X-Ray Structures of Two Photodimers of 2-Methyl-1,4-naphthoquinone (Menadione)

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The structures of the photodimers (I) and (II) of menadione (2-methyl-1,4-naphthoquinone, MNQ) were determined by X-ray analysis. It was confirmed that both dimers are structural isomers of the *cis-syn* and *cis-anti* forms, *i.e.*, 5a,5b-*cis*-dimethyl (I) and 5a,11a-*cis*-dimethyl (II) isomers of 5a,5b,11a,11b-tetrahydro-β,β'-*cis*-binaphthylene-5,6,11,12-tetrone. The dimer (II), which was twisted around the cyclobutane ring, was more deformed than the dimer (I). MM2 calculation indicated that such twisting decreases the steric energy of the dimer (II) more than that of the dimer (I).

Keywords menadione; 1,4-naphthoquinone photodimer; X-ray analysis; *cis-syn* form; *cis-anti* form

Menadione[1,2] (2-methyl-1,4-naphthoquinone, MNQ), a derivative of vitamin K, is very unstable in light, and its photoirradiation can produce four dimers as follows. Asahi[1] obtained two crystalline isomeric dimers (A and B) by the exposure of crystalline MNQ to sunlight, and assigned dimer (A) as a *trans-syn* form (III), and (B) as a *trans-anti* form (IV), since the *trans* forms (III and IV) seemed to be more stable structures than the *cis* forms (I and II). The present study set out to confirm these structures, but is showed that the structures are *cis-syn* (I) for (A) and *cis-anti* (II) for (B). To reveal what mechanism controls the photoreaction, it is very important to know the crystal structure of MNQ itself. However, it was impossible to perform an X-ray study of MNQ, because of the decomposition of the crystalline MNQ when exposed to an X-ray beam. In this paper, we reported the molecular structures of two photodimers of MNQ, (I) and (II), and described the stereochemistry of these two dimers.

Experimental

Two photodimers (I) and (II) of MNQ were prepared by the method previously reported[1] and recrystallized from their benzene solutions. X-Ray measurements were performed using a four-circle diffractometer Rigaku AFC-6B, equipped with MoK_α radiation ($\lambda = 0.71069$ Å) monochromatized by graphite. The unit cell dimensions of the dimers (I) and (II) were determined by least-squares calculations for 25 reflections in the range of $15° < 2\theta < 25°$. The intensities were measured applying the scan mode $2\theta/\omega$ with a scan rate of 2°/min, and corrected for Lorentz and polarization effects, but not for absorption. The initial structures of both non-hydrogen atoms were obtained by direct methods applying MULTAN[3] programs, and were refined by block-diagonal least-squares calculation with isotropic thermal parameters. After successive refinements of the structure using anisotropic thermal parameters, the positional parameters of the hydrogen atoms of dimers (I) and (II) were obtained by means of difference Fourier syntheses. Further refinements, including the positional parameters of the hydrogen atoms and their isotropic thermal parameters, were carried out until the parameter shifts attained were below their standard deviations. Experimental details are summarized in Table I.

The atomic scattering factors were taken from International Tables for X-Ray Crystallography.[4] The calculations were performed using the following program packages: RASA (by Rigaku Co.), MULTAN[3] and X-STANP (written by one of the authors, Z.T.) on a mini-computer, PANAFACOM U-1400.

Results

The fractional atomic coordinates of non-hydrogen atoms are given in Table II. The bond lengths and angles are listed in Tables III and IV, respectively. ORTEP drawings of the molecular structures are presented in Fig. 1, and the selective torsion angles are shown in Fig. 2, together with atom numbering schemes.

