

(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  $\beta$ . 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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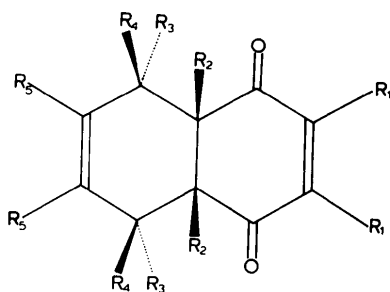
Crystals of *cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone are monoclinic, space group  $P2_1/c$ , with  $a = 5.266$ ,  $b = 24.267$ ,  $c = 14.506$  Å,  $\beta = 114.50^\circ$  and  $Z = 8$ . The structure contains two crystallographically independent types of molecule, one of which occurs in pairs related 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  $\beta$ -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.

Table 1. Derivatives whose structures have been determined



Derivative	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	Reference*
(I)	H	H	H	H	H	This work
(II)	Me	Me	H	H	Me	<i>a</i>
(III)	Me	Me	H	Me	H	<i>b</i>
(IV)	Me	H	H	H	Me	<i>c</i>
(V)	H	H	H	H	Ph	<i>d</i>
(VI)	H	CN	H	H	Me	<i>e</i>
(VII)	H	CN	Me	H	H	<i>f</i>
(VIII)	H	H	Me	H	H	Phillips & Trotter (1977a)

\* Reference column gives *x* in reference Phillips & Trotter (1976*x*).

### Experimental

Well-formed, yellow needles were obtained by recrystallization from a mixture of ether and petroleum spirit. The crystals proved unstable in the X-ray beam and two samples were needed to complete data collection. Both were sections (dimensions *ca* 0.08 × 0.03 × 0.02 cm) cut from a larger crystal. Each was mounted on a Datex-automated GE XRD 6 diffractometer with the *a*\* axis parallel to the  $\phi$  axis of the goniometer. Accurate unit-cell constants were obtained by least-squares refinement from the  $2\theta$  values of 16 manually centred reflexions.

### Crystal data

C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>, FW 162.19, monoclinic,  $a = 5.266(1)$ ,  $b = 24.267(5)$ ,  $c = 14.506(4)$  Å,  $\beta = 114.50(2)^\circ$ ;  $V = 1687.0(7)$  Å<sup>3</sup>,  $d_m = 1.26$  (floatation),  $Z = 8$ ,  $d_x = 1.277$  g cm<sup>-3</sup>. Space group  $P2_1/c$  ( $0k0$ ,  $k = 2n$ ;  $h0l$ ,  $l = 2n$ ). Cu  $K\alpha$  radiation, Ni-filtered;  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu(\text{Cu } K\alpha) = 7.3$  cm<sup>-1</sup>.

Intensities were collected in shells of reciprocal space to a maximum  $2\theta$  of  $120^\circ$ . The  $\theta$ - $2\theta$  scan technique was used with scan speed  $4^\circ \text{ min}^{-1}$  and 10 s background counts. The first shell ( $2\theta = 0$ - $90^\circ$ , 1362 reflexions) was collected with one crystal, 028 being measured after every fifty observations as a check on decomposition. After 100 observations in the second

shell ( $2\theta = 90$ - $120^\circ$ ) the intensity of 028 had fallen by 17%, and the second crystal was used for the remainder of the data collection. The standard intensity fell by 34% for the second crystal. The data were put on a common scale and the standard intensities were used to compensate for the decomposition. Of the 2496 independent reflexions collected, 2036 had intensities greater than  $3\sigma(I)$  above background [ $\sigma^2(I) = S + B + (0.05S)^2$ , where  $S = \text{scan}$  and  $B = \text{background count}$ ]. Lorentz and polarization corrections were applied and the structure amplitudes derived. No absorption correction was applied in view of the low value of the coefficient.

Table 2. Final positional parameters (fractional,  $\times 10^4$ , H  $\times 10^3$ ) with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	9955 (4)	2857 (1)	822 (2)
O(2)	836 (4)	1617 (1)	-364 (2)
C(1)	7745 (6)	2618 (1)	623 (2)
C(2)	7765 (6)	2067 (1)	1067 (2)
C(3)	5526 (6)	1747 (1)	727 (2)
C(4)	2923 (5)	1903 (1)	-122 (2)
C(5)	3020 (6)	2409 (1)	-707 (2)
C(6)	4049 (6)	2232 (1)	-1518 (2)
C(7)	4955 (6)	2709 (2)	-1952 (2)
C(8)	5412 (7)	3204 (2)	-1561 (3)
C(9)	5074 (8)	3359 (1)	-620 (3)
C(10)	4935 (5)	2855 (1)	-23 (2)
O(1')	5326 (5)	-557 (1)	1211 (2)
O(2')	-746 (5)	738 (1)	2461 (2)
C(1')	3656 (6)	-299 (1)	1427 (2)
C(2')	2735 (6)	255 (1)	991 (2)
C(3')	1307 (7)	585 (1)	1333 (3)
C(4')	715 (6)	439 (1)	2200 (2)
C(5')	2094 (6)	-71 (1)	2783 (2)
C(6')	4992 (7)	82 (1)	3595 (2)
C(7')	6745 (7)	-414 (1)	4034 (3)
C(8')	6192 (7)	-904 (1)	3629 (3)
C(9')	3729 (9)	-1036 (1)	2688 (3)
C(10')	2317 (6)	-526 (1)	2085 (2)
H(2)	948 (6)	196 (1)	162 (2)
H(3)	561 (6)	140 (1)	105 (2)
H(5)	115 (6)	255 (1)	-107 (2)
H(6a)	257 (7)	204 (1)	-205 (2)
H(6b)	566 (7)	197 (1)	-116 (2)
H(7)	528 (7)	261 (1)	-257 (3)
H(8)	598 (7)	349 (1)	-186 (3)
H(9a)	335 (8)	357 (2)	-82 (3)
H(9b)	669 (7)	359 (1)	-17 (3)
H(10)	427 (5)	296 (1)	49 (2)
H(2')	316 (7)	36 (1)	39 (2)
H(3')	54 (8)	93 (2)	98 (3)
H(5')	98 (7)	-22 (1)	313 (2)
H(6a')	470 (7)	28 (1)	412 (3)
H(6b')	597 (6)	34 (1)	330 (2)
H(7')	834 (7)	-35 (1)	465 (2)
H(8')	733 (8)	-118 (2)	398 (3)
H(9a')	229 (9)	-123 (2)	281 (3)
H(9b')	428 (7)	-123 (2)	223 (3)
H(10')	46 (6)	-61 (1)	158 (2)

