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Crystal Structure of a Cyclization Photoproduct* of 1-(4-Chlorophenyl)-2-cyclooctylethanone, and Reaction Pathway in Norrish Type II Cyclizations

By Sara Ariel, Miguel Garcia-Garibay, John R. Scheffer and James Trotter

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Y6

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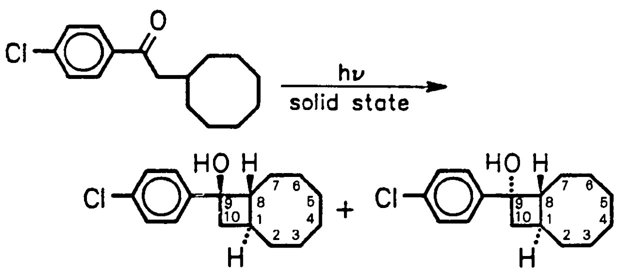
Abstract

The title compound is a minor solid-state photoproduct in the Norrish type II reaction of 1-(4-chlorophenyl)-2-cyclooctylethanone. $C_{16}H_{21}ClO$, $M_r = 264{\cdot}79$, triclinic, $P\bar{1}$, $a = 14{\cdot}335$ (3), $b = 15{\cdot}122$ (3), $c = 15{\cdot}611$ (2) Å, $\alpha = 76{\cdot}90$ (2), $\beta = 72{\cdot}27$ (1), $\gamma = 68{\cdot}00$ (1)°, $V = 2964$ (1) Å^3, $Z = 8$ (four molecules per asymmetric unit), $D_x = 1{\cdot}187$ g cm^{-3}, λ(Cu $K\alpha_1$) = 1·54053 Å, $\mu = 22{\cdot}1$ cm^{-1}, $F(000) = 1136$, $T = 295$ K, $R = 0{\cdot}069$ for 2958 observed reflections. The four crystallographically independent molecules form a tetrameric hydrogen-bonding pattern. In each of the four molecules the cyclobutanol ring is *trans*-fused to the cyclooctane ring, and the hydroxyl group is *cis* to the nearest bridgehead H atom. All four cyclooctane rings exhibit disorder of the outer atoms. On the basis of the above structure, the major photoproduct has been established as the *trans*-fused-*trans*-OH isomer. Furthermore, from the known conformation of the reactant, the detailed reaction pathway of the cyclization reaction has been constructed. The pathway involves γ-H abstraction by oxygen, followed by rotations about single bonds and angle bending, to allow overlap of radical p-orbitals and formation of a C—C bond. The motions required are minimum for the observed major *trans*-fused-*trans*-OH photoproduct, which can be formed in a topochemically controlled reaction.

Introduction

The present crystallographic work is part of a study (Ariel, Ramamurthy, Scheffer & Trotter, 1983) of the Norrish type II reaction, the light-induced cleavage and/or cyclization of organic carbonyl compounds possessing favourably oriented γ-H atoms. The geometric requirements for the Norrish type II reaction in the α-cycloalkylacetophenone system have been determined *via* a series of crystal structure determinations of appropriate model compounds (Ariel & Trotter, 1985, 1986*a,b*; Evans & Trotter, 1988). One major unresolved question concerns the configuration of the ring junction in the cyclization products. For example, solid-state photolysis of 1-(4-chlorophenyl)-2-cyclooctylethanone gives mainly cyclization, with two products which have been characterized by spectroscopic techniques, since many efforts to grow single crystals for X-ray study were unsuccessful. NMR studies (Harkness, 1986) have shown that both photoproducts have similar junctions between the four-membered and the eight-membered rings, but cannot distinguish between *cis*- and *trans*-fused configurations. NMR data also suggest that the OH group is *cis* to the ring-junction H(8) atom in the minor and *trans* in the major photoproduct. Recently single crystals of the minor photoproduct (I) were obtained, and determination of the crystal structure establishes the *trans* configuration at the ring junction, and thus provides more understanding of the mechanism of the solid-state Norrish type II reaction. In addition, the structural information now available on the reactant and photoproduct allows construction of the detailed molecular pathway of the cyclization reaction.



