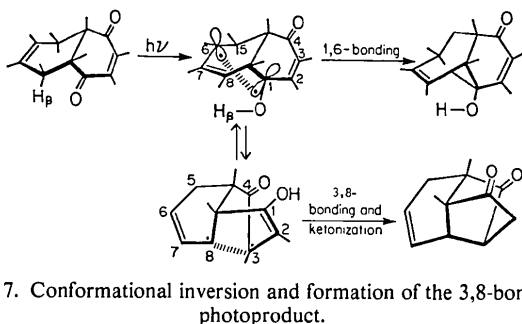


Fig. 7. Conformational inversion and formation of the 3,8-bonding photoproduct.

results indicate that the molecular geometries are favourable for β -H abstraction by O, and subsequent C(1)–C(6) bond formation with minimum atomic motion, to yield the principal enone-alcohol photoproducts found in the solid state and solution photolyses.

The additional solution photoproduct from (1) (Fig. 3) involves 3,8-bonding (Fig. 4). This is impossible from the twist conformation found in the solid state, and must involve a ring flip (*via* eclipsed bridgehead H substituents) to a conformation in which C(3) and C(8) are in closer proximity (Fig. 7). The formation of this additional photoproduct is topochemically forbidden in the solid state, since the conformational change is prevented by the constraints of the crystal lattice. Compounds (2) and (3) do not give the additional solution photoproduct; (2) presumably because 3,8-bonding would destroy the aromatic character of the benzene-like ring, and (3) possibly because the bulkier CN bridgehead substituents (relative to H) make the conformational change less facile.

γ -H abstraction by C

Naphthoquinones (4) and (5) give similar enone-alcohol-type photoproducts and in addition cyclobutanone products upon irradiation in the solid state or in solution. The enone-alcohol photoproducts arise *via* the same mechanism as previously discussed, the geometrical parameters (Table 1) being favourable, with short $H_\beta \cdots O$ and $C(1) \cdots C(6)$ distances, and very favourable τ_0 and Δ_0 angles.

The formation of the cyclobutanone photoproducts can be correlated with the solid-state conformation (Fig. 8), which is similar to that previously observed for

Table 1. Parameters relevant to β -H abstraction by O in the tetrahydronaphthoquinones (see text and Fig. 6)

Quinone	Photoproduct	$H_\beta \cdots O$ (Å)	τ_0	Δ_0	C(1) ... C(6) (Å)
(1)		2.46	3°	81.3°	3.51
(2)		2.57	5°	80.7°	3.46
(3)		2.58	8°	83.6°	3.38
(4)		2.47	0°	85.1°	3.35
(5)		2.26	1°	86.4°	3.33
Sum of van der Waals radii		2.72			3.40
Ideal angles			0°	90°	

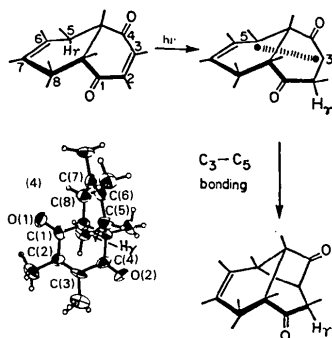


Fig. 8. γ -H abstraction by C and C(3)–C(5) bonding; the detailed geometry of (4) is shown.

the other derivatives (Fig. 5). The proposed mechanism involves γ -H abstraction by C [*i.e.* abstraction of a C(5) hydrogen atom by C(2)], followed by C(3)–C(5) bond formation (Fig. 8). Ideal geometry should again involve short $H_\gamma \cdots C(2)$ and $C(3) \cdots C(5)$ distances, with τ_c [angle subtended by the $C(2) \cdots H_\gamma$ vector and its projection on the plane of the $C(2)=C(3)$ double bond] and Δ_c [$C(3)=C(2) \cdots H_\gamma$] angles of 90° , since abstraction will be *via* the p orbital. The cyclobutanone photoproducts probably arise from a $(\pi, \pi^*)^3$ excited state, whose geometry at the double bond is likely to differ from the ground-state precursor; a reasonable twist of 45° would give an ideal τ_c of 45° , with little change in Δ_c or in the distances involved. The $H_\gamma \cdots C(2)$ (2.80, 2.66 Å) and $C(3) \cdots C(5)$ (3.17, 3.17 Å) distances are less than the van der Waals distances of 2.90 and 3.40 Å, and the τ_c (52° , 50°) and Δ_c (72.6° , 74.4°) are not far from ideal values (Table 2). The conformations are thus very favourable for the formation of the cyclobutanone photoproducts.