Table 3. Final thermal parameters and their estimated standard deviations

(a) Anisotropic thermal parameters ( $U_{ij} \times 10^3 \text{ \AA}^2$ ) in the expression:  
 $f = f^0 \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}kbc^*)]$ .

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
O(1)	53 (1)	73 (1)	68 (1)	-23 (1)	17 (1)	-5 (1)
O(2)	48 (1)	58 (1)	86 (2)	-14 (1)	23 (1)	0 (1)
C(1)	48 (2)	49 (2)	38 (1)	-7 (1)	19 (1)	-10 (1)
C(2)	44 (2)	56 (2)	39 (1)	5 (1)	12 (1)	5 (1)
C(3)	52 (2)	43 (2)	56 (2)	1 (1)	25 (1)	6 (1)
C(4)	40 (2)	42 (1)	55 (2)	-1 (1)	23 (1)	-4 (1)
C(5)	32 (1)	46 (2)	46 (1)	6 (1)	12 (1)	5 (1)
C(6)	50 (2)	62 (2)	35 (2)	2 (1)	9 (1)	-3 (1)
C(7)	56 (2)	84 (2)	44 (2)	5 (2)	21 (1)	14 (2)
C(8)	59 (2)	72 (2)	67 (2)	3 (2)	26 (2)	29 (2)
C(9)	72 (2)	42 (2)	83 (2)	5 (2)	37 (2)	11 (2)
C(10)	53 (2)	38 (1)	52 (2)	3 (1)	29 (1)	-1 (1)
O(1')	75 (2)	107 (2)	91 (2)	18 (1)	51 (1)	-12 (1)
O(2')	87 (2)	57 (1)	118 (2)	23 (1)	62 (2)	5 (1)
C(1')	43 (2)	69 (2)	52 (2)	0 (1)	18 (1)	-12 (1)
C(2')	54 (2)	77 (2)	56 (2)	-8 (2)	25 (2)	4 (2)
C(3')	57 (2)	53 (2)	74 (2)	3 (1)	29 (2)	12 (2)
C(4')	54 (2)	42 (2)	75 (2)	2 (1)	34 (2)	1 (1)
C(5')	53 (2)	37 (1)	67 (2)	1 (1)	37 (2)	2 (1)
C(6')	74 (2)	46 (2)	57 (2)	-6 (1)	31 (2)	-4 (1)
C(7')	61 (2)	65 (2)	63 (2)	-3 (2)	20 (2)	12 (2)
C(8')	64 (2)	50 (2)	86 (2)	11 (2)	33 (2)	23 (2)
C(9')	82 (3)	36 (2)	93 (3)	6 (2)	36 (2)	-3 (2)
C(10')	46 (2)	43 (2)	62 (2)	-2 (1)	22 (1)	-7 (1)

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

	$U(\text{Å}^2)$		$U(\text{Å}^2)$		$U(\text{Å}^2)$
H(2)	5 (1)	H(9a)	9 (1)	H(6b')	6 (1)
H(3)	7 (1)	H(9b)	8 (1)	H(7')	6 (1)
H(5)	6 (1)	H(10)	4 (1)	H(8')	10 (1)
H(6a)	6 (1)	H(2')	7 (1)	H(9a')	11 (1)
H(6b)	7 (1)	H(3')	9 (1)	H(9b')	9 (1)
H(7)	8 (1)	H(5')	7 (1)	H(10')	5 (1)
H(8)	8 (1)	H(6a')	8 (1)		

## Structure determination and refinement

A Wilson plot gave good centric statistics and 328  $E$  values  $> 1.5$  were derived. An automatic computer program (Long, 1965), applying a multiresolution procedure, was used to assign phases. The set with the highest consistency (75%) 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  $\sum w(|F_o| - |F_c|)^2$ , with weights  $w = 1/\sigma^2(F)$ ;  $\sigma(F)$  values were derived from the previously calculated  $\sigma(I)$  values.  $R$  at this point was 0.11 and a difference Fourier map gave the positions of all H atoms; these were included in the subsequent refinement with isotropic temperature factors. The whole structure was refined for four cycles, and analysis of weighting statistics showed five reflexions to be in poor agreement. 022 suffered from extinction and 0,9,10, 194, 1,12,  $\bar{1}$ , 327 had  $|F_o| - |F_c| > 4\sigma(F)$ . These planes were given zero weight in the final refinement cycles.