TABLE I. Crystal Data and Experimental Details for Photodimers of 2-Methyl-1,4-naphthoquinone

Compounds	I	II
Formula	$C_{22}H_{16}O_4$	$C_{22}H_{16}O_4$
M.W.	344.37	344.37
Lattice	Monoclinic	Triclinic
Space group	*C*2/*c*	$P\bar{1}$
a/Å	10.803 (2)	8.397 (2)
b/Å	11.611 (3)	8.400 (2)
c/Å	26.827 (4)	13.533 (4)
α/°	90	90.58 (2)
β/°	97.40 (1)	90.70 (2)
γ/°	90	117.05 (2)
U/Å^3	3336.9 (11)	851.2 (4)
Z	8	2
D_x/g·cm^{-3}	1.371	1.343
F(000)	1440	360
μ(MoK_α)/cm^{-1}	1.019	0.998
Crystal size/mm	0.3 × 0.4 × 0.3	0.3 × 0.3 × 0.3
2θmax/°	60	50
No. of unique reflections	5543	3131
No. of observed reflections	3310 ($F > 3\sigma F$)	1967 ($F > 3\sigma F$)
R	0.065	0.075
R_w	0.060	0.069

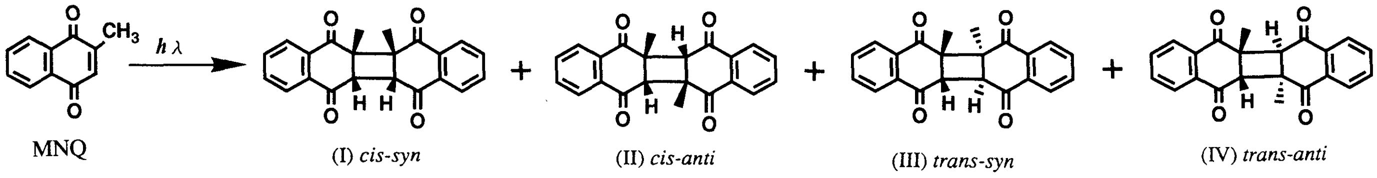


Chart 1

TABLE II. Fractional Coordinates (× 10^4) with Their Estimated Standard Deviations (E.S.D.) in Parentheses

a) Dimer (I)

Atoms	*x*	*y*	*z*
C(1)	11126 (3)	898 (3)	9085 (1)
C(2)	11599 (3)	582 (3)	8649 (1)
C(3)	10874 (3)	−19 (3)	8276 (1)
C(4)	9681 (3)	−336 (3)	8337 (1)
C(5)	9179 (2)	−26 (2)	8775 (1)
C(6)	7885 (3)	−389 (3)	8821 (1)
C(7)	7247 (2)	21 (2)	9256 (1)
C(8)	8012 (2)	883 (2)	9611 (1)
C(9)	9395 (2)	985 (2)	9607 (1)
C(10)	9900 (2)	603 (2)	9147 (1)
C(11)	6735 (3)	1719 (3)	7731 (1)
C(12)	7510 (4)	2365 (3)	7469 (1)
C(13)	8381 (3)	3102 (3)	7712 (1)
C(14)	8517 (3)	3196 (3)	8224 (1)
C(15)	7751 (2)	2552 (2)	8500 (1)
C(16)	7883 (2)	2702 (2)	9053 (1)
C(17)	7198 (2)	1899 (2)	9359 (1)
C(18)	6270 (2)	1023 (2)	9089 (1)
C(19)	5956 (3)	1176 (3)	8530 (1)
C(20)	6847 (3)	1821 (2)	8253 (1)
C(21)	6758 (3)	−1023 (2)	9511 (1)
C(22)	5082 (3)	966 (3)	9344 (1)
O(1)	10057 (2)	1397 (2)	9962 (1)
O(2)	7322 (3)	−1008 (3)	8506 (1)
O(3)	4988 (3)	790 (3)	8310 (1)
O(4)	8535 (2)	3446 (2)	9267 (1)

b) Dimer (II)