No additional solution photoproducts involving conformational changes are observed for (4) and (5), presumably because the bulky bridgehead methyl substituents inhibit conformational inversion [minor amounts of the 3,8-bonded product for (4) have been isolated in some solvents, and this must arise *via* conformational change (Fig. 7)].

Lack of cyclobutanone formation in the photochemistry of (1), (2) and (3) may be related to longer

Table 2. Parameters relevant to γ -H abstraction by C in the tetrahydronaphthoquinones

Quinone	Photoproduct	$H_\gamma \cdots C$ (Å)	τ_c	Δ_c	$C(3) \cdots C(5)$ (Å)
(4)		2.80	52°	72.6°	3.17
(5)		2.66	50°	74.4°	3.17
Sum of van der Waals radii		2.90			3.40
Ideal angles			$\sim 45^\circ$	90°	

Table 3. Summary of parameters relevant to β -H abstraction by O and to γ -H abstraction by C in the tetrahydronaphthoquinones

	β -H by O	γ -H by C
$H \cdots O$ or C (van der Waals)	2.3–2.6 Å (2.7)	2.7–2.8 Å (2.9)
$\tau_{O \text{ or } C}$ (Ideal)	0 – 10° (0)	50° ($\sim 45^\circ$)
$\Delta_{O \text{ or } C}$ (Ideal)	80 – 90° (90)	70° (90)
$C \cdots C$ (van der Waals)	3.4–3.5 Å (3.4)	3.2 Å (3.4)
Excited state	$(\pi, \pi^*)^1$	$(\pi, \pi^*)^3$

$H_\gamma \cdots C(2)$ distances of 2.97, 3.09, 2.86 Å; molecules (1), (2), and (3) are less tightly folded, with $C(5)–C(4a)–C(8a)–C(1)$ torsion angles of 64 – 68° , compared with 61° in (4) and (5) (compare Figs. 5 and 8) [for (2), cyclobutanone formation is unlikely as the aromatic character of the benzene ring would be destroyed]. The differences in the distances are, however, small, and an alternative explanation is a lowering of the energy of the $(\pi, \pi^*)^3$ state by the electron-releasing C(2) and C(3) methyl substituents in (4) and (5) (Scheffer, Jennings & Louwerens, 1976).

In summary (Table 3), two mechanisms appear to be operative in the photochemistry of these tetrahydronaphthoquinones, β -H abstraction by O and γ -H abstraction by C. $H \cdots O$ or C distances are slightly shorter than normal van der Waals distances, orientations are close to ideal, and $C \cdots C$ distances are of the order of normal van der Waals separations, with new C–C bonds being formed with minimum atomic movement. An additional solution photoproduct involves conformational change which is topochemically forbidden in the solid state.

Dimerization

The tetrahydronaphthoquinones (6), (7), and (8) (Fig. 9) undergo (2 + 2) *intermolecular* cycloaddition upon irradiation in the solid state, to yield four-membered-ring dimers.

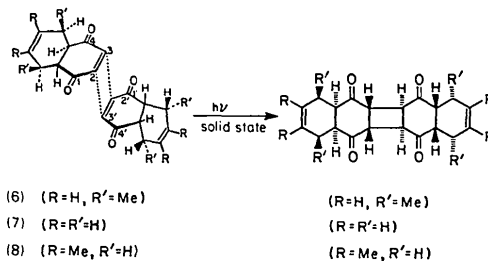


Fig. 9. Photodimerization of (6), (7), and (8).