The final  $R$  and  $R'$   $\{= [\sum w(|F_o| - |F_c|)^2] / \sum w|F_o|^2\}^{1/2}$  for the 2036 reflexions with  $I > 3\sigma(I)$  are 0.062 and 0.078 respectively. For all 2496 data\*  $R$  is 0.072 and  $R'$  is 0.085 (no planes zero weighted). The error in an observation of unit weight  $\{[\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}\}$  is 2.38. The largest change/error in the final cycle of refinement was 0.24, and the difference map showed random fluctuations with the highest peak at 0.27 e  $\text{Å}^{-3}$ . Atomic scattering

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32148 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

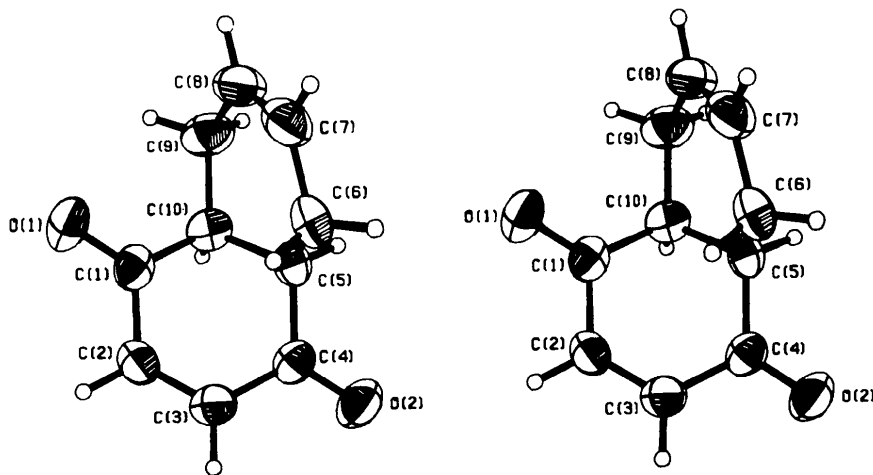


Fig. 1. Stereo diagram of molecule *A* showing the crystallographic numbering scheme. H atoms are labelled according to the C atoms to which they are bonded. Non-hydrogen atoms are shown with 50% probability vibration ellipsoids.

Table 4. Bond lengths ( $\text{\AA}$ ) in (I) corrected for libration

	Molecule <i>A</i>	Molecule <i>B</i>
O(1)—C(1)	1.229	1.226
O(2)—C(4)	1.226	1.229
C(1)—C(2)	1.487	1.487
C(1)—C(10)	1.508	1.516
C(2)—C(3)	1.330	1.337
C(3)—C(4)	1.471	1.468
C(4)—C(5)	1.511	1.512
C(5)—C(6)	1.555	1.547
C(5)—C(10)	1.542	1.547
C(6)—C(7)	1.494	1.497
C(7)—C(8)	1.315	1.315
C(8)—C(9)	1.504	1.484
C(9)—C(10)	1.524	1.528

factors for O and C atoms are those of Cromer & Mann (1968) and for H atoms those of Stewart, Davidson & Simpson (1965). Final positional and thermal parameters are listed in Tables 2 and 3. The two independent molecules (henceforth referred to as *A* and *B*) were given the same numbering scheme (see Fig. 1), except that designations for *B* have primes.

#### Thermal-motion analysis

The thermal motion has been analysed in terms of the rigid-body modes of translation, libration and screw motion (Schomaker & Trueblood, 1968) with the computer program *MGTLS*. For each molecule, the ten C atoms in the ring were taken to be a rigid body. R.m.s.  $\Delta U_{ij}$  values for *A* and *B* were 0.0021 and 0.0031  $\text{\AA}^2$  respectively, compared to the r.m.s.  $\sigma(U_{ij})$  from the least-squares refinement of 0.0016  $\text{\AA}^2$ . Thus the rigid bodies give a good approximation 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  $\Delta U_{ij}$  values (Busing & Levy, 1964; Johnson, 1970). Corrected bond lengths are given in

Table 4. Bond angles are not significantly affected and corrected values are not reported

## Results and discussion

### The structure of (I)

The crystal structure of (I) contains two crystallographically independent molecules (*A* and *B*). Layers of *A* molecules lie roughly in the planes  $y = \frac{1}{4}$  and  $y = \frac{3}{4}$ , alternating with layers of *B* molecules at  $y = 0$  and  $y = \frac{1}{2}$ . The layers are clearly shown in the packing diagram (Fig. 2).

Both *A* and *B* have the 'twist' conformation (see *A* in Fig. 1) observed for the other derivatives studied. Bond lengths are normal (see Tables 4 and 5 for corrected and uncorrected values), and most do not differ significantly between the two molecules. One exception is C(8)—C(9) which is 0.019  $\text{\AA}$  (uncorrected) longer in *A*, and the difference is maintained after the libration correction. Mean corrected bond lengths are as follows: C( $sp^3$ )—C( $sp^3$ ) 1.540 (5); C( $sp^3$ )—C( $sp^2$ ) 1.503 (4); C( $sp^2$ )—C( $sp^2$ ) 1.478 (5); C( $sp^2$ )=C( $sp^2$ ) 1.324 (6); O=C( $sp^2$ ) 1.227 (1); and C—H 0.975 (7)  $\text{\AA}$ . Bond angles are also as expected (see Table 6), the only significant difference between *A* and *B* being for C(4)—C(5)—C(6). Several torsion angles (see Table 7), however, show small but significant differences, the most interesting being the higher value of C(1)—C(2)—C(3)—C(4) in *B*. This may be related to the intermolecular interaction between C(2')=C(3') bonds in *B* molecules mentioned below. The effect also appears in the mean-plane calculations for C(1), C(2), C(3), C(4), giving  $\chi^2 = 17$  for *A* and 62 for *B*. Other calculations show all carbonyl groups to be slightly, but significantly, non-planar. C(6), C(7), C(8), C(9) groups are planar within experimental error.

