The Crystal and Molecular Structures of Solid-State Photodimers of Two
cis-4a,5,8,8a-Tetrahydro-1,4-naphthoquinone Derivatives

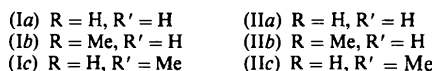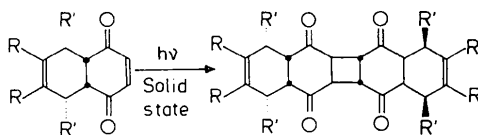By Simon E. V. Phillips and James Trotter

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Crystals of pentacyclo[10.8.0.0^{2,11}.0^{4,9}.0^{14,19}]eicosa-6,16-diene-3,10,13,20-tetrone are monoclinic, space group $P2_1/c$, with $a = 11\cdot7302$ (5), $b = 6\cdot4142$ (2), $c = 10\cdot9331$ (5) Å, $\beta = 114\cdot624$ (3)° and $Z = 2$. Crystals of the 6,7,16,17-tetramethyl derivative also have space group $P2_1/c$, with $a = 15\cdot247$ (1), $b = 6\cdot2776$ (6), $c = 10\cdot1949$ (7) Å, $\beta = 93\cdot19$ (1)°, $Z = 2$. The two structures are almost identical, the dimer molecules having crystallographic centres of symmetry and planar four-membered rings.

Introduction

A study of the photochemistry of various substituted *cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone systems in solution (Scheffer, Jennings & Louwerens, 1976) and the solid state (Dzakpasu, Phillips, Scheffer & Trotter, 1976) has revealed unusual reaction pathways. The solid-state dimerization of 5α,8α-dimethyl-4aβ,5,8,8aβ-tetrahydro-1,4-naphthoquinone (I*c*) has been described and the crystal structure determined, together with that of the dimer product (II*c*) (Phillips & Trotter, 1977*a*). Irradiation of crystals of *cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (I*a*) and 6,7-dimethyl-*cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (I*b*) also gives dimer products [(II*a*) and (II*b*)] (Dzakpasu & Scheffer, 1976).

(I*a*) R = H, R' = H	(II*a*) R = H, R' = H
(I*b*) R = Me, R' = H	(II*b*) R = Me, R' = H
(I*c*) R = H, R' = Me	(II*c*) R = H, R' = Me

The crystal structures of (II*a*) and (II*b*) have been determined to ascertain the stereochemistry of the four-membered rings.

Experimental

Dimer II*a*

Colourless, well-formed, rod-shaped crystals were obtained by recrystallization from acetonitrile. The crystal chosen for data collection (dimensions *ca* 0·05 × 0·03 × 0·03 cm) was mounted on a Datex-auto-mated GE XRD 6 diffractometer with its *b* axis parallel to the φ axis of the goniometer. Accurate unit-cell constants were obtained by least-squares refinement from the 2θ values of the α_1 and α_2 peaks of 15 manually centred reflexions.

Crystal data: $C_{20}H_{20}O_4$, FW 324·38; monoclinic, $a = 11\cdot7302$ (5), $b = 6\cdot4142$ (2), $c = 10\cdot9331$ (5) Å, $\beta = 114\cdot624$ (3)°; $V = 747\cdot79$ (6) Å^3, $d_m = 1\cdot44$ (flotation), $d_x = 1\cdot440$ g cm^{-3}, $Z = 2$. Space group $P2_1/c$ (0*k*0, $k = 2n$; *h0l*, $l = 2n$). Cu $K\alpha$ radiation, Ni-filtered; λ(Cu $K\alpha$) = 1·5418 Å; μ(Cu $K\alpha$) = 8·21 cm^{-1}.

