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Structures of Two Isomeric Intermediates to Nogaramycin

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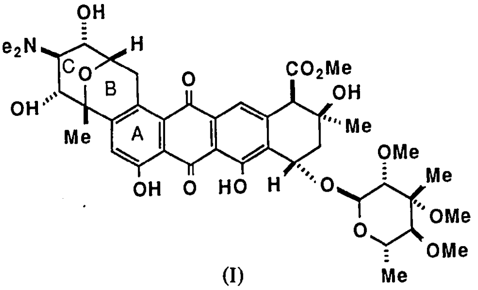
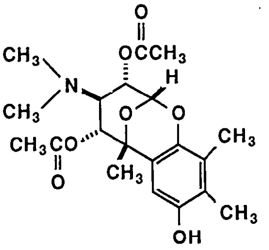
Abstract. (2*R*,3*S*,4*R*,5*R*,6*R*)-3,5-Diacetoxy-4-dimethylamino-3,4,5,6-tetrahydro-6,9-10-trimethyl-2,6-epoxy-2*H*-1-benzoxocin-8-ol (II), $C_{20}H_{27}NO_7$, M_r = 393·44, orthorhombic, $P2_12_12_1$, a = 14·432 (1), b = 19·712 (2), c = 7·2349 (5) Å, V = 2057·8 (3) Å^3, Z = 4, D_x = 1·27 g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ = 7·616 cm^{-1}, $F(000)$ = 840, T = 295 K, R = 0·052 for 2252 observed reflections. (2*S*,3*S*,4*R*,5*R*,6*S*)-3,5-Diacetoxy-4-dimethylamino-3,4,5,6-tetrahydro-6,9,10-trimethyl-2,6-epoxy-2*H*-1-benzoxocin-8-ol (III), $C_{20}H_{27}NO_7$, M_r = 393·44, orthorhombic, $P2_12_12_1$, a = 11·952 (1), b = 17·228 (1), c = 9·615 (1) Å, V = 1981·1 (3) Å^3, Z = 4, D_x = 1·32 g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ = 7·911 cm^{-1}, $F(000)$ = 840, T = 295 K, R = 0·046 for 1991 observed reflections. The oxolane ring in (II) and (III) takes a chair and a boat conformation, respectively. The benzene rings in both structures are almost planar. Ring *C* takes a chair conformation in (II) but a boat conformation in (III). Large differences between the isomers are found in the bond lengths and angles around ring *C*.

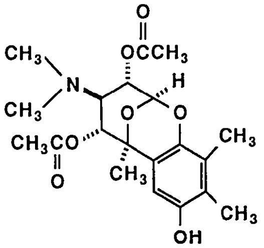
Introduction. Nogaramycin (I) is a very useful antitumor antibiotic because of its prominent antitumor activity and reduced cardiotoxicity. For total synthesis of (I) it is necessary to construct the bicyclic *ABC*-ring system in an optically active form. Kawasaki, Matsuda & Terashima (1985) prepared two isomeric compounds, (II) and (III), corresponding to the bicyclic *ABC*-ring system from D-arabinose. In the oxolane rings there are two pairs of *trans* protons and one pair of *gauche* protons. A boat conformation should be possible for the oxolane ring in (III) because it might relieve the steric hindrance. From considerations with the Dreiding model, however, the torsion angles H—C—C—H for the *gauche* protons are *ca* 60 and 120° in (II) and (III), respectively. This indicates that the coupling constants obtained by ^{1}H NMR spectra can not determine the structures unequivocally. Therefore we have undertaken the X-ray analyses of the two compounds to establish their configurations and conformations.



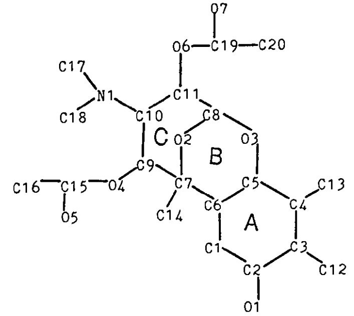
(I)



(II)



(III)