The mean O to  $\beta$ -H distance [O(1)  $\cdots$  H(9b)], over which photochemical abstraction occurs in solution, is 2.46  $\text{\AA}$  (individual values in Table 8). The change in molecularity of the reaction in going from solution to

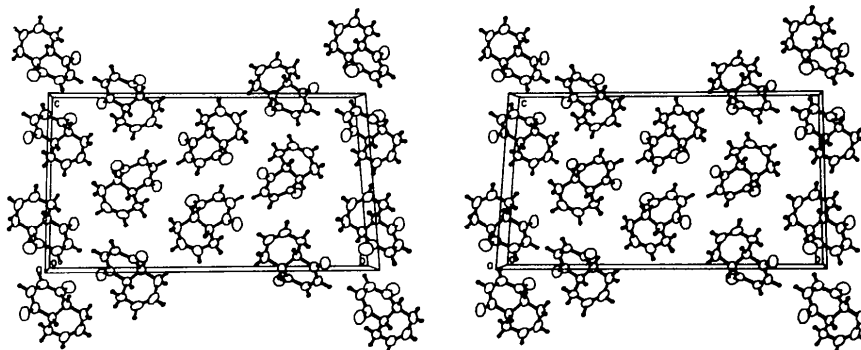


Fig. 2. An *a* projection of the structure.

Table 5. Bond lengths (Å) with estimated standard deviations in parentheses for derivatives I–VIII

	(Ia)	(Ib)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)
O(1)–C(1)	1.224 (3)	1.221 (4)	1.232 (6)	1.213 (4)	1.217 (4)	1.220 (2)	1.200 (2)	1.202 (2)	1.211 (2)
O(2)–C(4)	1.222 (3)	1.226 (3)	1.185 (6)	1.216 (4)	1.215 (4)	1.219 (2)	1.210 (2)	1.210 (2)	1.222 (2)
C(1)–C(2)	1.480 (4)	1.480 (4)	1.492 (7)	1.485 (5)	1.491 (6)	1.477 (3)	1.471 (3)	1.477 (3)	1.481 (3)
C(1)–C(10)	1.500 (4)	1.507 (4)	1.537 (7)	1.546 (4)	1.501 (5)	1.501 (3)	1.557 (3)	1.549 (3)	1.509 (2)
C(2)–C(3)	1.324 (4)	1.327 (4)	1.340 (7)	1.331 (5)	1.344 (5)	1.325 (3)	1.332 (3)	1.326 (3)	1.327 (2)
C(3)–C(4)	1.463 (4)	1.460 (4)	1.486 (7)	1.503 (5)	1.492 (5)	1.477 (3)	1.472 (3)	1.464 (3)	1.480 (2)
C(4)–C(5)	1.504 (4)	1.505 (4)	1.517 (7)	1.527 (4)	1.500 (6)	1.509 (3)	1.538 (3)	1.546 (3)	1.501 (2)
C(5)–C(6)	1.546 (4)	1.538 (4)	1.528 (7)	1.570 (4)	1.526 (5)	1.534 (3)	1.551 (2)	1.573 (3)	1.553 (2)
C(5)–C(10)	1.531 (4)	1.534 (4)	1.547 (6)	1.560 (4)	1.537 (5)	1.535 (3)	1.556 (2)	1.573 (3)	1.548 (2)
C(6)–C(7)	1.488 (4)	1.490 (4)	1.520 (8)	1.509 (5)	1.509 (6)	1.511 (3)	1.501 (3)	1.487 (4)	1.500 (3)
C(7)–C(8)	1.307 (5)	1.305 (5)	1.323 (7)	1.309 (5)	1.326 (5)	1.339 (3)	1.333 (3)	1.317 (4)	1.319 (3)
C(8)–C(9)	1.496 (5)	1.477 (5)	1.507 (8)	1.484 (5)	1.508 (6)	1.511 (3)	1.503 (3)	1.498 (4)	1.485 (3)
C(9)–C(10)	1.518 (4)	1.521 (4)	1.541 (8)	1.544 (5)	1.514 (6)	1.522 (3)	1.532 (5)	1.543 (3)	1.529 (3)

Table 6. Bond angles (°) with estimated standard deviations in parentheses for derivatives I–VIII

