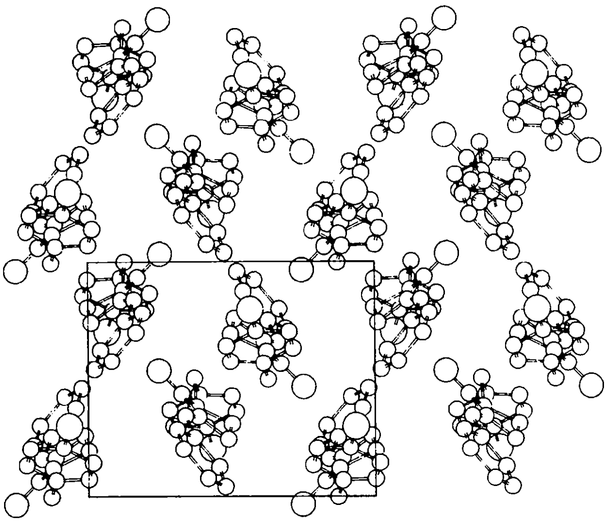

Fig. 3. The crystal structure viewed along *a*.

in the incipient dimer react topochemically to form a centrosymmetric cyclobutane ring.

We thank Dr J. D. C. McConnell and Mr T. Abraham for assistance with the intensity collection, Professor J. M. Thomas for discussions, and the SRC and the Oppenheimer Fund of the University of Cambridge for support.

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2-Benzyl-6-benzylidenecyclohexanone – a Photodimerizable Crystal

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(*Received* 2 *October* 1980; *accepted* 21 *October* 1980)

Abstract. $C_{20}H_{20}O$, M_r = 276·4, triclinic, $P\bar{1}$, a = 13·303 (3), b = 11·144 (2), c = 5·927 (3) Å, α = 72·11 (3), β = 82·55 (3), γ = 67·76 (2)°, Z = 2, D_x = 1·186 Mg m^{-3}. Final R = 0·055 for 2285 independent reflections. Molecules are packed in pairs across a centre of symmetry such that the reactive double bonds are separated by 3·792 (3) Å.

Introduction. Whilst the solid-state photodimerization of 2-benzyl-5-benzylidenecyclopentanone (BCCP) and 2-benzyl-5-(*p*-bromobenzylidene)cyclopentanone (B*p*BrBCP) proceed smoothly to yield highly perfect single crystals of product (Nakanishi, Jones & Thomas, 1980), 2-benzyl-6-benzylidenecyclohexanone (BBCH) has been reported to yield an amorphous photoproduct (Forward & Whiting, 1969). As part of a detailed study (Jones, Nakanishi, Theocharis & Thomas, 1980) of the topochemical and topotactic reactivity of BBCP, BBCH and their derivatives we have determined the crystal structure of BBCH.

BBCH was prepared following the method of Forward & Whiting (1969). Single crystals were obtained by evaporation of a light-petroleum (353–373 K) solution at room temperature (m.p. = 342–343 K). The specimen used for structure analysis was a fragment of a plate, 0·10 × 0·15 × 0·20 mm. The lattice constants and intensities were obtained from measurements on a Philips four-circle diffractometer

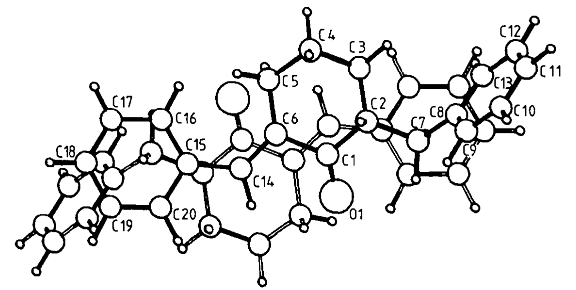

Fig. 1. Atomic numbering, and the interaction between molecules forming the incipient dimer, viewed along the normal to the mean plane of the carbonyl, ethylene and benzene groups.

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Table 1. *Fractional atomic coordinates* ($\times 10^4$), *with e.s.d.'s in parentheses, and equivalent isotropic thermal parameters*

