value of 118·5 (11)°, typical of phenyl rings bound to silicon (Domenicano, Vaciago & Coulson, 1975). The C—C distances range from 1·34 (3) to 1·45 (2) Å with a mean of 1·39 (2) Å.

The $(Ph_3Si)_2NH$ molecule has no internal symmetry in the crystal, as shown both by the Si—C distances (Table 2) and by the angles between the phenyl planes (Table 3).

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5-Benzylidene-2-(p-chlorobenzyl)cyclopentanone – a Photodimerizable Crystal

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Abstract. $C_{19}H_{17}ClO$, $M_r = 296·8$, monoclinic, $P2_1/c$, $a = 17·175$ (4), $b = 10·587$ (3), $c = 8·796$ (5) Å, $\beta = 76·33$ (9)°, $Z = 4$, $D_x = 1·269$ Mg m⁻³. Final $R = 0·055$ for 1728 independent reflections. Molecules form incipient dimers across centres of symmetry such that the intermolecular separation of reactive double bonds is 4·027 (5) Å.

Introduction. In a study of the growth of crystallographically oriented product in the topochemical dimerization of 2-benzyl-5-benzylidenecyclopentanone (BBCP) derivatives (Nakanishi, Jones & Thomas, 1980), we have observed that solid-state photoreactivity may be controlled by varying both the nature and position of substitution within the molecule. Thus, whilst 2-benzyl-5-(p-methylbenzylidene)cyclopentanone and its chloro analogue (BpClBCP) are photostable, 5-benzylidene-2-(p-methylbenzyl)cyclopentanone and its chloro analogue (pClBBCP) are photoreactive (Jones, Nakanishi, Theocharis & Thomas, 1980). The present study was undertaken as part of an investigation of the effect on crystal packing of varying the nature and position of substitution.

pClBBCP was prepared by a method similar to that described by Forward & Whiting (1969). Single crystals were grown by evaporation of a methanol–chloroform solution. The specimen used for structure analysis was a fragment of a plate, 0·15 × 0·20 × 0·20 mm. The lattice constants and intensities were obtained from measurements on a Philips four-circle diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. Reflections within the range $2\theta < 150°$ were collected in a 2θ–ω scan mode at a scanning rate of 4° min⁻¹. 1728 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 block-diagonal least squares. Isotropic H atoms were first located geometrically and then refined. Full-matrix refinement was carried out at the final stage to give $R = 0·055$.*

Table 1. *Fractional atomic coordinates* (×10⁴), *with e.s.d.'s in parentheses, and equivalent isotropic thermal parameters*

|	x	y	z	U_{eq}* (Å²)
O(1)	5824 (2)	7474 (4)	−343 (4)	0·091
C(1)	5802 (2)	8269 (4)	651 (4)	0·058
C(2)	6520 (2)	8761 (3)	1184 (4)	0·052
C(3)	6222 (2)	10021 (4)	1926 (5)	0·061
C(4)	5325 (2)	9888 (4)	2575 (4)	0·054
C(5)	5060 (2)	8851 (3)	1622 (4)	0·048
C(6)	7307 (2)	8708 (4)	−20 (4)	0·062
C(7)	8022 (2)	8865 (4)	678 (4)	0·056
C(8)	8382 (2)	10019 (4)	740 (5)	0·070
C(9)	9021 (3)	10165 (5)	1415 (6)	0·079
C(10)	9300 (2)	9139 (5)	2058 (5)	0·073
C(11)	8967 (3)	7982 (5)	2029 (5)	0·076
C(12)	8328 (3)	7848 (4)	1331 (5)	0·073
C(13)	4342 (2)	8392 (3)	1597 (4)	0·052
C(14)	3550 (2)	8706 (3)	2505 (4)	0·053
C(15)	3389 (2)	9571 (4)	3756 (5)	0·062
C(16)	2622 (2)	9780 (4)	4591 (5)	0·070
C(17)	1982 (2)	9173 (5)	4237 (5)	0·077
C(18)	2124 (2)	8321 (4)	3007 (6)	0·077
C(19)	2886 (2)	8101 (4)	2172 (5)	0·063
Cl(1)	90 (1)	9333 (2)	2966 (2)	0·119
H(2)	6621 (14)	8146 (18)	2006 (19)	
H(31)	6482 (15)	10285 (18)	2729 (19)	
H(32)	6335 (14)	10706 (18)	1079 (18)	
H(41)	5048 (15)	10685 (18)	2545 (19)	
H(42)	5187 (14)	9663 (18)	3688 (18)	
H(61)	7285 (14)	9395 (18)	−808 (19)	
H(62)	7313 (14)	7829 (18)	−493 (19)	
H(8)	8177 (14)	10753 (18)	340 (19)	
H(9)	9246 (14)	11068 (18)	1479 (18)	
H(11)	9213 (14)	7232 (18)	2436 (19)	
H(12)	8058 (14)	7033 (18)	1318 (18)	
H(13)	4383 (14)	7704 (18)	779 (18)	
H(15)	3812 (14)	10043 (18)	3999 (19)	
H(16)	2514 (14)	10394 (18)	5437 (19)	
H(17)	1415 (14)	9253 (18)	4880 (18)	
H(18)	1630 (15)	7877 (18)	2809 (19)	
H(19)	3048 (14)	7532 (18)	1306 (19)	