Atoms	*x*	*y*	*z*
C(1)	−7862 (7)	−3211 (7)	77 (4)
C(2)	−8175 (7)	−1774 (7)	206 (4)
C(3)	−7405 (7)	−337 (8)	−421 (5)
C(4)	−6314 (7)	−352 (7)	−1164 (4)
C(5)	−6002 (7)	−1833 (6)	−1317 (4)
C(6)	−4810 (7)	−1800 (7)	−2139 (4)
C(7)	−4308 (7)	−3311 (7)	−2244 (3)
C(8)	−5638 (7)	−5041 (6)	−1737 (3)
C(9)	−6605 (6)	−4944 (6)	−839 (3)
C(10)	−6812 (6)	−3301 (6)	−689 (3)
C(11)	−6764 (7)	−2135 (7)	−5080 (4)
C(12)	−8243 (8)	−1830 (7)	−5199 (4)
C(13)	−9679 (8)	−2585 (8)	−4575 (5)
C(14)	−9653 (7)	−3683 (7)	−3828 (4)
C(15)	−8153 (6)	−3991 (6)	−3683 (4)
C(16)	−8213 (7)	−5190 (7)	−2856 (3)
C(17)	−6686 (7)	−5689 (7)	−2745 (3)
C(18)	−4958 (7)	−4361 (7)	−3257 (3)
C(19)	−5045 (7)	−3393 (7)	−4163 (3)
C(20)	−6721 (6)	−3197 (6)	−4315 (3)
C(21)	−2309 (8)	−2573 (9)	−2002 (4)
C(22)	−7424 (8)	−7690 (7)	−3002 (4)
O(1)	−7210 (6)	−6162 (5)	−265 (3)
O(2)	−4187 (5)	−533 (5)	−2691 (3)
O(3)	−3828 (5)	−2797 (5)	−4738 (3)
O(4)	−9462 (5)	−5811 (6)	−2311 (3)

TABLE III. Bond Lengths (Å) with Their E.S.D.s in Parentheses

	I	II
C(1)–C(2)	1.385 (4)	1.357 (9)
C(1)–C(10)	1.398 (4)	1.394 (8)
C(2)–C(3)	1.378 (4)	1.386 (8)
C(3)–C(4)	1.370 (5)	1.373 (9)
C(4)–C(5)	1.403 (4)	1.397 (9)
C(5)–C(6)	1.480 (4)	1.499 (8)
C(5)–C(10)	1.391 (3)	1.407 (6)
C(6)–C(7)	1.507 (4)	1.514 (9)
C(6)–O(2)	1.212 (4)	1.219 (6)
C(7)–C(8)	1.546 (3)	1.547 (6)
C(7)–C(18)	1.596 (3)	1.575 (6)
C(7)–C(21)	1.521 (4)	1.531 (8)
C(8)–C(9)	1.500 (3)	1.493 (7)
C(8)–C(17)	1.571 (3)	1.567 (6)
C(9)–C(10)	1.480 (4)	1.480 (8)
C(9)–O(1)	1.213 (3)	1.209 (6)
C(11)–C(12)	1.382 (5)	1.385 (9)
C(11)–C(20)	1.395 (4)	1.385 (8)
C(12)–C(13)	1.373 (5)	1.383 (8)
C(13)–C(14)	1.367 (4)	1.383 (9)
C(14)–C(15)	1.396 (4)	1.408 (9)
C(15)–C(16)	1.482 (4)	1.500 (7)
C(15)–C(20)	1.395 (3)	1.390 (6)
C(16)–C(17)	1.499 (3)	1.526 (9)
C(16)–O(4)	1.211 (3)	1.203 (6)
C(17)–C(18)	1.542 (3)	1.549 (6)
C(17)–C(22)	—	1.538 (8)
C(18)–C(19)	1.505 (4)	1.499 (7)
C(18)–C(22)	1.531 (4)	—
C(19)–C(20)	1.491 (4)	1.501 (9)
C(19)–O(3)	1.218 (4)	1.210 (6)