Crystal structure study of (6) has shown that the molecules are arranged in pairs about centres of symmetry with antiparallel C=C bonds, with mid-points separated by 4.04 Å (Fig. 9). The dimerization is topochemically controlled, with least motion of the atoms in the formation of C(2)–C(3') and C(3)–C(2') bonds, the stereochemistry of the photodimer being that derived from the orientation of the monomer molecules in the crystal. Similar results are found for (7), except that that crystal contains two molecules per asymmetric unit. One of these forms pairs about centres of symmetry, with 3.76 Å between double bonds, again favourable for dimer formation; the other molecule has double-bond separations of 5.27 Å, unsuitable for dimer formation. Dimer yields of greater than 50% indicate that the process may be somewhat complex (Scheffer & Dzakpasu, 1978). Crystals of (8) were unsuitable for X-ray study.

In solution (7) and (8) give the expected photoproducts involving β -H abstraction by O, followed by 1,6-bonding and, after conformational change, 3,8- and 3,6-bonding [for the parent tetrahydronaphthoquinone, (7), the yields are low and the products mainly polymeric]. For (7), the parameters involved in the β -H abstraction are $H_{\beta}\cdots O = 2.46$ Å (average for the two molecules in the asymmetric unit), $\tau_0 = 4^\circ$, $\Delta_0 = 80.2^\circ$, $C(1)\cdots C(6) = 3.43$ Å (*cf.* Table 1). For (6) there is no abstractable β -H atom as a result of the C(8) methyl substituent. The observed photoproduct in solution appears to arise from abstraction of a methyl-group H by O, followed by conformational change, $C(3)\cdots CH_3$ bonding and ketonization. The parameters involved are $H\cdots O = 2.38$ Å, $\tau_0 = 15^\circ$, $\Delta_0 = 101.4^\circ$.

(2 + 2) Intramolecular cycloaddition

Irradiation of (9) in the solid state or in solution yields an oxetane photoproduct (Fig. 10). Crystal

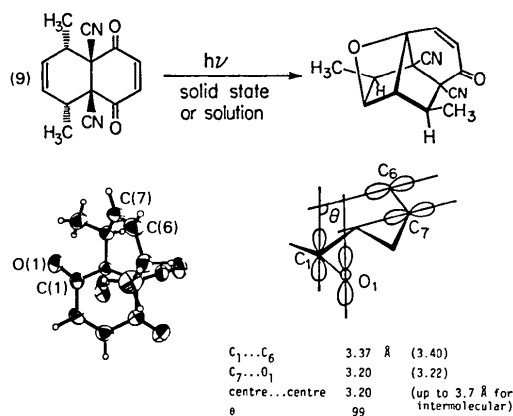


Fig. 10. Photolysis of (9), and details of molecular geometry (van der Waals distances and related observed centre...centre distances in parentheses).

structure study of (9) shows that the molecules are not suitably arranged for dimerization, and have the usual twist conformation (Fig. 10). As a result of the methyl substitution there is no β -H for abstraction by O nor γ -H for abstraction by C, nor are any of the methyl H atoms suitably positioned for abstraction. The photoproduct clearly arises from a (2 + 2) intramolecular cycloaddition involving bonding of C(1) to C(6) and O(1) to C(7); the arrangement and distances are favourable (Fig. 10). Since oxetane photoproducts are not observed in any of the photoirradiations where the other mechanisms are feasible, this appears to be the least-favoured reaction mode.

Summary

The foregoing crystallographic and photochemical results allow a hierarchy to be established of the various possible reactions (Fig. 11 – note that the photoproducts include all of those in Fig. 2). If the crystal has an arrangement with parallel C(2)=C(3) bonds in adjacent molecules with separations of <4.1 Å, then (2 + 2) intermolecular cycloadditions occur to form dimeric photoproducts (6)–(8).