Intensities were collected by the θ–2θ scan technique, with a scan speed of 4° min^{-1} and 10 s background counts, to a maximum 2θ of 146°. Reflexion $10,0,\bar{4}$, was measured after every fifty observations, its intensity fluctuating between limits of $\pm 3\%$ during data collection. Of the 1488 independent reflexions collected, 1385 had intensities greater than $3\sigma(I)$ above background [$\sigma^2(I) = S + B + (0\cdot06S)^2$, where $S = $ scan and $B = $ background count]. Lorentz and polarization corrections were applied and the structure amplitudes derived. No absorption correction was applied in view of the low value of the absorption coefficient.

Dimer II*b*

Colourless, elongated plate crystals were obtained from a mixture of chloroform and hexane. A piece (dimensions *ca* 0·007 × 0·025 × 0·075 cm) was cut from a larger crystal and mounted on the diffractometer as before. Ten reflexions were used in the cell-parameter refinement.

Crystal data: $C_{24}H_{28}O_4$, FW 380·48, monoclinic, $a = 15\cdot247$ (1), $b = 6\cdot2776$ (6), $c = 10\cdot1949$ (7) Å, $\beta = 93\cdot19$ (1)°; $V = 974\cdot3$ (1) Å^3, $d_m = 1\cdot28$ (flotation), $d_x = 1\cdot297$ g cm^{-3}, $Z = 2$. Space group $P2_1/c$. Cu $K\alpha$ radiation, Ni-filtered; μ(Cu $K\alpha$) = 7·06 cm^{-1}.

Intensities were collected as before, but with a scan speed of 2° min^{-1}. The standard reflexion 525 fluctuated between limits of $\pm 4\%$ during data collection. Of the 1443 independent reflexions with $2\theta < 120°$, 1011 had intensities greater than $3\sigma(I)$ above back-

ground [$\sigma(I)$ defined as before but with the constant set to 0·05]. Structure amplitudes were derived and no absorption correction was applied.

Structure determination and refinement

Dimer IIa

A Wilson plot gave good centric statistics and 203 E values greater than 1·5 were derived. An automatic computer program (Long, 1965), applying a multi-solution procedure, was used to assign phases to the E values. The set with the highest consistency was used to calculate an E map, which revealed the positions of all non-hydrogen atoms. Two cycles of isotropic, followed by two cycles of anisotropic, full-matrix least-squares refinement were carried out, where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with weights $w = 1/\sigma^2(F)$; $\sigma(F)$ values were derived from the previously calculated $\sigma(I)$ values. R at this point was 0·089 and a difference Fourier map gave the positions of all H atoms; these were included in subsequent refinement cycles with isotropic temperature factors. Further refinement showed the weighting scheme to be unsatisfactory, and it was replaced with the following: $\sqrt{w} = |F_o|/3·8$ for $|F_o| < 3·8$ and $\sqrt{w} = 3·8/|F_o|$ for $|F_o| \geq 3·8$. In the final stages of refinement, extinction effects were apparent in the data, and a correction was applied as described for (Ic) (Phillips & Trotter, 1977a). The

final refined value of the parameter E was 9 (2) × 10^{-8} and the correction produced a significant reduction in R.

The final R and $R'\{=[\Sigma w(|F_o| - |F_c|)^2/ \Sigma w|F_o|^2]^{1/2}\}$ for the 1385 reflexions with $I > 3\sigma(I)$ are 0·037 and 0·053 respectively. For all 1488 data, R is 0·039 and R' is 0·055.* The largest change/error in the final cycle of refinement was 0·04. The difference map showed random fluctuations with the highest peak at 0·39 e Å^{-3}. Atomic scattering factors for O and C atoms are those of Cromer & Mann (1968), and for H atoms those of Stewart, Davidson & Simpson (1965). The real and imaginary parts of the anomalous scattering factors for O and C atoms were taken from Cromer & Liberman (1970). Final positional and thermal parameters are listed in Tables 1 and 2.