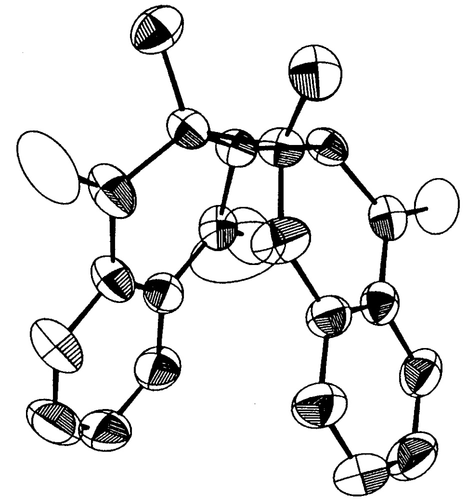
The Structure of the Dimer (I) Figure 1a shows that the dimer (I) has a *cis-syn* form, 5a,5b-*cis*-dimethyl-5a,5b,11a,11b-tetrahydro-*β*,*β′*-*cis*-binaphthylene-5,6,11,12-tetrone. The molecule was twisted around both inter-annular bonds, C(7)–C(18) and C(8)–C(17), connecting between 2,3-dihydronaphthoquinone rings, as indicated by the torsion angle C(6)–C(7)–C(18)–C(19) of 13.2°. An examination of the bond lengths and angles showed that the molecule possesses approximate mirror symmetry across two midpoints of the inter-annular bonds, but the torsion angles showed that the molecule has nearly a two-fold rotational symmetry around an axis through the center of the cyclobutane ring, as shown in Fig. 2. Such twisting may cause the larger torsion angles within the cyclobutane ring to be −10.9°, 11.3°, −10.9°, and 11.1° about bonds C(7)–C(8), C(8)–C(17), C(17)–C(18) and C(18)–C(7), respectively. Two methyl groups attached to the adjacent carbon atoms, C(7) and C(18), of the cyclobutane ring took an eclipsed form with a torsion angle C(21)–C(7)–C(18)–C(22) of 17.4°, and then were very close: a distance of 2.93 Å between the carbon atoms C(21) and C(22). The bond lengths and angles seemed to be almost normal except for the following: the bond angles around the methine carbon atoms were 120.0° and 116.1° at the atom C(8), and 119.3° and 114.5° at the atom C(17), which was much larger than the regular tetrahedral angle of 109.5°, and the bond lengths of the inter-annular ring, 1.596 and 1.571 Å, were also longer than the single bond lengths of 1.546 and 1.542 Å found in the intra-2,3-dihydrobenzoquinone ring. Such bond elongation has often been found in other photodimers,5,6) probably attributed to an effect of a through-bond coupling6) between two double bonds very closely facing each other, *i.e.*, between the sp^2 carbon atoms of C(6) and C(19), 2.80 Å, and between C(9) and C(16), 2.99 Å. The calculations of the least-squares planes showed that both benzene rings were essentially planar, because of the displacement under 0.011 Å from the plane, but the dihydro-*p*-benzoquinone rings were deformed, adopting a half-chair form, puckered