In the absence of such a molecular-packing arrangement unimolecular processes occur, the most favoured being β -H abstraction by O [(1)–(5); (7), (8) in solution], with $H\cdots O$ distances slightly smaller than a normal van der Waals distance and τ_0 and Δ_0 orientation angles of close to 0 and 90°, respectively;

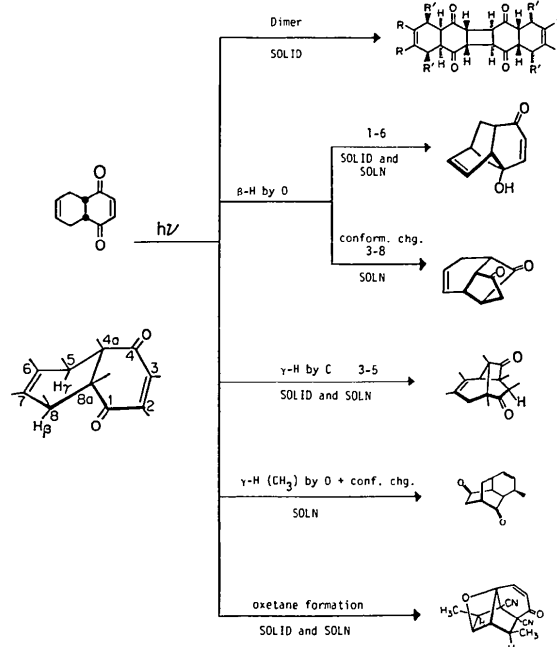


Fig. 11. Hierarchy of reaction mechanisms observed in the photolysis of tetrahydronaphthoquinones.

the biradical so formed forms a C(1)–C(6) bond by least motion from an initial C(1)···C(6) contact of the order of the normal van der Waals distance. In solution, additional photoproducts involving conformational change are formed for those reactants which lack bulky bridgehead substituents.

Molecules with C(2), C(3) methyl substituents also form photoproducts *via* γ -H abstraction by C, followed by C(3)···C(5) bonding [(4), (5)]. Distances involved are again of the order of van der Waals contacts, with orientation angles τ_C and Δ_C of about 45 and 90°, respectively, and minimum atomic movement is required in the bond formation.

Two molecules where these mechanisms are not possible react *via* methyl-H abstraction [(6) in solution, dimerization in the solid state] and by intramolecular cycloaddition [(9)].

Finally, the 2,3,6,7-tetramethyl derivative (10) is unusual in that no reaction occurs upon irradiation in the solid state. In solution the usual photoproducts are obtained, involving β -H abstraction by O and 1,6- and 3,8-bonding; the parameters are $H_\beta \cdots O = 2.42 \text{ \AA}$, $\tau_O = 3^\circ$, $\Delta_O = 81.9^\circ$, $C(1) \cdots C(6) = 3.49 \text{ \AA}$. No solution photoproduct is found corresponding to γ -H abstraction by C; since the compound contains 2,3-methyl substituents, lack of this reaction can only be ascribed to the larger $H_\gamma \cdots C(2)$ distance of 2.94 Å. The reason for the lack of reactivity in the solid state is not clear; C=O bonds in adjacent molecules are antiparallel with a separation of about 3.6 Å, and perhaps this results in a quenching of the excitation.

Tetrahydronaphthoquinols

Sodium borohydride reduction of the tetrahydronaphthoquinones yields a mixture of 4 α β ,5,8,8 $\alpha\beta$ -tetrahydro-1-naphthoquin-4 α -ols and -4 β -ols* (Fig. 12). Irradiation of these naphthoquin-4-ols in the solid state results in the formation of two different types of photoproduct (Fig. 12); that from the 4 α -ol series involves formation of a C(2)–C(5) bond, while in the 4 β -ol series, a C(2)–C(8) bond is formed (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980*b*). X-ray crystal structure studies lead to an understanding of the mechanisms by which these photoproducts are formed (Greenhough & Trotter, 1981; Secco & Trotter, 1982).