Dimer IIb

One hundred and ninety-six E values > 1·5 were derived and sets of phases assigned as for dimer IIa. The set with the highest consistency again gave an E map showing all non-hydrogen atoms. Four cycles of refinement were carried out as before, leading to $R =$

Table 1. *Final positional parameters for* (IIa) (*fractional*, ×10⁵, H ×10³) *with estimated standard deviations in parentheses*

The molecular centre is at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

	x	y	z
O(1)	30170 (10)	89987 (15)	38987 (11)
O(2)	41242 (9)	19862 (16)	67500 (10)
C(1)	33161 (10)	73845 (18)	45289 (11)
C(2)	41743 (10)	58570 (17)	42712 (11)
C(3)	43937 (10)	36761 (17)	49486 (11)
C(4)	37144 (11)	32221 (18)	58279 (11)
C(5)	25362 (10)	44701 (18)	55204 (11)
C(6)	14936 (12)	40104 (21)	41234 (13)
C(7)	4779 (11)	56328 (22)	37160 (13)
C(8)	5877 (12)	74338 (22)	43406 (14)
C(9)	17533 (12)	81097 (22)	55190 (14)
C(10)	28791 (11)	68109 (19)	56146 (11)
H(2)	394 (1)	578 (2)	330 (1)
H(3)	423 (1)	253 (3)	429 (2)
H(5)	225 (1)	414 (2)	623 (2)
H(6a)	183 (2)	386 (3)	344 (2)
H(6b)	113 (2)	263 (3)	413 (2)
H(7)	−26 (2)	525 (3)	298 (2)
H(8)	−15 (2)	838 (3)	404 (2)
H(9a)	162 (1)	790 (3)	633 (2)
H(9b)	194 (2)	959 (3)	544 (2)
H(10)	363 (1)	707 (3)	654 (2)

Table 2. *Final thermal parameters for* (IIa) *and their estimated standard deviations*

(a) Anisotropic thermal parameters ($U_{ij} \times 10^4$ Å²) in the expression:

$$f = f^0 \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	502 (6)	262 (5)	563 (6)	99 (4)	286 (5)	141 (4)
O(2)	383 (5)	406 (6)	439 (6)	67 (4)	192 (4)	225 (4)
C(1)	254 (5)	198 (6)	285 (6)	−16 (4)	97 (5)	4 (4)
C(2)	260 (5)	191 (5)	222 (6)	2 (4)	102 (4)	31 (4)
C(3)	269 (6)	166 (5)	250 (6)	−8 (4)	107 (4)	8 (4)
C(4)	271 (6)	205 (6)	264 (6)	−35 (4)	100 (4)	31 (4)
C(5)	271 (6)	259 (6)	267 (6)	−11 (4)	128 (5)	41 (4)
C(6)	296 (6)	277 (7)	344 (7)	−35 (5)	88 (5)	−8 (5)
C(7)	257 (6)	389 (8)	337 (7)	−5 (5)	73 (5)	66 (5)
C(8)	301 (6)	363 (7)	391 (7)	71 (5)	159 (5)	91 (6)
C(9)	355 (7)	315 (7)	393 (7)	42 (5)	195 (6)	−28 (5)
C(10)	271 (6)	253 (6)	257 (6)	0 (4)	108 (5)	−32 (4)

(b) Isotropic thermal parameters ($U \times 10^3$)

	U (Å²)		U (Å²)		U (Å²)
H(2)	28 (3)	H(6b)	49 (5)	H(9a)	40 (4)
H(3)	38 (4)	H(7)	45 (4)	H(9b)	57 (5)
H(5)	33 (4)	H(8)	45 (4)	H(10)	32 (4)
H(6a)	44 (4)				

Table 3. *Final positional parameters for* (IIb)
(*fractional,* ×10⁴, H ×10³) *with estimated standard deviations in parentheses*