Experimental. Single crystals of (II) and (III) were obtained from chloroform and chloroform–*n*-hexane solutions, respectively. Colourless crystals, (II) 0·6 × 0·5 × 0·1 mm and (III) 0·7 × 0·1 × 0·1 mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Cu $K\alpha$ radiation. Lattice parameters, (II) from 24 reflections ($35·2 \le \theta \le 49·3°$) and (III) from 21 reflections ($44·9 \le \theta \le 54·6°$). (II) ω–2θ scan ($2 < \theta < 75°$), 2425 unique reflections recorded ($0 \le h \le 18$, $0 \le k \le 24$, $0 \le l \le 9$), 2252 with $I > 3\sigma(I)$. (III) ω–2θ scan ($2 < \theta < 75°$), 2347 unique reflections recorded ($0 \le h \le 21$, $0 \le k \le 29$, $0 \le l \le 12$), 1991 with $I > 3\sigma(I)$. 3 standard reflections, no significant intensity variation. The two crystal structures were deter-

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mined with the use of *MULTAN*11/82 (Main *et al.*, 1982). 11 atoms including the phenyl group of structure (II) were used as a known group with random orientation in the *NORMAL* routine to solve the structure (III). The structures were refined by full-matrix least squares on F, with unit weight. H atoms directly bonded to the rings were located from the difference Fourier synthesis. The positions of other H atoms were calculated geometrically. The H atoms bonded directly to the ring were refined isotropically and other H atoms were not refined for structure (II). The H atoms were included in the structure factor calculations but not refined for structure (III). All non-H atom parameters were refined anisotropically. The secondary-extinction coefficient of (II) was also refined to $9{\cdot}4089 \times 10^{-6}$. (II) $R = 0{\cdot}052$ for 253 variables and 2252 observed data, (III) $R = 0{\cdot}046$ for 253 variables and 1991 observed data. $(\Delta/\sigma)_{\max}$ for the final least-squares cycles were 0·35 and 0·32, and the maximum final difference electron densities were +0·32 and +0·35 e Å^{-3}, respectively. No corrections for absorption. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The programs used throughout the analyses were provided by Enraf–Nonius, *i.e.*, CAD-4 *SDP-Plus*, version 1.1 (Frenz, 1983). Refined fractional atomic coordinates and estimated standard deviations for the two compounds are given in Table 1, non-H bond distances and angles in Table 2, and selected torsion angles in Table 3.*

Table 1. *Positional parameters of* (II) *and* (III) ($\times 10^4$) *and equivalent isotropic temperature factors* (Å^2) *for non*-H *atoms*