The tetrahydro-1-naphthoquin-4-ol ring system can exist in two low-energy conformations (Fig. 13, *A* and *B*); both have fused six-membered rings with half-chair conformations, and are folded and twisted about the C(4a)–C(8a) bond. They can be interconverted by ring 'flipping' involving single bond rotations *via* a higher-energy conformer (Fig. 13, *C*), which has eclipsed

bridgehead substituents and parallel double bonds. The flipping converts a pseudo-equatorial substituent at C(4) in the cyclohexenone ring of one conformer into a pseudo-axial substituent of the other conformer.

The two sets of derivatives, 4 α -ol and 4 β -ol, have different ring-flipped conformations, *A* and *B*, respectively, as shown in Fig. 14 [to illustrate the similarity of the fused ring systems in the two conformations, the molecules shown in Fig. 14 are enantiomorphic at the bridgehead C(4a) and C(8a) atoms; the crystals are racemic]. The hydroxyl groups occupy the more sterically favoured pseudo-equatorial

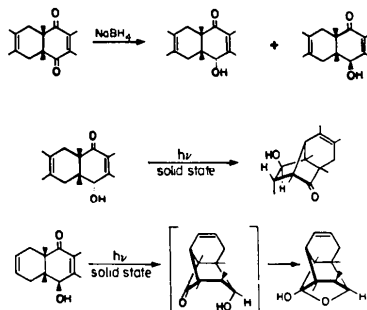


Fig. 12. Sodium borohydride reduction of tetrahydronaphthoquinones (top), and solid-state photolyses of tetrahydro-1-naphthoquin-4 α -ols (middle) and -4 β -ols (bottom).

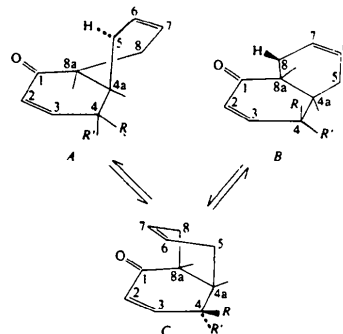


Fig. 13. Conformations of tetrahydro-1-naphthoquin-4-ols. Observed conformations in the crystal lattice are *A* for the 4 α -ols with $R = OH$, and *B* for the 4 β -ols with $R' = OH$.

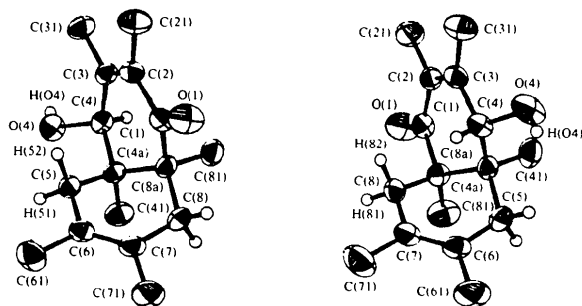


Fig. 14. Comparison of the molecular conformations of 2,3,4 α β ,6,7,8 α β -hexamethyl-4 α ,5,8,8 α -tetrahydro-1-naphthoquin-4 α -ol [(17), left] and 4 β -ol [(20), right].

* Systematic IUPAC nomenclature: 4 α - and 4 β -hydroxy-4 α β ,5,8,8 α β -tetrahydronaphthalen-1(4*H*)-one.

