

angles: N(1)—C(6)—C(1)—C(2), 121.2 (5)°; N(1)—C(6)—C(1)—N(2), -59.1 (5)°. These rotations move the H(2N) atoms away from the N(1) atom so that the H(2N)⋯N(1) distance is 2.81 (5) Å; there is no indication of intramolecular hydrogen bonding in the cation. Our result, that the three pyridine N atoms are protonated and the aliphatic N atom is not, is in agreement with the conclusions reached by Anderegg, Hubmann, Podder & Wenk (1977) on the basis of pH measurements and confirmed by Anderegg, Popov & Pregosin (1986) by ¹⁵N NMR studies.

The H(2N) atoms are involved in three-center hydrogen bonds with the O(12) and O(32) atoms (Fig. 2).^{*} Distances are H(2N)⋯O(12), 2.42 (5); H(2N)⋯O(32), 2.23 (5); N(2)⋯O(12), 3.040 (5); N(2)⋯O(32), 2.916 (5) Å. The H atom is 0.27 (5) Å out of the N(2)⋯O(12)⋯O(32) plane. These distances

^{*} We are indebted to a referee for pointing this out.

fit the criteria for three-center hydrogen bonds given by Jeffrey (1987).

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Structure and Photochemistry of a Cyclohexenone* and its Solid-State Photoproduct†

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Abstract. C₁₈H₁₅BrO, *M_r* = 327.23, *T* = 294 K, Mo *Kα*₁, λ = 0.70930 Å. Cyclohexenone, monoclinic, *P*2₁/*c*, *a* = 16.157 (2), *b* = 9.189 (3), *c* = 9.996 (3) Å, β = 95.80 (2)°, *V* = 1476 (1) Å³, *Z* = 4, *D_m* = 1.46, *D_x* = 1.472 g cm⁻³, *F*(000) = 664, μ = 27.5 cm⁻¹, *R* = 0.051 for 1807 reflections. Photoproduct, monoclinic, *I*2/*a*, *a* = 17.607 (4), *b* = 8.213 (2), *c* = 19.976 (5) Å, β = 93.09 (3)°, *V* = 2884.5 (12) Å³, *Z* = 8, *D_x* = 1.507 g cm⁻³, *F*(000) = 1328, μ = 28.1 cm⁻¹, *R* = 0.038 for 1651 reflections. In the cyclohexenone molecule the six-membered cyclohexene ring has a C5-sofa conformation with the *p*-bromophenyl substituent in a pseudo-axial site; the structure exhibits disorder, with the enantiomers randomly distributed (75:25 occupancies) at one site. Formation of the photoproduct involves migration of the *p*-bromophenyl substituent from position 4 to 3, and 2–4 bonding (cyclohexenone numbering); the

detailed molecular structure of the photoproduct can be derived with minimum atomic movement from that of the cyclohexenone reactant.

Introduction. Photolysis in solution of 4,4-diaryl substituted cyclohexenones (Fig. 1) gives photoproducts resulting from migration of one of the substituents and 2–4 bond formation (Zimmerman & Wilson, 1964; Zimmerman, Rieke & Scheffer, 1967; Schuster, 1980); for unsymmetrically substituted compounds there are two possible photoproducts (Fig. 1). The present work involves a study of the photolysis reaction in the solid state, and the crystal structures of the *p*-bromophenyl compound and of its major solid-state photoproduct have been determined to obtain quantitative information on the proposed reaction mechanism (Fig. 1).

Experimental. Crystals of the cyclohexenone were grown from diethyl ether/petroleum ether; the photoproduct sample was obtained by photolysis in

* 4-(4-Bromophenyl)-4-phenylcyclohex-2-en-1-one.