(I) 12%† 65%†

trans-fused-*cis*-OH *trans*-fused-*trans*-OH

Experimental

Colourless crystal from pentane, 0·1 × 0·1 × 0·3 mm, m.p. 361–362 K, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Cu $K\alpha$ radiation, lattice parameters from setting of 25 reflections with $15 \le \theta \le 24°$, 8767 reflections measured with $\theta \le 60°$, $h = -16 \to 16$, $k = -17 \to 17$, $l = 0 \to 17$; ω–2θ scan, ω

* (1α,8β)-9α-(4-Chlorophenyl)bicyclo[6.2.0]decan-9β-ol.

† Plus 18% cleavage photoproducts, 5% not identified, assumed to be *cis*-fused-*trans*(and *cis*)-OH (Ariel, Evans, Garcia-Garibay, Harkness, Omkaram, Scheffer & Trotter, 1988).

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Table 1. *Atom coordinates* ($\times 10^4$) *and temperature factors* ($\text{Å}^2 \times 10^3$)

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}	x	y	z	U_{eq}
		Molecule *A*				Molecule *C*		
Cl(1)	−1703 (2)	12470 (2)	5529 (2)	129	6802 (2)	3138 (2)	8768 (2)	155
O(1)	1467 (5)	8318 (5)	6917 (5)	85	2994 (5)	6716 (4)	7401 (4)	82
C(1)	572 (7)	10088 (7)	6062 (8)	80	4640 (6)	5564 (6)	8112 (8)	71
C(2)	−60 (9)	10882 (9)	5620 (7)	86	5268 (9)	4859 (9)	8603 (7)	90
C(3)	−904 (8)	11519 (7)	6114 (11)	86	5962 (7)	4079 (8)	8192 (9)	87
C(4)	−1109 (7)	11383 (8)	7029 (9)	83	6035 (7)	3997 (7)	7323 (9)	96
C(5)	−485 (8)	10593 (8)	7498 (7)	73	5395 (7)	4727 (8)	6846 (6)	78
C(6)	363 (7)	9942 (6)	6999 (8)	61	4661 (6)	5534 (6)	7238 (7)	64
C(7)	1053 (6)	9064 (6)	7493 (7)	67	3961 (7)	6370 (5)	6757 (6)	63
C(8)	628 (7)	8801 (6)	8503 (6)	81	3921 (6)	6225 (6)	5823 (6)	83
C(9)	1254 (7)	9332 (7)	8710 (7)	83	4756 (7)	6714 (6)	5371 (6)	75
C(10)	1926 (6)	9261 (6)	7746 (6)	67	4431 (6)	7186 (6)	6255 (5)	64
C(11)	2288 (7)	10097 (6)	7213 (6)	82	5265 (7)	7311 (7)	6603 (6)	90
C(12)	2826 (13)	10453 (10)	7632 (12)	225	5828 (11)	7919 (12)	5965 (11)	327
C(13)	3244 (12)	10287 (11)	8276 (10)	178	6026 (9)	8400 (10)	5222 (9)	152
C(14)	3370 (9)	9349 (11)	8944 (11)	162	5286 (13)	8675 (8)	4621 (9)	152
C(15)	2416 (11)	9320 (10)	9695 (8)	134	5389 (9)	7902 (8)	4089 (6)	119
C(16)	1733 (10)	8852 (9)	9523 (7)	116	4619 (7)	7370 (7)	4475 (6)	94
		Molecule *B*				Molecule *D*		
Cl(1)	4501 (2)	2960 (2)	10772 (2)	126	−1970 (2)	4919 (2)	5601 (1)	127
O(1)	1606 (5)	5746 (5)	7969 (4)	84	262 (4)	7199 (3)	7084 (3)	78
C(1)	2466 (7)	4745 (6)	9383 (7)	72	−620 (6)	6534 (5)	6128 (7)	72
C(2)	3035 (8)	4326 (8)	10048 (7)	85	−870 (6)	5993 (6)	5681 (6)	81
C(3)	3802 (7)	3450 (9)	9940 (7)	82	−1632 (7)	5610 (6)	6129 (7)	78
C(4)	3988 (7)	2982 (7)	9239 (9)	87	−2130 (6)	5720 (5)	7019 (7)	68
C(5)	3421 (8)	3390 (8)	8587 (7)	90	−1865 (6)	6257 (5)	7460 (5)	64
C(6)	2638 (7)	4277 (7)	8659 (7)	63	−1116 (6)	6679 (5)	7025 (6)	57
C(7)	1972 (6)	4730 (7)	7984 (6)	73	−816 (6)	7302 (6)	7458 (6)	62
C(8)	2407 (7)	4344 (6)	7069 (6)	82	−1164 (6)	7211 (6)	8487 (6)	85
C(9)	1734 (6)	3695 (6)	7384 (6)	82	−2138 (7)	8086 (7)	8391 (6)	90
C(10)	1054 (6)	4328 (5)	8143 (6)	69	−1552 (6)	8363 (6)	7425 (6)	70
C(11)	644 (7)	3862 (7)	9102 (6)	87	−2099 (7)	8790 (6)	6657 (6)	90
C(12)	50 (14)	3248 (14)	9169 (11)	245	−2660 (11)	9853 (10)	6610 (10)	184
C(13)	−304 (14)	2908 (12)	8686 (11)	214	−3567 (22)	10188 (17)	7435 (17)	340
C(14)	−390 (10)	3331 (13)	7738 (11)	153	−3551 (24)	10251 (13)	8175 (19)	353
C(15)	516 (11)	3035 (9)	7004 (9)	143	−3612 (11)	9572 (11)	9016 (10)	177
C(16)	1238 (8)	3616 (8)	6685 (6)	104	−2587 (9)	8781 (9)	9087 (8)	136