Table 4. Parameters relevant to the photochemical reactions of the tetrahydro-1-naphthoquin-4 α -ols and 4 β -ols

Methyl substituents	ol	H(5)···C(3)	τ_c	Δ_c	C(2)···C(5)	Reaction*	
						Solution	Solid
(11) None	4 α	2.81 Å	56°	82.2°	3.39 Å	1	2, 3
(12) 2,3-Di	4 α	2.84	54	79.7	3.42	1	2
(13) 5 α ,8 α -Di	4 α	—	—	—	—	1	None
(14) 6,7-Di	4 α	2.82	57	80.9	3.53	1	2, 3
(15) 2,3,4 α / β ,8 α / β -Tetra	4 α	2.78	52	77.5	3.30	1†	2†
(16) 2,3,6,7-Tetra	4 α	2.84	54	79.0	3.42	1	2
(17) 2,3,4 α / β ,6,7,8 α / β -Hexa	4 α	2.72	53	78.5	3.30	1	2
(18) 2,3,4 α / β ,6,7,8 α / β -Hepta	4 β	2.81	50	78.3	3.35	1	2
		H(8)···C(3)			C(2)···C(8)		
(19) 2,3,4 α / β ,8 α / β -Tetra	4 β	2.85	51	71.6	3.17	1	2
(20) 2,3,4 α / β ,6,7,8 α / β -Hexa	4 β	2.92	49	75.2	3.23	1	None
Sum of van der Waals radii		2.90			3.40		
Ideal angles			45	90			

* Primary photochemical reaction: 1 = intramolecular (2 + 2) cycloaddition, 2 = H abstraction by β -enone C(3), 3 = H abstraction by carbonyl O(1).

† The photoproduct composition is not well established for this compound.

positions in both series, and this is probably the main feature which controls the conformations. The consequence of these conformations is that there is a close intramolecular non-bonded approach in the 4 α -ol series of a H atom on C(5) to the enone C atoms C(2) and C(3), with well separated, non-parallel C=C bonds; in the 4 β -ol series the close approach is from a C(8) H atom to C(2) and C(3).

The solid-state photochemical reactions proceed *via* initial H-atom abstraction by β -enone carbon C(3). The H abstracted is from C(5) in the 4 α -ols and from C(8) in the 4 β -ols, and the resulting biradicals then collapse by formation of C(2)–C(5) and C(2)–C(8) bonds, respectively. The important parameters are similar to those discussed for the naphthoquinones: H(n)···C(3), τ_c , Δ_c , and C(2)···C(n) ($n = 5$ or 8, respectively) (Table 4).

For the 4 α -ol or *anti* series (4 α -ol *anti* or *trans* to the 4 β bridgehead substituents), the H(5)···C(3) distances are in the range 2.72–2.84 Å [Table 4, compounds (11), (12), (14)–(17)], slightly shorter than the van der Waals separation of 2.90 Å; $\tau_c = 52$ –57° and $\Delta_c = 77.5$ –82.2° are close to ideal values of 45° (estimated for the excited state) and 90°; C(2)···C(5) distances of 3.30–3.53 Å are close to the normal van der Waals separation of 3.40 Å. All of these compounds give rise to similar photoproducts *via* H(5) abstraction by β -enone C(3).

The 5 α ,8 α -dimethyl derivative gives no photoproduct in the solid state, presumably because the abstractable C(5) hydrogen atom has been replaced by a methyl substituent; one methyl H atom is not far from a possible abstractable position, but such a reaction is not observed.

Only two examples of the 4 β -ol or *syn* series have been studied [Table 4, (19) and (20)]. (19) reacts in the solid state by H(8) abstraction by C(3), followed by

C(2)–C(8) bonding; the appropriate parameters, 2.85 Å, 51°, 71.6°, 3.17 Å, are again favourable. No photoproduct is obtained in the solid state for the hexamethyl derivative (20); the only apparent reason for this is a slightly longer H(8)···C(3) distance of 2.92 Å.

All of the *anti* series have geometries which seem favourable for H(8) abstraction by O(1), *i.e.* the β -H abstraction by O mechanism found in the naphthoquinones. The appropriate photoproduct is found (Table 4) only for the two compounds with no 2,3-methyl substituents, (11) and (14) [(13) has no abstractable C(8) hydrogen atom as a result of the 8 α -methyl substituent]. All of the other *anti* compounds have electron-releasing 2,3-methyl substituents, which probably favour the mechanism involving abstraction by C, as for the naphthoquinones (4) and (5), apparently to the exclusion of abstraction by O in the 2,3-dimethylnaphthoquinol series.