† *trans*-6-(4-Bromophenyl)-5-phenylbicyclo[3.1.0]hexan-2-one.

acetone and crystallization, again from diethyl ether/petroleum ether. Crystal dimensions 0.14 × 0.30 × 0.50 (0.12 × 0.20 × 0.50) mm. Nonius CAD-4F diffractometer, monochromatized Mo K α radiation, lattice parameters from 20 reflections with $\theta = 10\text{--}15^\circ$. Intensities for $\theta \leq 27.5^\circ$, hkl : -20 to 20, 0 to 11, 0 to 12 (-22 to 22, 0 to 10, 0 to 25), ω -2 θ scan, ω scan width $(0.65 + 0.35 \tan \theta)^\circ$ at $1.1\text{--}20^\circ \text{ min}^{-1}$, extended 25% on each side for background measurement, three standard reflections showed no significant variation, Lp and absorption corrections [numerical integration, transmission factors 0.50–0.68 (0.55–0.72)]. 3361 (3290) unique reflections, 1807 (1651) with $I \geq 3\sigma(I)$. Structures by Patterson and Fourier methods, refined by full-matrix least-squares procedures, H atoms from difference maps. For the cyclohexenone, large thermal parameters and unusual molecular dimensions for C2 and C6 indicated disorder, which was modelled by splitting atoms C2, C6 and C1 into two sites each (occupancies adjusted to 75:25 gave reasonably consistent thermal parameters, lower occupancy C1 not refined, lower occupancy H atoms not included). Refinement on F , with $w = 1/\sigma(F)$, where $\sigma^2(I) = S + 4(B_1 + B_2) + (0.04I)^2$, $S = \text{scan}$, B_1 and $B_2 = \text{background counts}$, scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–102), locally written, or locally modified versions of standard computer programs. Final $R = 0.051$ (0.038), $wR = 0.064$ (0.045) for 1807 (1651) reflections with $I \geq 3\sigma(I)$, $S = 2.8$ (1.5), $\Delta/\sigma = 0.01$ (0.001) (mean), 0.19 (0.003) (maximum), $\Delta\rho = -0.57$ to $+0.77$ (-1.25 to $+0.72$) e \AA^{-3} .

Discussion. Positional parameters are given in Table 1, interatomic distances and angles in Table 2, and views of the molecules in Fig. 2.*

The cyclohexenone crystal structure exhibits disorder, with two enantiomers (75:25 occupancies) randomly occupying each site. The torsion angles in the six-membered cyclohexene ring (Table 2) indicate a C5-sofa conformation (C5 displaced from the plane of the other five ring atoms), with the *p*-bromophenyl substituent pseudo-axial and the phenyl substituent pseudo-equatorial at C4 (Fig. 2). The aromatic rings of the two substituents have fairly symmetrical but different orientations: that of the *p*-bromophenyl group lies across the cyclohexene ring, *i.e.* approximately parallel to the C3...C5 vector, while the phenyl ring plane is rotated about 90° from such an

* Lists of anisotropic thermal parameters, hydrogen positions, bond lengths and angles, torsion angles, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54292 (50 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

orientation and bisects the cyclohexene ring, *i.e.* it is approximately parallel to C4...C1.

Solid-state photolysis produces two photoproducts, in the ratio 1.3:1 (2:1 in solution) (Fig. 1). The general molecular shape and conformational features of the major photoproduct are remarkably similar to those of the cyclohexenone (Fig. 2). The photoreaction involves: (i) migration of the *p*-bromophenyl substituent, with breaking of the C4—C7 bond and formation of a C3—C7 bond [the C3...C7 distance of 2.51 (1) \AA in the cyclohexenone is reduced to 1.49 (1) \AA in the photoproduct]; (ii) formation of a C2—C4 bond [C2...C4 changing from

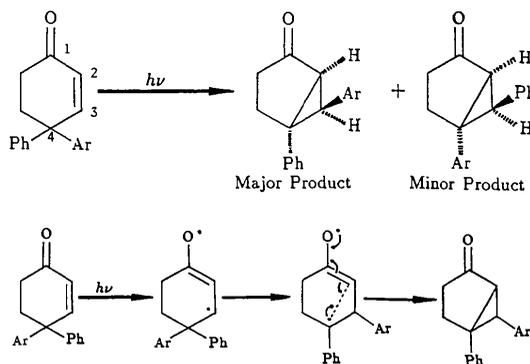


Fig. 1. Photochemistry of cyclohexenones and proposed reaction mechanism.