The molecular centre is at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

	x	y	z
O(1)	3472 (2)	8485 (5)	3886 (3)
O(2)	4069 (2)	1147 (5)	6412 (3)
C(1)	3695 (3)	6955 (6)	4535 (3)
C(2)	4520 (3)	5758 (6)	4287 (4)
C(3)	4649 (3)	3491 (6)	4862 (4)
C(4)	3926 (3)	2618 (6)	5665 (4)
C(5)	3057 (3)	3721 (7)	5529 (4)
C(6)	2566 (3)	3257 (7)	4213 (4)
C(7)	1744 (3)	4582 (7)	4021 (4)
C(8)	1610 (3)	6336 (8)	4721 (4)
C(9)	2283 (3)	7185 (9)	5728 (5)
C(10)	3174 (3)	6144 (7)	5668 (4)
C(11)	1104 (4)	3781 (11)	2946 (6)
C(12)	792 (4)	7705 (12)	4572 (8)
H(2)	464 (2)	584 (7)	336 (4)
H(3)	479 (3)	241 (8)	415 (4)
H(5)	272 (3)	318 (6)	621 (4)
H(6a)	296 (2)	349 (6)	349 (4)
H(6b)	240 (3)	162 (8)	413 (4)
H(9a)	204 (3)	690 (7)	661 (5)
H(9b)	236 (3)	876 (8)	556 (4)
H(10)	353 (2)	646 (5)	650 (4)
H(11a)	89 (5)	267 (15)	321 (8)
H(11b)	60 (4)	477 (10)	272 (6)
H(11c)	139 (4)	381 (11)	203 (8)
H(12a)	92 (8)	904 (22)	379 (15)
H(12b)	63 (5)	831 (12)	535 (7)
H(12c)	40 (6)	677 (16)	418 (10)

Table 4. *Final thermal parameters for* (IIb) *and their estimated standard deviations*

(*a*) Anisotropic thermal parameters (U_{ij} × 10³ Å²)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	63 (2)	42 (2)	50 (2)	16 (2)	−3 (1)	11 (2)
O(2)	56 (2)	49 (2)	60 (2)	−1 (2)	−8 (2)	27 (2)
C(1)	42 (2)	33 (2)	28 (2)	0 (2)	−13 (2)	−2 (2)
C(2)	41 (2)	33 (2)	23 (2)	1 (2)	−4 (2)	2 (1)
C(3)	44 (2)	33 (2)	26 (2)	2 (2)	−6 (2)	−4 (2)
C(4)	46 (3)	34 (2)	30 (2)	0 (2)	−9 (2)	3 (2)
C(5)	41 (2)	47 (3)	30 (2)	2 (2)	3 (2)	5 (2)
C(6)	44 (2)	39 (2)	43 (2)	−3 (2)	−3 (2)	0 (2)
C(7)	40 (2)	50 (3)	43 (2)	1 (2)	−2 (2)	10 (2)
C(8)	35 (2)	53 (3)	56 (3)	7 (2)	9 (2)	10 (2)
C(9)	49 (3)	58 (3)	48 (3)	7 (2)	8 (2)	−2 (2)
C(10)	46 (2)	43 (2)	28 (2)	4 (2)	−1 (2)	−4 (2)
C(11)	50 (3)	74 (4)	65 (3)	−4 (3)	−14 (3)	5 (3)
C(12)	54 (3)	76 (4)	101 (5)	25 (3)	0 (3)	−3 (4)

(*b*) Isotropic thermal parameters (U × 10²)

	U (Å²)		U (Å²)		U (Å²)
H(2)	5 (1)	H(9a)	6 (1)	H(11c)	12 (2)
H(3)	6 (1)	H(9b)	5 (1)	H(12a)	26 (6)
H(5)	4 (1)	H(10)	3 (1)	H(12b)	12 (3)
H(6a)	3 (1)	H(11a)	14 (3)	H(12c)	16 (4)
H(6b)	5 (1)	H(11b)	9 (2)		

0·11. A difference Fourier map then revealed the positions of all but four H atoms, those missing being located on a subsequent difference map. Refinement continued as before and a new weighting scheme and extinction correction were again necessary. Weights were assigned as follows: $\sqrt{w} = |F_o|/8\cdot5$ for $|F_o| <$ 8·5 and $\sqrt{w} = 8\cdot5/|F_o|$ for $|F_o| \geq 8\cdot5$. The final value of E was 3 (1) × 10⁻⁷.