Table IV. Bond Angles (°) with Their E.S.D.s in Parentheses

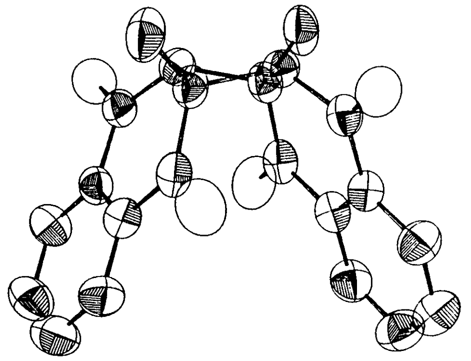
	I	II
C(2)–C(1)–C(10)	119.6 (3)	121.6 (5)
C(1)–C(2)–C(3)	120.7 (3)	119.7 (6)
C(2)–C(3)–C(4)	120.3 (3)	120.4 (7)
C(3)–C(4)–C(5)	120.1 (3)	120.6 (5)
C(4)–C(5)–C(6)	117.9 (2)	119.0 (4)
C(4)–C(5)–C(10)	119.6 (2)	118.7 (5)
C(6)–C(5)–C(10)	122.5 (2)	122.3 (5)
C(5)–C(6)–C(7)	120.4 (2)	119.3 (4)
C(5)–C(6)–O(2)	120.4 (3)	120.4 (6)
C(7)–C(6)–O(2)	119.3 (3)	120.2 (5)
C(6)–C(7)–C(8)	114.8 (2)	112.9 (5)
C(6)–C(7)–C(18)	111.4 (2)	112.8 (5)
C(6)–C(7)–C(21)	108.4 (2)	108.4 (4)
C(8)–C(7)–C(18)	89.0 (2)	87.4 (3)
C(8)–C(7)–C(21)	115.4 (2)	118.6 (5)
C(18)–C(7)–C(21)	116.9 (2)	115.6 (5)
C(7)–C(8)–C(9)	120.0 (2)	120.4 (4)
C(7)–C(8)–C(17)	89.8 (2)	88.8 (3)
C(9)–C(8)–C(17)	116.1 (2)	119.5 (5)
C(8)–C(9)–C(10)	117.2 (2)	117.0 (4)
C(8)–C(9)–O(1)	120.8 (2)	121.5 (5)
C(10)–C(9)–O(1)	122.0 (2)	121.4 (4)
C(9)–C(10)–C(1)	118.8 (2)	119.6 (4)
C(9)–C(10)–C(5)	121.5 (2)	121.5 (4)
C(1)–C(10)–C(5)	119.6 (2)	118.9 (5)
C(12)–C(11)–C(20)	119.0 (3)	119.2 (5)
C(11)–C(12)–C(13)	121.3 (2)	121.1 (6)
C(12)–C(13)–C(14)	120.4 (3)	119.6 (7)
C(13)–C(14)–C(15)	119.7 (3)	120.4 (5)
C(14)–C(15)–C(16)	118.7 (2)	117.5 (4)
C(14)–C(15)–C(20)	120.0 (2)	118.7 (5)
C(16)–C(15)–C(20)	121.2 (2)	123.8 (5)
C(15)–C(16)–C(17)	119.0 (2)	118.5 (4)
C(15)–C(16)–O(4)	122.2 (2)	121.5 (6)
C(17)–C(16)–O(4)	118.8 (2)	120.0 (5)
C(16)–C(17)–C(18)	119.3 (2)	112.9 (5)
C(16)–C(17)–C(8)	114.5 (2)	113.0 (4)
C(18)–C(17)–C(8)	90.0 (2)	87.6 (3)
C(16)–C(17)–C(22)	—	108.0 (4)
C(18)–C(17)–C(22)	—	117.9 (5)
C(8)–C(17)–C(22)	—	116.4 (5)
C(17)–C(18)–C(19)	116.1 (2)	121.0 (5)
C(17)–C(18)–C(7)	89.0 (2)	88.5 (3)
C(19)–C(18)–C(7)	116.1 (2)	119.8 (5)
C(17)–C(18)–C(22)	110.5 (2)	—
C(19)–C(18)–C(22)	110.8 (2)	—
C(7)–C(18)–C(22)	113.9 (2)	—
C(18)–C(19)–C(20)	118.6 (2)	116.3 (4)
C(18)–C(19)–O(3)	120.6 (3)	121.8 (6)
C(20)–C(19)–O(3)	120.8 (3)	121.9 (5)
C(19)–C(20)–C(11)	118.6 (3)	117.8 (4)
C(19)–C(20)–C(15)	121.7 (2)	121.1 (4)
C(11)–C(20)–C(15)	119.6 (3)	121.0 (5)

at the atom C(8) or C(18). The dihedral angle between the least-squares planes of both dihydronaphthoquinone moieties was 35.2°.

The Structure of the Dimer (II) Figure 1b shows that dimer (II) has a *cis-anti* form, 5a,11a-*cis*-dimethyl-5a,5b,11a,11b-tetrahydro-*β*,*β*′-*cis*-binaphthylene-5,6,11,12-tetrone. The molecule was also twisted around both inter-annular bonds, C(7)–C(18) and C(8)–C(17), connected between the dihydronaphthoquinone rings, as showing by the torsion angle C(6)–C(7)–C(18)–C(19) of 32.4°. The bond lengths and angles showed that the molecule has approximately a two-fold rotational symmetry around an

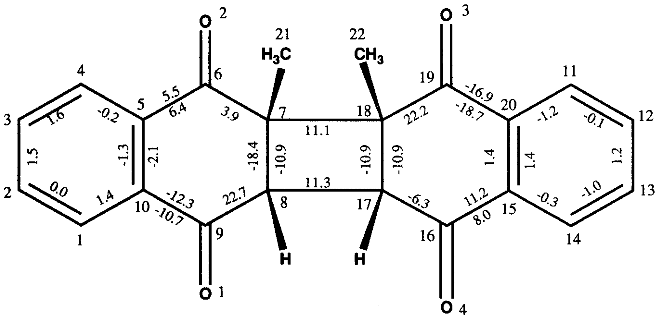


(a) dimer (I)