In solution (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980a) entirely different products are obtained (Fig. 15), the photochemical reactions for all the tetrahydronaphthoquinols proceeding *via* intramolecular (2 + 2) cycloaddition of C(2)=C(3) and C(6)=C(7) double bonds. In the solid state these bonds are non-parallel with separations in the range 4.35–

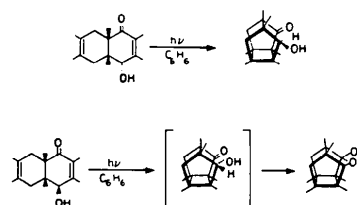
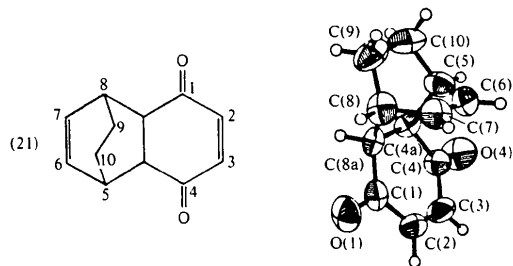


Fig. 15. Solution photochemistry of tetrahydro-1-naphthoquin-4 α -ols (upper) and -4 β -ols (lower).



2 + 2 cycloaddition – SOLID and SOLUTION
Centre...centre = 3.53 Å

Fig. 16. Conformation and photochemistry of the ethano-bridged tetrahydronaphthoquinone, (21).

4.44 Å, and reaction in solution probably proceeds *via* the higher-energy conformers, *C* (Fig. 13), which better fulfil the geometric requirements for intramolecular cycloaddition. Parameters relevant to (2 + 2) intramolecular cycloaddition are available for compound (21) (Fig. 16), where such a photochemical reaction is observed in solution and in the solid state. The C(9)–C(10) bridge constrains the C=C double bonds to be parallel with a separation of 3.53 Å (Greenhough & Trotter, 1980).

Hence for the tetrahydronaphthoquinols in solution, where conformational equilibration is facile, rapid (kinetically controlled) (2 + 2) photocycloaddition occurs *via* minor higher-energy conformers, whereas the solid-state reactions are topochemically controlled.

This lattice control can be exploited by designing a molecule so that its lowest-energy conformation (in which it is most likely to crystallize) is one which predisposes the molecule towards a specific reaction, *i.e.* crystal engineering (Schmidt, 1971). The heptamethyl derivative (18) (Table 4) is a member of the 4 β -ol or *syn* series; it has, however, a bulkier 4 α -methyl substituent which should constrain the molecule to adopt conformation *A* (Fig. 13) exhibited by the *anti* series, with the 4 α -methyl group pseudo-equatorial and the 4 β -ol group pseudo-axial. X-ray crystal structure analysis and photochemical studies (Jiang, Scheffer, Secco & Trotter, 1981; Secco & Trotter, 1982), indicate that the molecule does indeed have such a conformation in the solid state, which permits H(5) abstraction and formation of an *anti*-type photoproduct from this *syn*-series molecule; in solution, (2 + 2) cycloaddition again is dominant.

Summary

The crystal structure studies of the tetrahydronaphthoquin-4 α -ols and -4 β -ols have shown that the two series exhibit different molecular conformations in the solid state, such that the hydroxyl substituents occupy sterically favourable pseudo-equatorial posi-

tions. Photochemical reaction proceeds *via* H(*n*) abstraction by C(3) followed by C(2)···C(*n*) bonding, with *n* = 5 and 8 for the 4 α - and 4 β -ols, respectively; the distances and angles involved are favourable for the reaction process. In solution, reaction proceeds *via* a kinetically favourable (2 + 2) cycloaddition, involving a higher-energy conformer which is topochemically forbidden in the solid state. Lattice control of the photochemical reaction has been exploited for a 4 α -methyl-4 β -ol derivative, where the bulkier 4 α -methyl substituent occupies the pseudo-equatorial position, the molecule thus assuming the conformation typical of the 4 α -ol series and giving the appropriate 4 α -ol-type photoproduct.