scan width $(0{\cdot}70 + 0{\cdot}14\tan\theta)°$, extended 25% on each side for background measurement, horizontal aperture $(2{\cdot}0 + \tan\theta)$ mm, vertical aperture 4 mm, Lp and analytical absorption corrections (transmission factors from 0·628 to 0·726). Three standard reflections (440, 443, 204) were monitored every hour of exposure time for random intensity fluctuations (4% isotropic decay correction applied), and every 150 reflections for orientation control. The structure was solved by direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by block-diagonalized least squares, minimizing $\sum w(|F_o| - |F_c|)^2$ using *SHELX*76 (Sheldrick, 1976). Hydroxyl H atoms were located in a difference synthesis and were refined isotropically. All other H atoms were placed in calculated positions, and their temperature factors were refined isotropically. 745 parameters consisting of 228 positional parameters, 432 anisotropic temperature factors, 84 isotropic temperature factors, and a scale factor. Convergence at $R = 0{\cdot}069$, $wR = 0{\cdot}060$ for 2958 observed reflections for which $F \geq 3\sigma(F)$, where $\sigma^2(I) = S + 2B + [0{\cdot}04 \times (S{-}B)]^2$, S = scan count, B = time-averaged background count. $R = 0{\cdot}156$, $wR = 0{\cdot}080$ for all data, $w = 1/\sigma^2(F)$, $(\Delta/\sigma)_{max} = 1{\cdot}0$, highest $\Delta\rho$ peak in final difference synthesis $= 0{\cdot}23$ e Å^{-3}. Atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965).

Discussion

Final atomic coordinates are in Table 1, and bond distances, bond angles and selected torsion angles in Table 2.*

The four independent molecules have a similar configuration, with the four-membered and the eight-membered rings *trans*-fused (Fig. 1); the substituent H atoms of the C(9)—C(10) bond (crystallographic atom numbering, see Fig. 1) have torsion angle H(9)—C(9)—C(10)—H(10) = 124, −124, 126, 126°, for molecules *A*, *B*, *C* and *D*, respectively (molecule *B* has the opposite chirality to molecules *A*, *C* and *D*, but the material is racemic, so that both enantiomers of all four independent molecules are present in the crystal). The four-membered cyclobutanol rings have the usual

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51397 (22 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), *bond angles* (°), *selected torsion angles* (°) *and* H-*bonding geometry for molecules A, B, C and D*