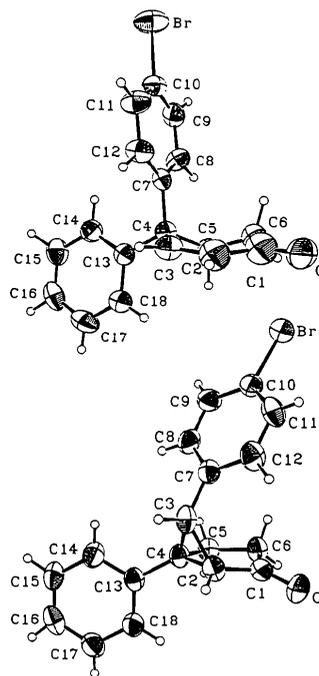


Fig. 2. Views of the cyclohexenone (75% molecule, upper) and photoproduct (lower).

Table 1. *Positional (fractional) and equivalent isotropic thermal ($\text{\AA}^2 \times 10^3$) parameters*

$U_{eq} = 1/3(\text{trace of diagonalized } U \text{ tensor}).$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U_{iso}
Cyclohexenone				
Br	-0.01924 (3)	0.75880 (6)	0.17480 (6)	76
O	0.4800 (3)	0.7234 (4)	0.0767 (6)	99
C1*	0.4272 (5)	0.6260 (10)	0.0666 (10)	81 (3)
C2*	0.4239 (6)	0.5388 (10)	0.1949 (10)	71 (2)
C3	0.3670 (3)	0.4339 (5)	0.2120 (6)	51
C4	0.2986 (2)	0.4011 (5)	0.0995 (4)	40
C5	0.3336 (3)	0.4401 (5)	-0.0333 (5)	50
C6*	0.3684 (5)	0.5895 (9)	-0.0435 (8)	59 (2)
C7	0.2206 (3)	0.4896 (4)	0.1187 (4)	36
C8	0.1656 (3)	0.5286 (5)	0.0088 (5)	47
C9	0.0932 (3)	0.6068 (5)	0.0265 (5)	49
C10	0.0772 (2)	0.6465 (5)	0.1533 (5)	47
C11	0.1292 (3)	0.6062 (6)	0.2632 (5)	55
C12	0.2006 (3)	0.5283 (5)	0.2459 (5)	52
C13	0.2810 (3)	0.2365 (4)	0.1010 (4)	40
C14	0.2027 (3)	0.1788 (5)	0.1136 (4)	48
C15	0.1898 (3)	0.0289 (5)	0.1187 (5)	59
C16	0.2548 (4)	-0.0646 (6)	0.1097 (5)	61
C17	0.3327 (4)	-0.0105 (6)	0.0951 (6)	66
C18	0.3461 (3)	0.1390 (5)	0.0918 (5)	53
C1†	0.4309	0.6247	0.0962	10 (2)
C2†	0.4011 (16)	0.5939 (29)	0.2258 (31)	77 (7)
C6†	0.3965 (14)	0.5509 (23)	-0.0169 (22)	49 (5)
Photoproduct				
Br	0.39622 (3)	-0.07849 (6)	0.06624 (2)	60
O	0.0177 (2)	0.2961 (4)	0.0033 (2)	65
C1	0.0661 (2)	0.3634 (5)	0.0383 (2)	47
C2	0.0628 (2)	0.3904 (5)	0.1116 (2)	46
C3	0.1332 (3)	0.3508 (5)	0.1566 (2)	46
C4	0.1220 (2)	0.5211 (5)	0.1316 (2)	39
C5	0.1615 (3)	0.5657 (6)	0.0681 (2)	43
C6	0.1357 (3)	0.4444 (6)	0.0139 (2)	49
C7	0.1965 (2)	0.2429 (5)	0.1372 (2)	43
C8	0.2716 (3)	0.2842 (6)	0.1522 (2)	55
C9	0.3310 (3)	0.1903 (5)	0.1332 (2)	53
C10	0.3156 (3)	0.0482 (5)	0.0983 (2)	47
C11	0.2422 (3)	-0.0001 (6)	0.0857 (3)	56
C12	0.1825 (3)	0.0942 (5)	0.1041 (2)	55
C13	0.1065 (2)	0.6564 (5)	0.1788 (2)	41
C14	0.1486 (3)	0.6746 (6)	0.2388 (2)	52
C15	0.1373 (3)	0.8073 (6)	0.2801 (2)	60
C16	0.0837 (3)	0.9205 (7)	0.2623 (2)	59
C17	0.0402 (3)	0.9052 (6)	0.2030 (3)	57
C18	0.0521 (3)	0.7740 (6)	0.1611 (2)	51