The studies of the photochemistry of the tetrahydronaphthoquinones and quinols represent a very fruitful combination of the techniques of organic photochemistry and X-ray crystal analysis. The crystal structure determinations have given detailed information on the geometries of the reacting molecules, and have allowed an interpretation of the mechanisms of the solid-state photochemical reactions in terms of H-atom abstractions and formation of new C–C bonds.

The solid-state results also shed light on the mechanisms of the photochemical reactions in solution. For the tetrahydronaphthoquinones, the solid-state photoproducts are also found in the solution studies, so that the reactions in solution presumably involve the same molecular conformations and same mechanisms as found in the solid state. Additional photoproducts in solution arise by initial H abstraction in the same molecular conformation as in the solid state, followed by conformational change (which is topochemically forbidden in the crystal), and then new C–C bond formation. For the tetrahydronaphthoquinols the solution photoproducts are completely different from those in the solid-state reactions, and are formed *via* kinetically favourable reactions involving a different higher-energy conformer whose presence in the solid state is topochemically forbidden.

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Triclinic Lattice Constants of Saturated Mono-Acid Triglycerides

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Abstract

Different triclinic crystal modifications of saturated, mono-acid triglycerides [$C_{3n+3}H_{2(3n+1)}O_6$], especially of trilaurin, were investigated. Calculated results show good correspondence with the measured diffraction data. Besides the known stable β modification (space group $P\bar{1}$), at least four further triclinic crystal forms are theoretically possible, and their existence is supported by evidence from the present experiments. Unit cells, subcells, chain distances, angles of chain tilts of the molecules and densities were determined for all crystal structures.

1. Introduction

On the basis of electron and X-ray diffractometric studies, it has been known for some time that triglycerides may exist in three major modifications: the α , β' and the β forms. This so-called polymorphism is characteristic of the crystallization of fats. It means that they can exist in different energetically favourable molecular arrangements with the same chemical composition.

The molecular form of triglycerides is more complicated than that of normal paraffins or fatty acids. While the latter consist primarily of unbranched chains, the triglyceride molecule contains a glycerol group linked with three fatty-acid chains. This conjugated structure is why relatively little is known about the

crystal structure of a number of modifications of triglycerides.

The α , β' and β forms have hexagonal (H), orthorhombic ($O\perp$) and triclinic ($T\parallel$) chain packings. The studies on single crystals by Larsson (1964), Jensen & Mabis (1963, 1966), as well as Buchheim & Knoop (1969) and Buchheim (1970), on the β and β' forms, led to the exact atomic arrangement of the triclinic modification as well as the unit-cell parameters of the orthorhombic modification.

In an earlier report (Frede & Precht, 1977), we pointed out that the β modification of saturated mono-acid triglycerides can occur in at least five different chain packings (space group $P\bar{1}$). These crystal forms have more or less the same $T\parallel$ subcell packings. They differ primarily in the angle of tilt of the molecules.

We started from the proposition that – as is the case in the well known stable β structure (*cf.* Larsson, 1964; Jensen & Mabis, 1966), which we designated as the β_{III} form – the molecules are arranged head-to-head with the two equivalent fatty-acid chains in the so-called 2 position. A report by de Jong & van Soest (1978) further includes in a model relative shifts of mono-molecular layers. In our investigations of binary triglyceride mixtures (Precht & Greiff, 1978), we were able to establish the existence of larger quantities of the β_{IV} form.

The results of de Jong & van Soest (1978), as well as the occurrence of β_{IV} reflections of relatively high intensity in our X-ray diffraction patterns, has induced us to undertake a study on the various arrangements existing for the β_n modifications of triglycerides.

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