The final R and R' for the 1101 reflexions with $I >$ $3\sigma(I)$ are 0·064 and 0·077 respectively. For all 1443 data, R is 0·100 and R' is 0·082.* The largest change/error in the final cycle of refinement was 0·34 and the highest difference-map peak was 0·36 e Å⁻³. Scattering factors were as before, except that no correction was made for anomalous scattering. Final positional and thermal parameters are listed in Tables 3 and 4.

Thermal-motion analysis

The thermal motion has been analysed in terms of the rigid-body modes of translation and libration (Schomaker & Trueblood, 1968) with the computer program *MGTLS*. In each case, the ten unique atoms in the ring system were taken to be a rigid body and the origin was fixed at the centre of symmetry. The r.m.s. ΔU_{ij} values for (IIa) and (IIb) are 0·0016 and 0·0032 Å² respectively, compared to the least-squares r.m.s. $\sigma(U_{ij})$ values of 0·0006 and 0·0024 Å². Thus the rigid bodies give good approximations to the thermal motion. Bond lengths in the rings have been corrected for libration (Cruickshank, 1956, 1961) with the shape parameter 0·08 for all atoms. Bonds outside the ten-atom core were further corrected for independent motion based on the ΔU_{ij} values (Busing & Levy, 1964;

* See previous footnote.

Table 5. *Bond lengths* (Å) *with estimated standard deviations in parentheses for non-hydrogen atoms*

	(IIa)		(IIb)	
	Uncorrected	Corrected	Uncorrected	Corrected
O(1)—C(1)	1·212 (2)	1·214	1·205 (5)	1·206
O(2)—C(4)	1·213 (2)	1·215	1·209 (5)	1·209
C(1)—C(2)	1·513 (2)	1·515	1·499 (6)	1·501
C(1)—C(10)	1·521 (2)	1·524	1·526 (6)	1·529
C(2)—C(3)	1·553 (2)	1·557	1·548 (5)	1·551
C(2)—C(3ⁱ)	1·564 (2)	1·565	1·567 (5)	1·569
C(3)—C(4)	1·511 (2)	1·513	1·512 (6)	1·514
C(4)—C(5)	1·509 (2)	1·510	1·495 (6)	1·496
C(5)—C(6)	1·536 (2)	1·539	1·528 (5)	1·531
C(5)—C(10)	1·547 (2)	1·550	1·538 (6)	1·541
C(6)—C(7)	1·503 (2)	1·505	1·507 (6)	1·509
C(7)—C(8)	1·321 (2)	1·324	1·334 (6)	1·338
C(8)—C(9)	1·500 (2)	1·502	1·509 (6)	1·511
C(9)—C(10)	1·528 (2)	1·529	1·511 (6)	1·512
C(7)—C(11)	—	—	1·513 (7)	1·515
C(8)—C(12)	—	—	1·515 (7)	1·517

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Table 6. *Bond angles* (°) *with estimated standard deviations in parentheses for non-hydrogen atoms*

	(IIa)	(IIb)
O(1)–C(1)–C(2)	120·3 (1)	121·4 (4)
O(1)–C(1)–C(10)	122·6 (1)	122·6 (4)
C(2)–C(1)–C(10)	117·1 (1)	116·0 (3)
C(1)–C(2)–C(3)	119·0 (1)	119·2 (3)
C(1)–C(2)–C(3^i)	114·9 (1)	114·6 (3)
C(3)–C(2)–C(3^i)	89·2 (1)	89·2 (3)
C(2)–C(3)–C(4)	116·8 (1)	117·2 (3)
C(2)–C(3)–C(2^i)	90·8 (1)	90·8 (3)
C(4)–C(3)–C(2^i)	114·9 (1)	113·6 (3)
O(2)–C(4)–C(3)	121·6 (1)	120·4 (4)
O(2)–C(4)–C(5)	122·7 (1)	122·7 (4)
C(3)–C(4)–C(5)	115·7 (1)	116·8 (3)
C(4)–C(5)–C(6)	113·3 (1)	112·5 (3)
C(4)–C(5)–C(10)	108·2 (1)	110·6 (3)
C(6)–C(5)–C(10)	109·3 (1)	108·5 (3)
C(5)–C(6)–C(7)	111·5 (1)	111·8 (4)
C(6)–C(7)–C(8)	123·9 (1)	122·5 (4)
C(7)–C(8)–C(9)	123·7 (1)	122·4 (4)
C(8)–C(9)–C(10)	110·7 (1)	113·5 (4)
C(1)–C(10)–C(5)	110·2 (1)	108·8 (3)
C(1)–C(10)–C(9)	112·2 (1)	113·2 (4)
C(5)–C(10)–C(9)	109·4 (1)	109·4 (4)
C(6)–C(7)–C(11)	—	114·1 (4)
C(8)–C(7)–C(11)	—	123·3 (4)
C(7)–C(8)–C(12)	—	124·4 (5)
C(9)–C(8)–C(12)	—	113·1 (5)