* $U_{eq} = \frac{1}{3}$ trace $\tilde{U}$.
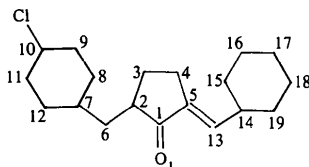
Fig. 1. Atom numbering.

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

All calculations were performed on an IBM 370-65 computer with *SHELX* 76 (G. M. Sheldrick) and *PLUTO* 78 (W.D.S. Motherwell).

Discussion. Bond lengths and angles are listed in Table 2; the values agree well with those of the non-substituted 2-benzyl-5-benzylidenecyclopentanone (BBCP) (Nakanishi, Jones, Thomas, Hursthouse & Motevalli, 1981). The moiety consisting of the carbonyl and ethylene groups and the benzene ring *B* [C(14)–C(19)] is planar with a maximum deviation of 0·13 Å. With this mean plane, the benzene ring *A* [C(7)–C(12)] makes a dihedral angle of 69·9 (4)°.

The molecules form incipient dimer pairs across centres of symmetry with a plane-to-plane perpendicular distance of 4·036 (5) Å [*cf.* 4·174 (5) Å for BBCP]. The intermolecular distance between double bonds within the pair is 4·027 (5) Å [4·166 (5) Å for BBCP], a value similar to that generally found for such 2+2 dimerizations (Schmidt, 1971). It is expected, therefore, that upon photo-irradiation, the double bonds
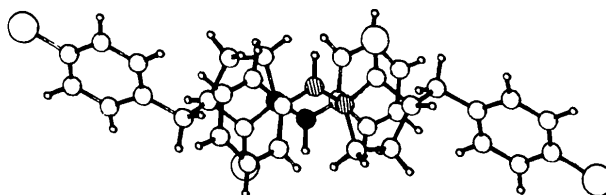
Fig. 2. The interaction between molecules forming the incipient dimer, viewed along the normal to the mean plane of the carbonyl, ethylene and benzene groups.

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

C(1)–O(1)	1·208 (5)	C(2)–C(1)	1·510 (7)
C(5)–C(1)	1·490 (6)	C(3)–C(2)	1·520 (7)
C(4)–C(3)	1·518 (7)	C(5)–C(4)	1·514 (7)
C(13)–C(5)	1·331 (5)	C(6)–C(2)	1·508 (7)
C(7)–C(6)	1·508 (7)	C(8)–C(7)	1·376 (6)
C(12)–C(7)	1·382 (6)	C(9)–C(8)	1·374 (6)
C(10)–C(9)	1·364 (7)	C(11)–C(10)	1·354 (7)
Cl(1)–C(10)	1·742 (6)	C(12)–C(11)	1·385 (7)
C(14)–C(13)	1·443 (6)	C(15)–C(14)	1·408 (6)
C(19)–C(14)	1·398 (6)	C(16)–C(15)	1·366 (6)
C(17)–C(16)	1·371 (7)	C(18)–C(17)	1·386 (7)
C(19)–C(18)	1·362 (6)		