$$B_{\text{eq}} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
(II)				
O(1)	4095 (1)	−1182 (1)	1078 (4)	4·93 (6)
O(2)	4318 (2)	1583 (1)	4549 (3)	3·94 (5)
O(3)	3581 (2)	1427 (1)	1701 (1)	3·97 (5)
O(4)	6567 (2)	816 (1)	3543 (4)	3·87 (5)
O(5)	7539 (2)	1326 (2)	5544 (5)	7·41 (8)
O(6)	4741 (2)	2322 (1)	6 (4)	4·22 (5)
O(7)	4287 (2)	3370 (1)	675 (5)	6·28 (7)
N(1)	6673 (2)	2039 (2)	1418 (5)	5·20 (8)
C(1)	4910 (2)	−191 (2)	2670 (5)	3·36 (6)
C(2)	4566 (2)	−528 (2)	1307 (5)	3·58 (7)
C(3)	3864 (2)	308 (2)	121 (5)	3·69 (7)
C(4)	3541 (2)	−344 (2)	295 (5)	3·62 (7)
C(5)	3925 (2)	774 (2)	1627 (5)	3·28 (6)
C(6)	4595 (2)	545 (2)	2854 (5)	3·11 (6)
C(7)	4958 (2)	1025 (2)	4324 (5)	3·24 (6)
C(8)	4084 (2)	1877 (2)	2840 (5)	3·71 (7)
C(9)	5890 (2)	1351 (2)	3751 (5)	3·30 (6)
C(10)	5800 (2)	1704 (2)	1892 (5)	3·53 (7)
C(11)	4946 (3)	2171 (2)	1918 (5)	3·51 (7)
C(12)	3474 (3)	−801 (2)	−1286 (7)	5·6 (1)
C(13)	2782 (3)	619 (2)	−957 (6)	5·3 (1)
C(14)	5020 (3)	695 (2)	6216 (5)	4·49 (8)
C(15)	7371 (3)	880 (2)	4519 (6)	4·76 (9)
C(16)	7994 (3)	298 (3)	4029 (8)	7·1 (1)
C(17)	6847 (3)	2091 (4)	−528 (8)	9·6 (2)
C(18)	6842 (3)	2674 (2)	233 (1)	8·9 (2)
C(19)	4424 (3)	2930 (2)	−428 (6)	4·36 (8)
C(20)	4265 (4)	3006 (3)	−2441 (6)	6·5 (1)
(III)				
O(1)	7140 (3)	9005 (2)	2729 (3)	3·54 (6)
O(2)	5057 (2)	8927 (2)	−3037 (3)	2·60 (5)
O(3)	3900 (2)	9380 (2)	−1273 (3)	2·79 (6)
O(4)	6516 (2)	7330 (2)	−3154 (3)	2·42 (5)
O(5)	7903 (3)	7261 (2)	−1561 (3)	3·73 (7)
O(6)	2687 (2)	7794 (2)	−2691 (3)	2·85 (5)
O(7)	1699 (3)	8455 (2)	−1100 (4)	5·17 (9)
N(1)	4279 (3)	6648 (2)	−2366 (4)	2·52 (6)
C(1)	6533 (3)	8780 (2)	353 (4)	2·52 (8)
C(2)	6372 (4)	9092 (2)	1675 (5)	2·70 (8)
C(3)	5402 (4)	9517 (2)	2001 (5)	2·77 (8)
C(4)	4571 (4)	9593 (2)	999 (5)	2·50 (8)
C(5)	4752 (3)	9276 (2)	−314 (4)	2·38 (7)
C(6)	5725 (3)	8888 (2)	−655 (4)	2·18 (7)
C(7)	5912 (3)	8599 (2)	−2137 (4)	2·33 (7)
C(8)	3993 (3)	8868 (2)	−2418 (4)	2·57 (7)
C(9)	5780 (3)	7698 (2)	−2153 (4)	2·08 (7)
C(10)	4596 (3)	7463 (2)	−2615 (4)	1·98 (6)
C(11)	3728 (3)	8018 (2)	−2018 (4)	2·18 (7)
C(12)	5319 (4)	9863 (3)	3457 (5)	3·7 (1)
C(13)	3479 (4)	10003 (3)	1255 (5)	3·59 (9)
C(14)	6993 (4)	8892 (2)	−2756 (5)	3·27 (9)
C(15)	7543 (3)	7110 (2)	−2699 (5)	2·75 (8)
C(16)	8136 (4)	6681 (3)	−3841 (6)	4·4 (1)
C(17)	4611 (5)	6355 (3)	−994 (6)	5·0 (1)
C(18)	4639 (4)	6119 (3)	−3490 (6)	4·9 (1)
C(19)	1722 (4)	8050 (3)	−2110 (5)	3·47 (9)
C(20)	739 (4)	7766 (3)	−2939 (7)	5·3 (1)

Discussion. The present analyses have definitely confirmed the initially presumed configurations and conformations of (II) and (III). *ORTEP*II drawings (Johnson, 1976) of the molecules are shown in Fig. 1. The benzene rings in both structures are almost planar. The rings *B* in both compounds take twisted conformations. The magnitudes of the deviations of the O(2) and C(8) atoms from the least-squares planes defined by O(3), C(5), C(6) and C(7) atoms [(II): $0{\cdot}7181x + 0{\cdot}3038y - 0{\cdot}6261z = 8{\cdot}0267$, (III): $0{\cdot}4073x + 0{\cdot}8765y - 0{\cdot}2565z = 16{\cdot}3875$] are remarkably different in the rings: (II) O(2) 0·432 (2) Å, C(8) −0·276 (4) Å; (III) O(2) 0·307 (3) Å, C(8) −0·453 (4) Å. The conformations of rings *C* are quite different as expected. In (II) it takes a chair conformation, but in (III) it is in a boat conformation. The *d* (Å) values (Hirayama, Shirahata, Ohashi & Sasada, 1980) are as follows: (II) O(2) 0·701 (2), C(10) −0·586 (4), C(7) −0·773 (3), C(11) 0·537 (3), C(8) −0·611 (4), C(9) 0·689 (3); (III) O(2) 0·685 (3), C(10) 0·587 (4), C(7) −0·489 (4), C(11) −0·455 (4), C(8) −0·183 (4), C(9) −0·148 (4) Å, respectively. The values of (III) indicate that the O(2) and C(10) atoms are bows, but the boat conformation is significantly deformed, apparently due to the steric effect of the large substituents.

Bond lengths and angles are normal, but the large differences between the two isomers are seen especially around ring *C*. C(8)–C(11) and C(7)–C(9) bond lengths in (III) are significantly longer than those in (II).