* Occupancy 0.75; isotropic.

† Occupancy 0.25; isotropic; positional parameters of C1' were not refined; C2' and C6' are located close to C2 and C6, respectively, so that the double bond is numbered C5=C6' in the lower occupancy molecule.

2.49 (1) to 1.53 (1) \AA). In the resulting photoproduct the *p*-bromophenyl substituent occupies an *endo* site (still 'axial', although the nomenclature is not really applicable). The *p*-bromophenyl aromatic ring has rotated away from parallelism with the C3...C5 vector, but is again approximately symmetrically oriented across the new three-membered ring; the phenyl ring retains an orientation very close to that in the cyclohexenone [the C6—C5—C4—C13 and C5—C4—C13—C18 torsion angles change by only 20 and 10°, respectively (Table 2)]. The five-membered ring of the photoproduct has a shallow C6-envelope conformation [maximum ring torsion angle 18 (1)°].

Thus the photochemical transformation of the disubstituted cyclohexenone to the major photoproduct can be realized with a minimum of atomic

Table 2. *Selected interatomic distances (\AA) and angles (°)*

For the cyclohexenone, only dimensions of the 75% occupancy site are given here (values for the other site are similar but less accurate); full listing in the supplementary material.

	Cyclohexenone	Photoproduct
Br—C	1.899 (4)	1.900 (4)
C=O	1.23 (1)	1.207 (5)
C1—C2	1.52 (1)	1.484 (6)
C2—C3	1.36 (1)	1.527 (6)
C2—C4	[2.49 (1)]	1.533 (6)
C3—C4	1.53 (1)	1.495 (6)
C4—C5	1.54 (1)	1.524 (6)
C5—C6	1.49 (1)	1.522 (6)
C6—C1	1.42 (1)	1.499 (7)
C3—C7	[2.51 (1)]	1.491 (6)
C4—C7	1.53 (1)	[2.63 (1)]
Mean C—C(ar)	1.384	1.380
C1—C2—C3	124 (1)	118.4 (4)
C1—C2—C4	—	107.4 (4)
C3—C2—C4	—	58.5 (3)
C2—C3—C4	120 (1)	61.0 (3)
C2—C4—C3	—	60.6 (3)
C2—C4—C5	—	106.6 (3)
C3—C4—C5	106.8 (4)	116.4 (4)
Mean C—C—C(ar)	120	120
	($\sigma \sim 1^\circ$)	($\sigma \sim 0.5^\circ$)
C6—C1—C2—C3	-3	-50
C1—C2—C3—C4	-2	+94
C2—C3—C4—C5	+28	-95
C3—C4—C5—C6	-53	+56
C4—C5—C6—C1	+51	+16
C5—C6—C1—C2	-21	-18
C6—C1—C2—C4	—	+12
C1—C2—C4—C5	—	-2
C2—C4—C5—C6	—	-9
C6—C5—C4—C13	-170	-151
C5—C4—C13—C18	+60	+70
C5—C4—C13—C14	-121	-106

motion. Formation of the minor photoproduct (Fig. 1) requires larger but still relatively small motions: inversion of the conformation of the cyclohexenone ring, which requires movement mainly of C5, brings the phenyl substituent into a pseudo-axial orientation, which is suitable for phenyl group migration to produce the minor photoproduct.

Other features of the molecular structures, bond lengths and angles are normal (Table 2); the measured dimensions of the cyclohexenone are somewhat unreliable in the disordered region. Intermolecular distances correspond to normal van der Waals interactions.

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