See Table 5 for symmetry code.

Johnson, 1970). Corrected bond lengths for both molecules are given in Table 5. Bond angles are not significantly affected and only uncorrected values are shown in Table 6.

Results and discussion

The crystal structures of the photodimers IIa and IIb were studied to determine the stereochemistry of the dimerization reaction. Stereo diagrams of the two molecules are shown in Figs. 1 and 2, together with the crystallographic numbering schemes. Both have crystallographic centres of symmetry and *trans–syn* stereochemistry, and are therefore similar to (IIc) (Phillips & Trotter, 1977a; Dzakpasu, Phillips, Scheffer & Trotter, 1976). The crystal structure of (Ia) has been determined (Phillips & Trotter, 1977b) and the intermolecular contacts between neighbouring C(2)= C(3) bonds are almost identical to those in (Ic). Crystals of (Ib) suitable for X-ray analysis have not been obtained.

Bond lengths and angles in the molecules (Tables 5 and 6) are mostly as expected. The rather short C(9)– C(10) bond is also found in related cis-4a,5,8,8a-tetrahydro-1,4-naphthoquinone monomers with H atoms at the bridgeheads. Mean $C(sp^3)$–$C(sp^3)$ and $C(sp^3)$– $C(sp^2)$ distances after thermal-motion correction are 1·548 (6) and 1·511 (3) Å for (IIa) and 1·541 (10) and 1·511 (4) Å for (IIb). Mean C–H distances are 0·987 (7) and 0·99 (2) Å respectively. There are, however, significant differences in bond angles, notably C(4)–C(5)–C(10) and C(8)–C(9)–C(10). The internal angles at C(7) and C(8) show a reduction of 1·4° with methyl substitution, and several other angles differ by 3σ or more. Relatively large differences are apparent in the intra-annular torsion angles (see Table 7), particularly those in the quinone rings. This suggests the changes may be related to crystal packing, as sub-
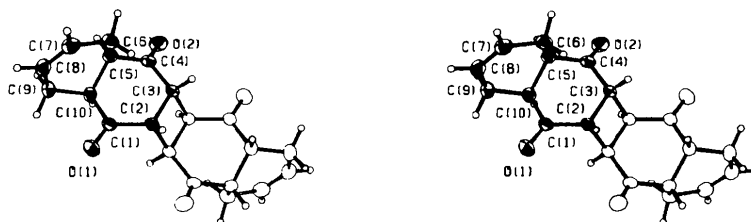

Fig. 1. Stereo diagram of (IIa) showing the crystallographic numbering scheme. H atoms are labelled according to the C atoms to which they are bonded. Non-hydrogen atoms are shown with 50% probability vibration ellipsoids, shaded for the asymmetric unit and open for symmetry-related atoms.
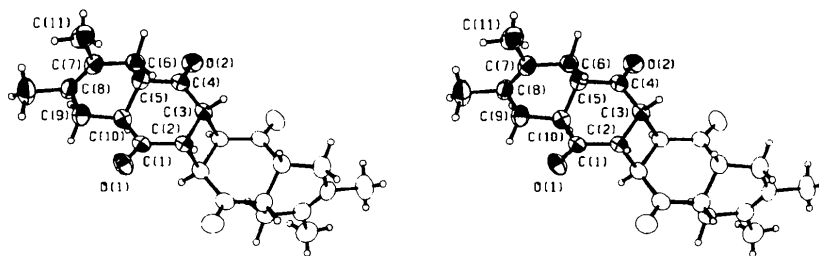