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51382 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

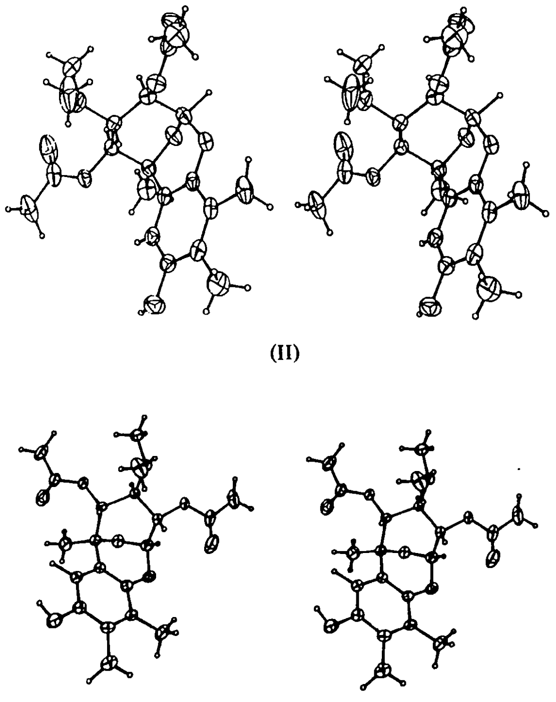
Table 2. *Bond lengths* (Å) *and angles* (°): *numbers in parentheses are e.s.d.'s in the least significant digits*

	(II)	(III)
O1–C2	1·388 (5)	1·375 (5)
O2–C7	1·445 (4)	1·454 (5)
O2–C8	1·407 (5)	1·408 (5)
O3–C8	1·412 (5)	1·415 (5)
O4–C9	1·446 (5)	1·450 (4)
O4–C15	1·364 (5)	1·358 (5)
O5–C15	1·175 (6)	1·205 (5)
O6–C11	1·446 (5)	1·455 (5)
O6–C19	1·319 (5)	1·354 (5)
O7–C19	1·195 (6)	1·197 (6)
N1–C10	1·464 (5)	1·475 (5)
N1–C17	1·433 (8)	1·467 (6)
N1–C18	1·438 (8)	1·478 (6)
C1–C2	1·378 (6)	1·395 (6)
C1–C6	1·373 (6)	1·381 (6)
C2–C3	1·398 (5)	1·406 (6)
C3–C4	1·372 (6)	1·391 (6)
C3–C12	1·516 (6)	1·526 (6)
C4–C5	1·399 (6)	1·392 (6)
C4–C13	1·521 (6)	1·505 (6)
C5–C6	1·388 (5)	1·381 (5)
C6–C7	1·517 (6)	1·527 (6)
C7–C9	1·546 (5)	1·562 (5)
C7–C14	1·519 (6)	1·510 (6)
C8–C11	1·525 (6)	1·547 (5)
C9–C10	1·519 (6)	1·537 (5)
C10–C11	1·538 (6)	1·523 (5)
C15–C16	1·499 (7)	1·501 (6)
C19–C20	1·482 (7)	1·502 (7)
C7–O2–C8	111·5 (3)	110·8 (3)
C5–O3–C8	115·0 (3)	112·4 (3)
C9–O4–C15	117·1 (4)	117·2 (3)
C11–O6–C19	119·1 (4)	117·3 (3)
C10–N1–C17	114·4 (5)	113·8 (4)
C10–N1–C18	115·5 (4)	113·2 (4)
C17–N1–C18	111·1 (6)	111·5 (4)
C2–C1–C6	120·8 (4)	119·4 (4)
O1–C2–C1	121·0 (4)	122·6 (4)
O1–C2–C3	118·0 (4)	116·3 (4)
C1–C2–C3	121·0 (4)	121·2 (4)
C2–C3–C4	118·7 (4)	118·9 (4)
C2–C3–C12	118·9 (4)	117·5 (4)
C4–C3–C12	122·4 (4)	123·6 (4)
C3–C4–C5	119·8 (4)	118·7 (4)
C3–C4–C13	121·6 (4)	123·4 (4)
C5–C4–C13	118·6 (4)	117·9 (4)
O3–C5–C4	116·7 (4)	116·1 (4)
O3–C5–C6	122·0 (4)	121·5 (4)
C4–C5–C6	121·3 (4)	122·4 (4)
C1–C6–C5	118·3 (4)	119·2 (4)
C1–C6–C7	122·6 (4)	120·6 (4)
C5–C6–C7	119·1 (4)	120·2 (4)
O4–C15–O5	124·8 (5)	123·7 (4)
O4–C15–C16	108·5 (5)	109·2 (4)
O5–C15–C16	126·7 (5)	127·1 (4)
O2–C7–C6	109·4 (3)	109·1 (3)
O2–C7–C9	105·6 (3)	108·0 (3)
O2–C7–C14	105·2 (3)	103·7 (3)
C6–C7–C9	111·9 (3)	108·6 (3)
C6–C7–C14	112·6 (3)	112·6 (4)
C9–C7–C14	111·6 (4)	114·5 (3)
O2–C8–O3	112·2 (3)	110·8 (3)
O2–C8–C11	110·2 (4)	111·0 (3)
O3–C8–C11	113·8 (4)	112·4 (4)
O4–C9–C7	108·2 (3)	112·3 (3)
O4–C9–C10	107·4 (3)	104·6 (3)
C7–C9–C10	110·7 (3)	110·9 (3)
N1–C10–C9	109·9 (4)	116·1 (3)
N1–C10–C11	115·0 (3)	111·2 (3)
C9–C10–C11	109·3 (3)	110·7 (3)
O6–C11–C8	109·3 (4)	108·3 (3)
O6–C11–C10	106·0 (3)	104·5 (3)
C8–C11–C10	115·5 (3)	111·2 (3)
O6–C19–O7	123·9 (5)	123·0 (5)
O6–C19–C20	112·3 (5)	109·9 (5)
O7–C19–C20	123·8 (5)	127·1 (5)