	(Ia)	(Ib)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)
O(1)–C(1)–C(2)	119.5 (3)	120.0 (3)	121.3 (5)	119.5 (3)	119.9 (4)	120.7 (2)	123.6 (2)	122.6 (2)	120.1 (1)
O(1)–C(1)–C(10)	124.0 (2)	123.5 (3)	121.6 (5)	121.5 (3)	122.5 (4)	123.5 (2)	121.1 (2)	123.4 (2)	125.4 (2)
C(2)–C(1)–C(10)	116.4 (2)	116.4 (2)	117.1 (5)	118.7 (3)	117.5 (3)	115.8 (2)	115.3 (2)	113.9 (2)	114.5 (1)
C(1)–C(2)–C(3)	121.5 (3)	121.7 (3)	122.0 (4)	121.6 (3)	121.1 (4)	122.0 (2)	122.1 (2)	121.3 (2)	122.2 (1)
C(2)–C(3)–C(4)	122.7 (3)	122.1 (3)	120.0 (5)	119.7 (3)	121.1 (4)	121.7 (2)	122.6 (2)	123.2 (2)	121.4 (2)
O(2)–C(4)–C(3)	120.8 (2)	120.5 (3)	120.2 (5)	119.5 (3)	121.5 (4)	120.7 (2)	122.8 (2)	122.9 (2)	120.1 (2)
O(2)–C(4)–C(5)	122.6 (3)	122.2 (3)	121.9 (5)	122.1 (3)	120.9 (4)	122.3 (2)	120.5 (2)	119.7 (2)	122.1 (1)
C(3)–C(4)–C(5)	116.6 (2)	117.2 (2)	117.4 (5)	118.4 (3)	117.4 (3)	117.0 (2)	116.7 (2)	117.3 (2)	117.8 (1)
C(4)–C(5)–C(6)	107.9 (2)	109.0 (2)	110.5 (5)	107.3 (2)	109.5 (4)	110.0 (2)	108.3 (1)	109.6 (2)	111.6 (1)
C(4)–C(5)–C(10)	112.2 (2)	111.9 (2)	107.3 (5)	108.3 (2)	112.8 (3)	110.8 (2)	111.3 (1)	111.1 (2)	111.6 (1)
C(6)–C(5)–C(10)	110.2 (2)	110.9 (2)	109.2 (4)	108.9 (2)	109.8 (3)	109.5 (2)	108.3 (1)	111.9 (2)	112.3 (1)
C(5)–C(6)–C(7)	112.4 (3)	112.0 (3)	115.9 (6)	110.3 (3)	116.0 (4)	112.6 (2)	114.3 (2)	111.4 (2)	110.5 (2)
C(6)–C(7)–C(8)	124.4 (3)	124.1 (3)	121.2 (6)	125.0 (3)	121.6 (4)	122.3 (2)	122.6 (2)	126.1 (2)	125.4 (2)
C(7)–C(8)–C(9)	123.8 (3)	124.1 (3)	122.8 (5)	124.7 (3)	122.3 (4)	122.5 (2)	122.8 (2)	124.5 (2)	124.4 (2)
C(8)–C(9)–C(10)	111.7 (3)	112.8 (3)	114.7 (5)	112.4 (3)	115.1 (4)	114.8 (2)	114.0 (2)	109.9 (2)	110.6 (2)
C(1)–C(10)–C(5)	110.3 (2)	109.9 (2)	109.6 (4)	107.7 (2)	109.7 (3)	110.1 (2)	107.2 (1)	106.6 (1)	109.1 (2)
C(1)–C(10)–C(9)	113.4 (2)	114.6 (3)	108.3 (4)	108.7 (2)	114.2 (4)	114.1 (2)	113.2 (1)	115.6 (2)	118.6 (1)
C(5)–C(10)–C(9)	112.0 (2)	111.1 (3)	109.5 (5)	112.4 (2)	111.2 (3)	111.2 (2)	110.5 (1)	110.6 (2)	110.5 (1)

Table 7. Torsion angles (°) with estimated standard deviations in parentheses for derivatives I–VIII