Fig. 2. Stereo diagram of (IIb).

stitution at C(7) and C(8) would be expected to affect the cyclohexene ring more strongly. All six-membered rings have half-chair conformation, as predicted for cyclohexene by minimum-energy calculations (Bucourt & Hainaut, 1965). The largest deviations from these calculated values occur for the (IIa) quinone ring where the conformation is far from symmetrical, e.g. C(2)–C(3)–C(4)–C(5) differs from C(10)–C(1)–C(2)–C(3) by 15·0°. The four-membered ring is constrained to be planar by the centre of symmetry. Interannular torsion angles vary little between the two molecules.

Mean-plane calculations show the C(1),C(2),C(3), C(4) groups to be planar within experimental error in each case; O(1), O(2) deviate from the plane by 0·153 (1) and −0·469 (1) Å for (IIa) and 0·295 (3) and −0·341 (3) Å for (IIb), reflecting the asymmetry in (IIa). Carbonyl groups deviate slightly, but significantly, from planarity.

The crystal structures of the two molecules are almost identical, as shown by the packing diagrams in Figs. 3 and 4. Molecules lie parallel to **a**, on crystallographic centres of symmetry ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$). In the structure of

Table 7. *Torsion angles (°) with estimated standard deviations in parentheses*

A positive angle corresponds to a clockwise rotation of the nearest to eclipse the furthest bond.

|	(IIa)	(IIb)
C(1)–C(2)–C(3)–C(4)	0·4 (1)	−0·7 (4)
C(2)–C(3)–C(4)–C(5)	24·3 (1)	16·5 (4)
C(3)–C(4)–C(5)–C(10)	−56·6 (1)	−48·6 (4)
C(4)–C(5)–C(10)–C(1)	64·7 (1)	64·2 (4)
C(5)–C(10)–C(1)–C(2)	−41·7 (1)	−48·9 (4)
C(10)–C(1)–C(2)–C(3)	9·3 (1)	18·0 (4)
C(5)–C(6)–C(7)–C(8)	13·1 (1)	18·0 (4)
C(6)–C(7)–C(8)–C(9)	1·4 (2)	2·3 (5)
C(7)–C(8)–C(9)–C(10)	17·4 (2)	11·7 (5)
C(8)–C(9)–C(10)–C(5)	−49·4 (1)	−44·6 (4)
C(9)–C(10)–C(5)–C(6)	64·7 (1)	64·5 (4)
C(10)–C(5)–C(6)–C(7)	−45·0 (1)	−50·4 (4)
C(6)–C(5)–C(10)–C(1)	−59·0 (1)	−59·7 (4)
C(4)–C(5)–C(10)–C(9)	−171·5 (1)	−171·7 (3)
C(1)–C(2)–C(3)–C(2ⁱ)	−118·3 (1)	−117·9 (3)
C(4)–C(3)–C(2)–C(3ⁱ)	118·6 (1)	117·3 (3)
H(5)–C(5)–C(10)–H(10)	64 (1)	66 (3)