	x	y	z	U_{eq}* (Å^2)
O(1)	796 (1)	793 (2)	7445 (3)	0·062
C(1)	395 (2)	1619 (2)	5610 (3)	0·043
C(2)	968 (2)	2524 (2)	4040 (3)	0·046
C(3)	777 (2)	2776 (2)	1442 (4)	0·058
C(4)	−421 (2)	3404 (3)	922 (4)	0·065
C(5)	−1034 (2)	2520 (3)	2318 (4)	0·061
C(6)	−714 (2)	1816 (2)	4873 (3)	0·042
C(7)	2163 (2)	2036 (2)	4678 (4)	0·055
C(8)	2673 (2)	3079 (2)	3503 (4)	0·047
C(9)	2563 (2)	4088 (2)	4530 (4)	0·062
C(10)	3010 (2)	5058 (3)	3447 (5)	0·077
C(11)	3561 (2)	5054 (3)	1333 (5)	0·076
C(12)	3677 (2)	4062 (3)	304 (4)	0·071
C(13)	3241 (2)	3080 (2)	1389 (4)	0·058
C(14)	−1323 (2)	1317 (2)	6594 (3)	0·041
C(15)	−2436 (2)	1346 (2)	6606 (3)	0·042
C(16)	−3069 (2)	1762 (3)	4603 (4)	0·062
C(17)	−4128 (2)	1799 (3)	4842 (4)	0·072
C(18)	−4571 (2)	1403 (3)	7003 (5)	0·073
C(19)	−3958 (2)	944 (3)	9000 (4)	0·076
C(20)	−2900 (2)	919 (2)	8788 (4)	0·057
H(2)	567 (8)	3447 (8)	4334 (9)	
H(31)	1096 (8)	1813 (8)	1035 (9)	
H(32)	1182 (8)	3398 (8)	361 (9)	
H(41)	−536 (8)	3687 (8)	−907 (9)	
H(42)	−725 (8)	4309 (8)	1422 (9)	
H(51)	−877 (8)	1803 (8)	1505 (9)	
H(52)	−1852 (8)	3084 (8)	2301 (9)	
H(71)	2599 (8)	1159 (8)	4095 (9)	
H(72)	2170 (8)	1765 (8)	6551 (9)	
H(9)	2138 (8)	4091 (8)	6164 (9)	
H(10)	2918 (8)	5723 (8)	4247 (9)	
H(11)	3875 (8)	5783 (8)	465 (9)	
H(12)	4071 (8)	4067 (8)	−1317 (9)	
H(13)	3315 (8)	2391 (8)	638 (9)	
H(14)	−990 (8)	835 (8)	8248 (9)	
H(16)	−2766 (8)	2055 (8)	2912 (9)	
H(17)	−4544 (8)	2104 (8)	3311 (9)	
H(18)	−5345 (8)	1444 (8)	7170 (9)	
H(19)	−4250 (8)	597 (8)	10723 (9)	
H(20)	−2466 (8)	587 (8)	10315 (9)	

* $U_{eq} = \frac{1}{3}\,\mathrm{trace}\,\tilde{\mathbf{U}}$.

with graphite-monochromatized Cu $K\alpha$ radiation. All reflections within the range $2\theta < 140°$ were collected in a 2θ–ω scan mode at a scanning rate of 4° min^{-1}. 2285 independent reflections had $|F_o| > 5\sigma(F_o)$ and were used for the determination. No correction was made for absorption.

The structure was determined by direct methods and refined by full-matrix least squares. Isotropic H atoms were first located geometrically and then refined. The final R was 0·055.*

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Final atomic coordinates are given in Table 1 and the atom numbering in Fig. 1.

Discussion. Bond lengths and angles are listed in Table 2. The C(1)—C(6) length of 1·509 (5) Å suggests that delocalization between the carbonyl and ethylene groups is weak. The moiety consisting of the carbonyl and ethylene groups and the benzene ring B [C(15)–C(20)] is approximately planar, the maximum deviation from the mean plane being 0·22 Å. The benzene ring A [C(8)–C(13)] makes a dihedral angle of 109·1 (2)° with this plane, however, and consequently the molecule as a whole is not planar.

In the crystal, the molecules are so oriented that the long molecular axis is nearly parallel to a (Fig. 2). Additionally, the molecules form incipient dimers across centres of symmetry (Fig. 2), where the plane-to-plane perpendicular distance of 3·028 (5) Å suggests an extremely strong interaction between the π-conjugation systems of the molecules. The shortest intermolecular contact between double bonds is found for these dimeric molecules, with C(6)—C(14′) = 3·792 (5) Å. Upon photo-irradiation those double bonds related by a centre of symmetry may react to form a centrosymmetric cyclobutane ring. The plane-to-plane perpendicular distance of 3·028 (5) Å may not allow sufficient room for the molecules to relax after