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

	(Ia)	(Ib)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)
O(1)–C(1)–C(2)–C(3)	–166.6 (3)	–168.4 (3)	–170.1 (5)	–172.4 (3)	–163.7 (4)	–163.2 (2)	–158.5 (2)	–150.7 (2)	–158.9 (2)
C(10)–C(1)–C(2)–C(3)	15.6 (3)	14.6 (3)	18.3 (6)	12.8 (3)	17.8 (4)	18.3 (3)	21.3 (2)	28.7 (2)	22.0 (2)
O(1)–C(1)–C(10)–C(5)	140.6 (3)	141.1 (3)	141.8 (5)	143.1 (3)	138.9 (4)	136.7 (2)	130.9 (2)	125.0 (2)	132.0 (2)
O(1)–C(1)–C(10)–C(9)	14.1 (3)	15.2 (4)	22.8 (6)	21.1 (3)	13.3 (5)	10.8 (3)	8.9 (2)	1.6 (2)	4.4 (2)
C(2)–C(1)–C(10)–C(5)	–41.7 (3)	–42.1 (3)	–46.8 (5)	–42.2 (3)	–42.6 (4)	–44.9 (2)	–48.9 (2)	–54.4 (2)	–48.9 (2)
C(2)–C(1)–C(10)–C(9)	–168.3 (3)	–167.9 (3)	–165.7 (5)	–164.2 (3)	–168.2 (3)	–170.7 (2)	–170.9 (2)	–177.7 (2)	–176.5 (1)
C(1)–C(2)–C(3)–C(4)	2.0 (3)	4.2 (4)	0.0 (6)	1.9 (4)	0.2 (4)	0.1 (3)	2.1 (3)	0.0 (3)	2.4 (2)
C(2)–C(3)–C(4)–O(2)	–174.3 (3)	–175.8 (3)	–164.5 (5)	–164.6 (3)	–173.7 (4)	–170.6 (2)	–177.2 (2)	178.1 (2)	–177.9 (2)
C(2)–C(3)–C(4)–C(5)	9.2 (3)	7.5 (4)	13.7 (5)	16.4 (4)	9.9 (4)	10.6 (3)	5.8 (2)	1.2 (3)	3.4 (2)
O(2)–C(4)–C(5)–C(6)	–91.1 (3)	–89.8 (3)	–105.7 (6)	–107.7 (3)	–90.0 (4)	–95.1 (2)	–93.9 (2)	–82.6 (2)	–84.0 (2)
C(4)–C(5)–C(6)–C(10)	147.3 (3)	147.2 (3)	134.9 (5)	134.9 (3)	147.4 (4)	143.6 (2)	147.2 (2)	153.1 (2)	149.4 (2)
C(3)–C(4)–C(5)–C(6)	85.3 (3)	86.9 (3)	76.0 (5)	71.2 (3)	86.5 (4)	83.6 (2)	83.2 (2)	94.4 (2)	94.7 (2)
C(3)–C(4)–C(5)–C(10)	–36.3 (3)	–36.1 (3)	–43.4 (5)	–46.1 (3)	–36.1 (4)	–37.7 (2)	–35.7 (2)	–29.8 (2)	–31.9 (2)
C(4)–C(5)–C(6)–C(7)	–164.5 (2)	–166.4 (3)	–164.9 (5)	–164.3 (3)	–166.2 (3)	–171.2 (2)	–166.1 (2)	–159.3 (2)	–164.9 (1)
C(10)–C(5)–C(6)–C(7)	–41.7 (3)	–42.8 (3)	–45.5 (5)	–47.3 (3)	–41.9 (4)	–49.1 (2)	–45.3 (2)	–35.5 (2)	–38.7 (2)
C(4)–C(5)–C(10)–C(1)	51.4 (3)	51.9 (3)	57.3 (5)	55.6 (3)	51.0 (4)	53.6 (2)	54.9 (2)	54.0 (2)	53.4 (1)
C(4)–C(5)–C(10)–C(9)	178.7 (2)	179.7 (3)	177.1 (4)	175.3 (2)	178.3 (3)	–178.9 (2)	178.6 (2)	–179.6 (2)	–174.6 (1)
C(6)–C(5)–C(10)–C(1)	–68.9 (2)	–70.0 (3)	–61.4 (5)	–60.7 (3)	–71.4 (4)	–67.9 (2)	–64.0 (2)	–69.0 (2)	–72.8 (1)
C(6)–C(5)–C(10)–C(9)	58.5 (3)	57.8 (3)	58.4 (5)	58.9 (3)	55.9 (4)	59.6 (2)	59.7 (2)	57.5 (2)	59.3 (2)
C(4)–C(5)–C(6)–C(8)	13.8 (3)	15.2 (4)	16.1 (7)	19.7 (3)	14.3 (4)	17.3 (2)	15.5 (2)	8.8 (2)	10.5 (2)
C(6)–C(7)–C(8)–C(9)	–0.2 (4)	–0.9 (4)	0.2 (6)	0.4 (4)	0.2 (5)	5.8 (2)	1.7 (2)	2.9 (3)	–1.6 (3)
C(7)–C(8)–C(9)–C(10)	15.7 (4)	15.3 (4)	14.8 (6)	9.2 (4)	15.0 (5)	4.9 (2)	13.5 (2)	23.8 (3)	20.8 (2)
C(8)–C(9)–C(10)–C(1)	81.0 (3)	82.0 (3)	73.8 (5)	79.8 (3)	81.5 (4)	87.6 (2)	75.8 (2)	71.7 (2)	78.9 (2)
C(8)–C(9)–C(10)–C(5)	–44.7 (3)	–43.2 (3)	–44.1 (5)	–39.2 (3)	–43.3 (4)	–37.6 (2)	–44.4 (2)	–49.5 (2)	–48.0 (2)

the solid state is readily explained on the basis of the crystal structure. *B* molecules occur in pairs, across centres of symmetry (0,0,0), with close intermolecular contacts between neighbouring  $C(2')=C(3')$  bonds (see Fig. 3).  $C(1')-C(2')=C(3')-C(4')$  groups lie in parallel planes with an interplanar separation of 3.232 Å. The closest contact,  $C(2')\cdots C(2')[-x, -y, -z]$ , is 3.351(6) Å;  $C(2')\cdots C(3')[-x, -y, -z]$  being 3.755(6) Å (also the separation of double-bond mid-points). The mid-point separation is well within the range 3.6–4.1 Å found to be photo-active for dimeriza-

tion of *trans*-cinnamic acids (Schmidt, 1964). Viewed perpendicular to the plane, the two  $C(2')$  atoms are almost eclipsed. The arrangement is identical to that found in (VIII), except that only half the molecules in the structure are involved. Bond formation between  $C(2')$  and neighbouring  $C(3')$  atoms gives the *trans-syn* dimer observed as the product after recrystallization. *A* molecules show no significant intermolecular interactions of this type, the closest contact between the bond mid-points being equal to the a cell translation of 5.266 Å with no overlap of  $\pi$  systems.