This may obviously come from the steric repulsions between HC9 and C(6) atoms [HC(9)···C(6) 2·37 Å] and HC11 and O(3) atoms [HC(11)···O(3) 2·49 Å].

Table 3. *Selected torsion angles* (°) *in* (II) *and* (III)

	(II)	(III)
C8–O2–C7–C6	−50·0	−45·5
C8–O2–C7–C9	70·6	72·4
C8–O2–C7–C14	−171·2	−165·7
C7–O2–C8–O3	65·8	70·4
C7–O2–C8–C11	−62·1	−55·1
C8–O3–C5–C4	−170·0	−163·1
C8–O3–C5–C6	12·3	17·6
C5–O3–C8–O2	−44·7	−54·0
C5–O3–C8–C11	81·2	70·7
C15–O4–C9–C7	−125·9	90·8
C15–O4–C9–C10	114·6	−148·9
C19–O6–C11–C8	90·4	−77·9
C19–O6–C11–C10	−144·5	163·5
O3–C5–C6–C7	0·2	3·3
C1–C6–C7–O2	−162·4	−168·1
C1–C6–C7–C9	80·9	74·4
C1–C6–C7–C14	−45·8	−53·5
C5–C6–C7–O2	18·4	10·6
C5–C6–C7–C9	−98·3	−106·9
C5–C6–C7–C14	135·0	125·1
O2–C7–C9–O4	178·8	95·4
O2–C7–C9–C10	−63·8	−21·1
C6–C7–C9–O4	−62·3	−146·4
C6–C7–C9–C10	55·2	96·9
C14–C7–C9–O4	65·0	−19·6
C14–C7–C9–C10	−177·6	−136·2
O2–C8–C11–O6	166·5	−123·7
O2–C8–C11–C10	47·1	−9·5
O3–C8–C11–O6	39·4	111·7
O3–C8–C11–C10	79·9	−134·1
O4–C9–C10–N1	−65·0	72·4
O4–C9–C10–C11	167·9	−159·6
C7–C9–C10–N1	177·1	−166·3
C7–C9–C10–C11	30·0	38·3
N1–C10–C11–O6	72·8	−57·1
N1–C10–C11–C8	−166·1	−173·7
C9–C10–C11–O6	−163·1	172·3
C9–C10–C11–C8	−41·9	55·6



(II)

(III)

Fig. 1. Stereoscopic drawings of (II) and (III) with 30% probability ellipsoids.