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)—O(1)	1·216 (3)	C(2)—C(1)	1·512 (5)
C(6)—C(1)	1·509 (5)	C(3)—C(2)	1·515 (5)
C(7)—C(2)	1·530 (5)	C(4)—C(3)	1·508 (5)
C(5)—C(4)	1·500 (4)	C(6)—C(5)	1·508 (5)
C(14)—C(6)	1·336 (4)	C(8)—C(7)	1·508 (5)
C(9)—C(8)	1·388 (4)	C(13)—C(8)	1·377 (4)
C(10)—C(9)	1·376 (4)	C(11)—C(10)	1·367 (5)
C(12)—C(11)	1·370 (5)	C(13)—C(12)	1·378 (4)
C(15)—C(14)	1·468 (4)	C(16)—C(15)	1·400 (4)
C(20)—C(15)	1·385 (4)	C(17)—C(16)	1·382 (4)
C(18)—C(17)	1·355 (4)	C(19)—C(18)	1·375 (4)
C(20)—C(19)	1·386 (4)		
C(2)—C(1)—O(1)	121·2 (3)	C(6)—C(1)—O(1)	121·1 (3)
C(6)—C(1)—C(2)	117·7 (3)	C(3)—C(2)—C(1)	111·2 (3)
C(7)—C(2)—C(1)	112·3 (3)	C(7)—C(2)—C(3)	114·4 (3)
C(4)—C(3)—C(2)	110·8 (3)	C(5)—C(4)—C(3)	112·5 (3)
C(6)—C(5)—C(4)	116·0 (3)	C(5)—C(6)—C(1)	118·7 (3)
C(14)—C(6)—C(1)	115·4 (3)	C(14)—C(6)—C(5)	125·9 (3)
C(8)—C(7)—C(2)	112·5 (3)	C(9)—C(8)—C(7)	120·2 (3)
C(13)—C(8)—C(7)	121·7 (3)	C(13)—C(8)—C(9)	118·1 (3)
C(10)—C(9)—C(8)	120·5 (3)	C(11)—C(10)—C(9)	120·7 (3)
C(12)—C(11)—C(10)	119·3 (3)	C(13)—C(12)—C(11)	120·3 (3)
C(12)—C(13)—C(8)	121·1 (3)	C(15)—C(14)—C(6)	131·7 (2)
C(16)—C(15)—C(14)	125·7 (3)	C(20)—C(15)—C(14)	117·2 (3)
C(20)—C(15)—C(16)	117·1 (3)	C(17)—C(16)—C(15)	120·5 (3)
C(18)—C(17)—C(16)	121·2 (3)	C(19)—C(18)—C(17)	119·7 (3)
C(20)—C(19)—C(18)	119·7 (3)	C(19)—C(20)—C(15)	121·8 (3)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35766 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

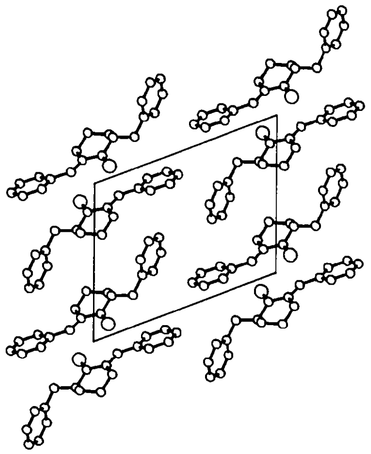

Fig. 2. The crystal structure viewed along *c*.

dimerization and may account for the loss of crystallinity upon dimerization (Forward & Whiting, 1969). This distance should be compared with the 4·174 (5) Å found for BBCP (Nakanishi, Jones, Thomas, Hursthouse & Motevalli, 1981), a structure shown to undergo a single-crystal → single-crystal photodimerization (Nakanishi, Jones & Thomas, 1980). An additional factor contributing to the loss of crystallinity upon reaction may be found in the relatively low melting point of the solid. Melting-point depression as a result of formation of product may well lead to the loss of topochemical control upon the reaction (Nakanishi, Ueno & Sasada, 1976).

We thank the SRC and the Oppenheimer Fund of the University of Cambridge for support, and Dr J. D. C. McConnell and Mr T. Abraham for assistance with the intensity collection, and we appreciate the stimulus provided by Professor J. M. Thomas.

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Acta Cryst. (1981). B**37**, 760–763

Vincamine 2-Oxoglutarate (Oxovinca). Two independent X-ray Structure Determinations

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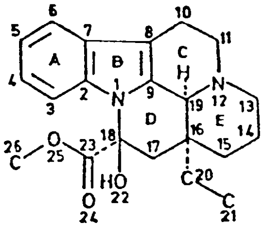
(*Received* 7 *October* 1980; *accepted* 28 *October* 1980)

Abstract. $C_{21}H_{27}N_2O_3^+.C_5H_5O_5^-$, $M_r = 500·5$, orthorhombic, $P2_12_12_1$, $a = 20·058$ (4), $b = 7·556$ (1), $c = 16·249$ (4) Å, $Z = 4$, $D_c = 1·35$ Mg m^{-3}, μ(Cu $K\alpha$) = 0·79 mm^{-1}. Final $R = 0·098$ and $R_w = 0·121$ for 1204 observed reflexions. The title compound is a more efficient brain vasodilator drug than pure vincamine. The two molecules are similar, except for the methyl ester radical which is rotated ~180° from one molecule to the other. Cations and anions are linked through NH···O and OH···O hydrogen bonds forming continuous chains parallel to **c**.

Introduction. Vincamine (I) is a well known brain vasodilator drug. To increase its action time, several derivatives were obtained in the ELMU Laboratory of Madrid. One of them, the title compound, hereafter oxovinca, has a half-life three times greater than that of vincamine, and shows less and shorter hypotensic secondary action. Gas-chromatography studies on the residual drugs in urine (Montoro, Vilar, Calatayud, de



(I)