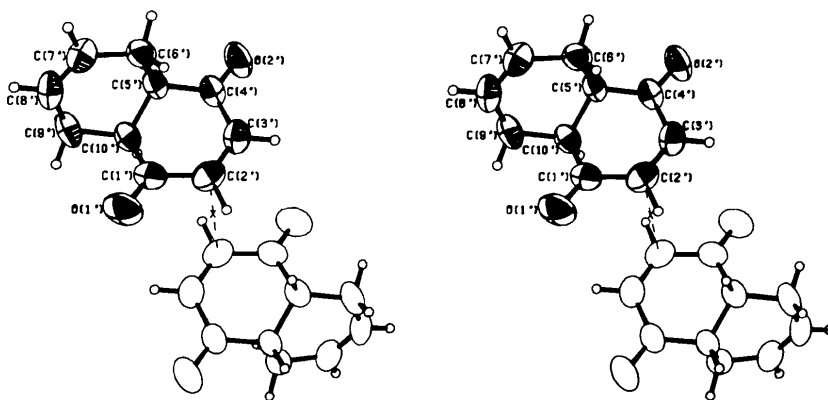
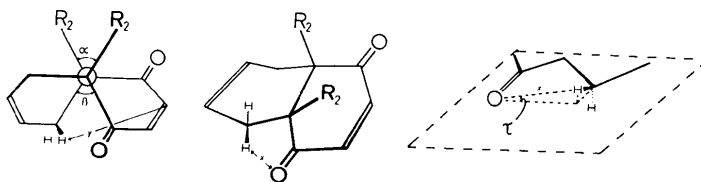


Fig. 3. View of molecule *B* (shaded ellipsoids) and its nearest neighbour related by the centre of symmetry (indicated by the cross).

Table 8. *Structural parameters relevant to photochemical activity for derivatives I–VIII*



$\alpha = R_2-C(5)-C(10)-R_2$ .  $\beta = C(6)-C(5)-C(10)-C(1)$ .  $x = O(1)\cdots\beta-H$  [at  $C(9)$ ].  $y = C(3)\cdots H$  [at  $C(6)$ ].  $\tau =$  angle subtended by  $O\cdots H$  vector ( $x$ ) and its projection on the  $O(1)$  carbonyl mean plane.

	$\alpha(^{\circ})$	$\beta(^{\circ})$	$x(\text{\AA})$	$y(\text{\AA})$	$\tau(^{\circ})$	Reaction <sup>†</sup>	
						Solution	Solid
(Ia)	63 (2)	68.9 (2)	2.49 (3)	2.82 (3)	4	1	5
(Ib)	62 (3)	70.0 (3)	2.42 (3)	2.95 (3)	3		
(II)	60.0 (6)	61.4 (5)	2.47 (6)	2.80 (6)	0	1, 2	1, 2
(III)	62.6 (3)	60.7 (3)	2.26 (3)	2.66 (3)	1	1, 2	1, 2
(IV)	56 (3)	71.4 (4)	2.42 (6)	2.94 (6)	3	1	None
(V)	62 (2)	67.9 (2)	2.46 (3)	2.97 (3)	3	1	1
(VI)	60.9 (2)	64.0 (2)	2.58 (3)	2.86 (3)	8	1	1
(VII)	57.1 (2)	69.0 (2)	2.41 (3)*	2.94 (3)*	24*	4	4
(VIII)	61 (2)	72.8 (1)	2.38 (3)*	2.92 (2)*	15*	3	5

\* Indicates Me hydrogen atom.

<sup>†</sup> Photochemical reaction pathways: (1)  $\beta$ -H abstraction by O. (2) H abstraction by enone C. (3)  $\gamma$ -H abstraction by O. (4) Oxetane formation (intramolecular). (5) Dimerization.

*Molecular geometry of derivatives (I)–(VIII)*

Determination of crystal structures for the series of derivatives allows comparisons to be made of the effect of substitution at various positions around the rings. Changes in geometry may be attributed to hybridization effects, as reported for substituted benzene derivatives (Domenicano, Vaciago & Coulson, 1975), steric effects, or some combination of the two.

Inspection of bond lengths and angles around C(7) and C(8) reveals trends related to substitution (see Tables 5 and 6\*). Derivatives with Me groups at these positions (see Table 1) have smaller internal angles, C(6)–C(7)–C(8) and C(7)–C(8)–C(9), than those with H. The decrease averages 2.5°. Bonds C(6)–C(7), C(7)=C(8) and C(8)–C(9) also show increases in length averaging 0.016 Å. This is consistent with expected changes in hybridization of the ring C atoms with substitution by electron-donating Me groups. Purely steric effects would be expected to affect the C(6)–C(7) and C(8)–C(9) bonds less than C(7)–C(8). External angles (not shown in the tables) C(7)=C(8)–R<sub>s</sub> and C(8)=C(7)–R<sub>s</sub>, however, show a mean increase of almost 4° with Me substitution, suggesting Me–Me steric interactions.

The longest C(7)=C(8) with R<sub>s</sub> = Me is for (VI), and inspection of this structure shows that the Me groups are not 'staggered' to minimize H···H interactions. This unusual arrangement is presumably the result of packing effects, and produces a close intramolecular H···H contact of 1.99 Å between Me groups. This C=C bond is even longer in (V) where the Me groups are replaced by Ph. Similar, but less marked, changes are apparent at C(2)=C(3) bonds.