See Table 5 for symmetry code.
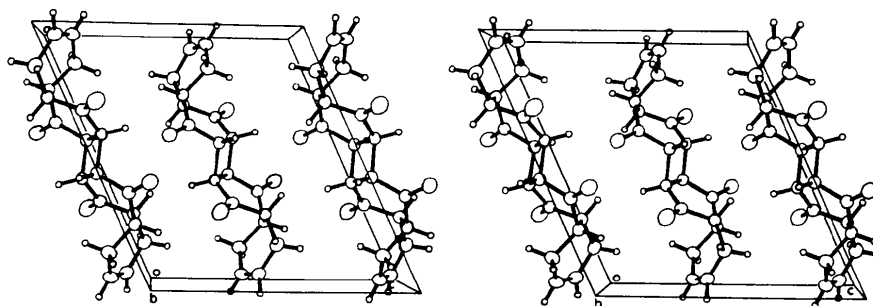
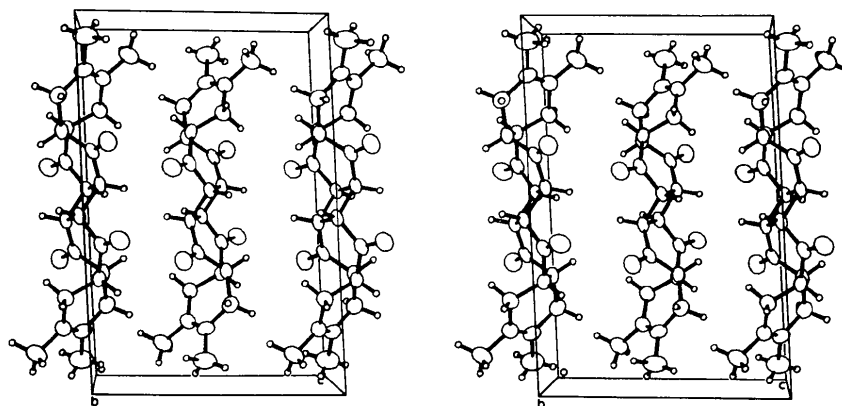Fig. 3. A **b** projection of the (IIa) structure.

Fig. 4. A **b** projection of the (IIb) structure.

(IIa), the arrangement is such that neighbouring C(7)= C(8) bonds are in close contact across centres of symmetry, in a manner reminiscent of that in (Ic) for C(2)=C(3) bonds prior to dimerization. The interplanar separation is 3·435 Å and the closest contact is 3·487 Å for C(7)···C(8)[−x, 1 − y, 1 − z] (also equal to the separation of the bond mid-points). Hindrance introduced by the methyl groups in (IIb) increases the separation to > 4 Å, with a resultant increase in length of the a axis and decrease in β. The efficient close packing of (IIa) is shown by its higher density and lower thermal-vibration parameters, compared to (IIb) and (IIc). This is reflected by the lower solubility in organic solvents displayed by (IIa). Other intermolecular contacts correspond to van der Waals interactions.

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The Crystal and Molecular Structure of cis-4a,5,8,8a-Tetrahydro-1,4-naphthoquinone and Comparison with some of its Derivatives

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Crystals of cis-4a,5,8,8a-tetrahydro-1,4-naphthoquinone are monoclinic, space group $P2_1/c$, with $a = 5·266$, $b = 24·267$, $c = 14·506$ Å, $\beta = 114·50°$ and $Z = 8$. The structure contains two crystallographically independent types of molecule, one of which occurs in pairs related by centres of symmetry. Irradiation of the crystals with ultraviolet light causes linking of the pairs to form dimers. Comparisons are made with other derivatives whose crystal structures are known.

Introduction

A study of the photochemistry of cis-4a,5,8,8a-tetrahydro-1,4-naphthoquinone [(I) in Table 1] and its derivatives, in solution (Scheffer, Jennings & Louwerens, 1976) and the solid state (Dzakpasu, Phillips, Scheffer & Trotter, 1976), has revealed unusual reaction pathways. Photolysis of (I) in solution gives products resulting from intramolecular β-H abstraction. Irradiation of the crystals, however, induces dimerization (Dzakpasu & Scheffer, 1976), and recrystallization of the crude product from acetonitrile gives crystals of the trans–syn dimer, whose structure has been reported (Phillips & Trotter, 1977b). The molecular formulae of other derivatives whose structures have been determined are shown in Table 1. Knowledge of these structures allows a comparison of molecular geometry and solid-state photochemical activity for a series of related compounds.