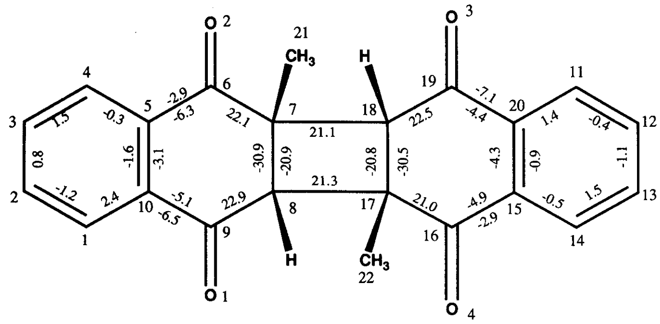


(b) dimer (II)

Fig. 1. ORTEP Drawings of Dimers (I) and (II)



(a) dimer (I)



(b) dimer (II)

Fig. 2. The Selective Torsional Angles of Dimers (I) and (II)

axis through the center of the cyclobutane ring. The twisting was larger than that of dimer (I), as shown by the torsion angle C(6)–C(7)–C(18)–C(19) of 32.4°. The torsion angles within the cyclobutane ring were −20.8°, 21.3°, −20.8° and 21.1° about the bonds C(7)–C(8), C(8)–C(17), C(17)–C(18) and C(18)–C(7), respectively. These values showed that the ring is more puckered than that of dimer (I). The bond lengths and angles seemed to be almost normal except for the following: the bond angles at the methine carbon atoms were 120.4° and 119.5° at C(8), and 121.0° and 119.8° at C(18), which were again greater than the normal tetrahedral angle. The lengths of 1.575 and 1.567 Å for the inter-annular bonds within the cyclobutane ring were also elongated, because of the contribution of the through-bond coupling$^{6)}$ between the sp^2 carbon atoms of C(6) and C(19), 3.00 Å, and between C(9) and C(16), 2.99 Å. The dihydrobenzoquinone rings were also more deformed, adopting a half-chair form, puckered at atom C(8) or C(18). These larger puckerings might reflect the larger twisting around the cyclobutane ring mentioned above. The dihedral angle between the least-squares planes of both dihydronaphthoquinone moieties was 46.2°.

Discussion

According to the studies of physical properties and structural stability,$^{1)}$ two photoproducts, (A) and (B), were determined to be the dimers (III) and (IV), respectively. However, as mentioned above, we found that dimer (A) is the *cis-syn* form (I), and (B) the *cis-anti* form (II). These are the structural isomers for two methyl groups attached to the cyclobutane ring, and the corresponding lengths and angles were similar to each other. As mentioned above, the twisting in dimer (II) was larger than that in dimer (I), and the values of the angle between both dihydronaphthoquinone moieties showed that dimer (II) has a more open structure than that of dimer (I). Since such twisting can decrease the overlapping between the two dihydronaphthoquinone rings, dimer (II) seemed to be more stabilized than dimer (I).

To confirm the results of these X-ray analyses, steric energies of the four isomers and those of two isomers without any of the methyl groups were calculated by the molecular mechanics of MM2.$^{7)}$ The steric energies were calculated to be 62.93 for isomer (I), 59.84 for (II), 58.18 for (III), 58.65 for (IV), 57.02 for the *cis* form, and 53.84 kcal/mol for the *trans* form. Therefore, as assumed by Asahi,$^{1)}$ the *trans* forms are more stable than the *cis* forms, but none of them were formed by the photoreaction. This may indicate that the photoreaction in the solid state is caused by factors other than the energetic condition, *e.g.* a topochemical factor,$^{5)}$ so that MNQ crystal contains two kinds of molecular stacts related with mirror and two-fold rotational symmetries, wherein their molecules are approached under 4.1 Å. Unfortunately, we could not reveal the real reason, because of the failure of X-ray analysis of MNQ, as mentioned above. However, MM2 calculations did clarify that isomer (I) is less stable than isomer (II) by 3.1 kcal/mol. This agreed well with the result of X-ray analyses.

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