The geometry at C(6) and C(9) again shows similar trends. While Me groups at these positions do not interfere with each other, there are steric interactions with other parts of the molecule. An interesting feature is the difference in length of chemically equivalent C(5)–C(6) and C(9)–C(10) bonds. The former is longer in all cases except (II), where the difference is not significant and the crystal structure is disordered. The length of C(9)–C(10) seems dependent on the bridgehead substituents at C(5) and C(10). With H at these positions it is consistently shorter than a normal C(sp<sup>3</sup>)–C(sp<sup>3</sup>) bond. Bridgehead Me or CN groups also lengthen the C(5)–C(10) bond, but only Me groups markedly affect bond angles C(4)–C(5)–C(10), which show a mean reduction of 4° over the value observed with H. The external angles (not shown in tables) C(5)–C(10)–R<sub>2</sub> and C(10)–C(5)–R<sub>2</sub> average 108° for R<sub>2</sub> = H or CN and 113° for R<sub>2</sub> = Me, reflecting the bulk of the Me groups. Bridgehead CN substituents

\* Distances and angles in Tables 5, 6 and 7 have not been corrected for thermal motion. Correction for (II) would be unreliable in view of the disorder, and uncorrected values for all derivatives are quoted for consistency.

also appear to affect the carbonyl groups, C=O distances becoming very short, together with increases in bond angles O(1)–C(1)–C(2) and O(2)–C(4)–C(3).

All six-membered rings have half-chair conformations as predicted for cyclohexene by minimum-energy calculations (Bucourt & Hainaut, 1965). Torsion angles in the molecules (see Table 7) vary by up to 25°, but agree qualitatively with calculated values within the rings. Of the two torsion angles at the bridgehead given as  $\alpha$  and  $\beta$  in Table 8, the surprising observation is that the internal angle  $\beta$  varies with substitution and  $\alpha$  seems relatively unaffected. Torsion angles about C(4)–C(5) are also altered by bridgehead Me groups.

The photochemistry of these derivatives has been discussed elsewhere (Dzakpasu, Phillips, Scheffer & Trotter, 1976; Scheffer *et al.*, 1976), but Table 8 summarizes the reaction pathways and relevant structural parameters. The most common reaction pathway observed is  $\beta$ -H abstraction by carbonyl O. O(1) abstracts the nearer H atom at C(9) and the resulting diradical collapses to form a tricyclic product. In all cases the O···H separation ( $x$ ) is less than the van der Waals radius sum and the low values of  $\tau$  show that the H lies close to the plane of the O *n* orbital. A second pathway involves H abstraction by enone carbon C(2) or C(3), again leading to a tricyclic product *via* a diradical intermediate. Abstraction of H[C(6)] by enone C occurs only for (II) and (III) where the relevant C···H distance ( $y$ ) and torsion angle ( $\beta$ ) are at a minimum.

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## Crystal Structure of 3-*O*-Acetyl-1,2-*O*-isopropylidene-5-*O*-tosyl- $\alpha$ -D-gulofuranose-4,6-carbolactone

BY SIMON E. V. PHILLIPS AND JAMES TROTTER

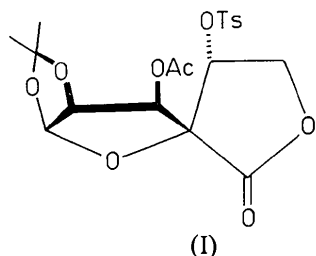
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Crystals of 3-*O*-acetyl-1,2-*O*-isopropylidene-5-*O*-tosyl- $\alpha$ -D-gulofuranose-4,6-carbolactone are orthorhombic, space group  $P2_12_12_1$ , with  $a = 9.782$ ,  $b = 10.455$ ,  $c = 19.976$  Å and  $Z = 4$ . The structure was solved by direct methods and refined by full-matrix least squares to  $R = 0.041$ . Bond lengths and angles are close to normal values.

### Introduction

Photoamidation of 3-*O*-acetyl-1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-erythro-hex-3-enofuranose afforded two products in 65 and 26% yields. Treatment of the major product with 5% hydrochloric acid, followed by tosylation, gave 3-*O*-acetyl-1,2-*O*-isopropylidene-5-*O*-tosyl- $\alpha$ -D-gulofuranose-4,6-carbolactone (I) (Rosenthal & Ratcliffe, 1976).



The crystal structure of (I) was studied in order to determine the configurations at C(3) and C(4).

### Experimental

A small piece (dimensions *ca* 0.040 × 0.024 × 0.012 cm) was cut from a large needle and used for data collection. Unit-cell and intensity data were measured on a Datex-automated GE XRD 6 diffractometer with Cu  $K\alpha$  radiation and the  $\theta$ - $2\theta$  scan technique. Unit-cell parameters were refined by least squares from the observed  $2\theta$  values of 15 reflexions.

### Crystal data

$C_{19}H_{22}O_{10}S$ , FW 442.44;  $a = 9.782$  (2),  $b = 10.455$  (4),  $c = 19.976$  (6) Å;  $V = 2043$  (1) Å<sup>3</sup>,  $d_m = 1.42$  (floatation),  $d_x = 1.438$  g cm<sup>-3</sup>,  $Z = 4$ . Space group  $P2_12_12_1$  ( $h00$ ,  $h = 2n$ ;  $0k0$ ,  $k = 2n$ ;  $00l$ ,  $l = 2n$ ). Cu  $K\alpha$  radiation, Ni-filtered;  $\lambda$ (Cu  $K\alpha$ ) = 1.5418 Å,  $\mu$ (Cu  $K\alpha$ ) = 18.7 cm<sup>-1</sup>.

Of the 2331 independent reflexions with  $2\theta < 146^\circ$ , 2016 had intensities greater than  $3\sigma(I)$  above background [ $\sigma^2(I) = S + B + (0.05S)^2$ , where  $S$  = scan and  $B$  = background count]. Lorentz and polarization corrections were applied and the structure amplitudes derived. No absorption correction was applied.