C(2)–C(1)–O(1)	125·2 (5)	C(5)–C(1)–O(1)	125·4 (4)
C(5)–C(1)–C(2)	109·2 (4)	C(3)–C(2)–C(1)	102·7 (4)
C(6)–C(2)–C(1)	115·5 (4)	C(6)–C(2)–C(3)	119·2 (4)
C(4)–C(3)–C(2)	106·8 (4)	C(5)–C(4)–C(3)	105·6 (4)
C(4)–C(5)–C(1)	106·8 (4)	C(13)–C(5)–C(1)	120·7 (4)
C(13)–C(5)–C(4)	132·4 (3)	C(7)–C(6)–C(2)	113·1 (4)
C(8)–C(7)–C(6)	122·0 (5)	C(12)–C(7)–C(6)	120·7 (5)
C(12)–C(7)–C(8)	117·2 (5)	C(9)–C(8)–C(7)	121·9 (5)
C(10)–C(9)–C(8)	119·0 (5)	C(11)–C(10)–C(9)	121·4 (5)
Cl(1)–C(10)–C(9)	119·0 (5)	Cl(1)–C(10)–C(11)	119·6 (5)
C(12)–C(11)–C(10)	118·9 (5)	C(11)–C(12)–C(7)	121·5 (5)
C(14)–C(13)–C(5)	131·5 (3)	C(15)–C(14)–C(13)	124·6 (4)
C(19)–C(14)–C(13)	119·1 (4)	C(19)–C(14)–C(15)	116·2 (4)
C(16)–C(15)–C(14)	120·8 (5)	C(17)–C(16)–C(15)	121·7 (5)
C(18)–C(17)–C(16)	118·7 (5)	C(19)–C(18)–C(17)	120·2 (5)
C(18)–C(19)–C(14)	122·4 (5)		
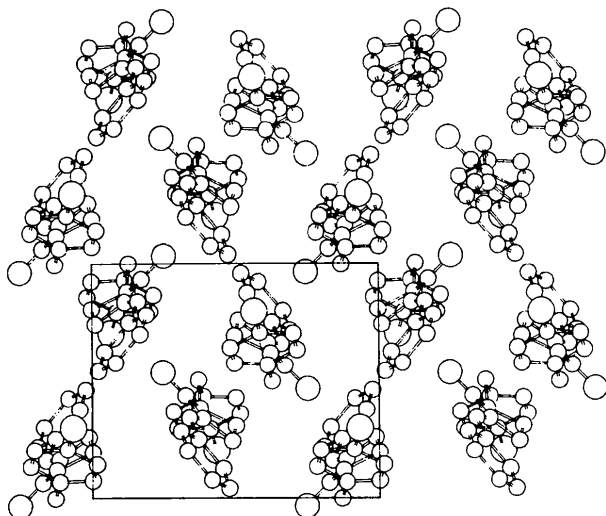
Fig. 3. The crystal structure viewed along a.

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

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2-Benzyl-6-benzylidenecyclohexanone – a Photodimerizable Crystal

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

Introduction. Whilst the solid-state photodimerization of 2-benzyl-5-benzylidenecyclopentanone (BCCP) and 2-benzyl-5-(p-bromobenzylidene)cyclopentanone (BpBrBCP) 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
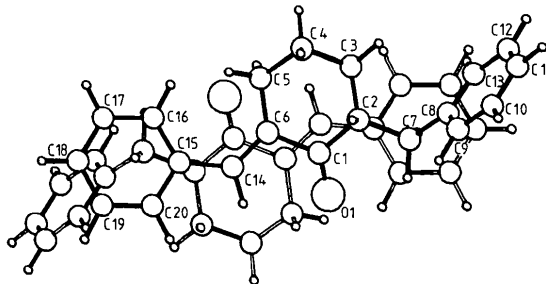

Fig. 1. Atomic numbering, and the interaction between molecules forming the incipient dimer, viewed along the normal to the mean plane of the carbonyl, ethylene and benzene groups.