In the crystal structure of (II), there is an intermolecular hydrogen bond between O(1) (x, y, z) and O(7) ($1-x, \frac{1}{2}+y, \frac{3}{2}-z$) atoms, but in (III) the hydrogen bond is made between O(1) (x, y, z) and N(1) ($\frac{1}{2}+x, \frac{3}{2}-y, -z$) atoms. Their distances and angles are as follows: O(1)···O(7) = 2·768 (5) Å, O(1)—H···O(7) = 173°, O(1)···N(1) = 2·815 (5) Å, O(1)—H···N(1) = 148°. The significant lengthening of N(1)—C(17) and N(1)—C(18) bonds in (III) may be due to the effect of the intermolecular hydrogen bond. The N atom in (III) is more pyramidal than that in (II). The deviations of the N atoms from the plane defined by C10, C17, and C18 atoms are 0·370 (3) and 0·402 (3) Å in (II) and (III), respectively.

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Topochemical Studies. X.* Structures of 4-Methyl-*trans*-cinnamic Acid and 4,4′-Dimethyl-α-truxillic Acid

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Abstract. 4-Methyl-*trans*-cinnamic acid (1), $C_{10}H_{10}O_2$, $M_r = 162{\cdot}19$, triclinic, $P\bar{1}$, $a = 7{\cdot}968\,(2)$, $b = 9{\cdot}144\,(2)$, $c = 7{\cdot}733\,(2)$ Å, $\alpha = 106{\cdot}87\,(2)$, $\beta = 125{\cdot}46\,(2)$, $\gamma = 86{\cdot}87\,(2)°$, $V = 434{\cdot}5\,(2)$ Å^3, $Z = 2$, $D_m = 1{\cdot}20$, $D_x = 1{\cdot}240$ Mg m^{-3}, $\mu = 0{\cdot}71$ mm^{-1}, $F(000) = 172$, $R = 0{\cdot}061$ for 1395 unique reflections. 4,4′-Dimethyl-α-truxillic acid (2) [2,4-bis(*p*-tolyl)-1,3-cyclobutanedicarboxylic acid], $C_{20}H_{20}O_4$, $M_r = 324{\cdot}38$, monoclinic, $P2_1/a$, $a = 17{\cdot}767\,(3)$, $b = 8{\cdot}431\,(2)$, $c = 5{\cdot}578\,(2)$ Å, $\beta = 92{\cdot}94\,(2)°$, $V = 834{\cdot}4\,(4)$ Å^3, $Z = 2$, $D_m = 1{\cdot}27$, $D_x = 1{\cdot}291$ Mg m^{-3}, $\mu = 0{\cdot}74$ mm^{-1}, $F(000) = 344$, $R = 0{\cdot}086$ for 1338 unique reflections. $T = 295$ K, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å. Structures have been determined on a photoreactive compound (1) and its photodimer (2) formed in the solid state. In the crystals of (1) the C=C double bonds of the nearest neighbours are related by $\bar{1}$ with C···C distance of 4·133 (4) Å. The molecule of (2) has $\bar{1}$ symmetry in the crystal, indicating the topochemical formation of (2).

Introduction. The space groups and lattice parameters for the crystals of (1) and (2) have been reported by Schmidt and his co-workers in their early works on topochemistry (Cohen, Schmidt & Sonntag, 1964; Schmidt, 1964). However, the three-dimensional structures have been left to be solved. In order to elucidate the mechanism of the solid-state photoreaction in detail, it is desirable to know the crystal and molecular structures of both the reactants and the products. We have undertaken X-ray structure analysis of photoreactive monomers and their products as an extension of studies of molecular overlapping and packing of unsaturated organic compounds in crystals (Haisa, Kashino, Yuasa & Akigawa, 1976). We report results for a classical pair of compounds, (1) and (2).

Experimental. Experimental details for (1) and (2) are listed in Table 1. Crystals of (1) grown from an ethanol solution by slow evaporation. Photodimer (2) prepared following the method described by Cohen, Schmidt & Sonntag (1964); crystals of (1) exposed to sunlight for two months. Single crystals of (2) grown from an ethanol solution of the irradiated sample by slow evaporation. D_m by flotation in aqueous KI. Rigaku AFC-5 four-circle diffractometer equipped with rotating anode; ω–2θ scan method (scan speed 4° min^{-1} in ω, scan range in ω: $1{\cdot}2° + 0{\cdot}15° \tan\theta$); Ni-filtered Cu $K\alpha$, 40 kV, 200 mA; background measured for 4 s on either side of the peak; three standard reflections recorded every 57 reflections; Lorentz and polarization corrections; no absorption correction. All unique

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* Part IX: Haisa, Kashino, Yuasa & Akigawa (1976).

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