	A	*B*	*C*	*D*
C(1)–C(2)	1·39 (1)	1·40 (2)	1·37 (1)	1·38 (2)
C(2)–C(3)	1·37 (1)	1·37 (1)	1·37 (2)	1·36 (1)
Cl(1)–C(3)	1·74 (1)	1·74 (1)	1·75 (1)	1·74 (1)
C(3)–C(4)	1·35 (2)	1·34 (2)	1·36 (2)	1·37 (1)
C(4)–C(5)	1·40 (1)	1·38 (2)	1·38 (1)	1·39 (2)
C(5)–C(6)	1·39 (1)	1·39 (1)	1·40 (1)	1·38 (1)
C(1)–C(6)	1·38 (2)	1·38 (2)	1·37 (2)	1·39 (1)
C(6)–C(7)	1·53 (1)	1·51 (1)	1·50 (1)	1·52 (2)
O(1)–C(7)	1·44 (1)	1·42 (1)	1·43 (1)	1·44 (1)
C(7)–C(8)	1·53 (1)	1·53 (1)	1·54 (2)	1·52 (1)
C(8)–C(9)	1·55 (2)	1·53 (2)	1·55 (1)	1·54 (1)
C(9)–C(10)	1·52 (1)	1·54 (1)	1·56 (1)	1·54 (1)
C(7)–C(10)	1·56 (2)	1·58 (2)	1·57 (1)	1·55 (1)
C(10)–C(11)	1·52 (1)	1·54 (1)	1·54 (2)	1·52 (1)
C(11)–C(12)	1·45 (3)	1·45 (3)	1·46 (2)	1·50 (2)
C(12)–C(13)	1·25 (3)	1·30 (3)	1·23 (2)	1·55 (3)
C(13)–C(14)	1·54 (2)	1·50 (2)	1·51 (2)	1·19 (4)
C(14)–C(15)	1·51 (2)	1·45 (2)	1·52 (2)	1·47 (3)
C(15)–C(16)	1·52 (3)	1·50 (2)	1·51 (2)	1·52 (2)
C(9)–C(16)	1·53 (2)	1·52 (2)	1·54 (1)	1·51 (2)
C(6)–C(1)–C(2)	120 (1)	121 (1)	124 (1)	122 (1)
C(3)–C(2)–C(1)	120 (1)	118 (1)	118 (1)	119 (1)
C(2)–C(3)–Cl(1)	118 (1)	117 (1)	121 (1)	121 (1)
C(4)–C(3)–Cl(1)	122 (1)	121 (1)	117 (1)	118 (1)
C(4)–C(3)–C(2)	120 (1)	122 (1)	122 (1)	122 (1)
C(5)–C(4)–C(3)	122 (1)	120 (1)	119 (1)	119 (1)
C(6)–C(5)–C(4)	118 (1)	121 (1)	122 (1)	122 (1)
C(5)–C(6)–C(1)	120 (1)	118 (1)	116 (1)	117 (1)
C(7)–C(6)–C(1)	121 (1)	120 (1)	119 (1)	118 (1)
C(7)–C(6)–C(5)	120 (1)	123 (1)	125 (1)	124 (1)
C(6)–C(7)–O(1)	106 (1)	109 (1)	108 (1)	110 (1)
C(8)–C(7)–O(1)	118 (1)	117 (1)	118 (1)	115 (1)
C(10)–C(7)–O(1)	112 (1)	112 (1)	113 (1)	114 (1)
C(8)–C(7)–C(6)	118 (1)	116 (1)	116 (1)	115 (1)
C(10)–C(7)–C(6)	114 (1)	115 (1)	115 (1)	113 (1)
C(10)–C(7)–C(8)	88 (1)	87 (1)	88 (1)	89 (1)
C(9)–C(8)–C(7)	89 (1)	90 (1)	89 (1)	88 (1)
C(10)–C(9)–C(8)	89 (1)	89 (1)	88 (1)	89 (1)
C(16)–C(9)–C(8)	115 (1)	116 (1)	115 (1)	119 (1)
C(16)–C(9)–C(10)	121 (1)	119 (1)	119 (1)	121 (1)
C(9)–C(10)–C(7)	88 (1)	88 (1)	88 (1)	87 (1)
C(11)–C(10)–C(7)	119 (1)	119 (1)	119 (1)	119 (1)
C(11)–C(10)–C(9)	120 (1)	120 (1)	120 (1)	121 (1)
C(12)–C(11)–C(10)	117 (1)	117 (1)	114 (1)	115 (1)
C(13)–C(12)–C(11)	144 (2)	143 (2)	152 (2)	116 (1)
C(14)–C(13)–C(12)	122 (2)	123 (2)	118 (1)	130 (3)
C(15)–C(14)–C(13)	115 (1)	118 (2)	116 (1)	131 (2)
C(16)–C(15)–C(14)	116 (1)	119 (1)	116 (1)	114 (1)
C(15)–C(16)–C(9)	116 (1)	117 (1)	114 (1)	116 (1)

	A	*B′**	*C*	*D*
C(2)–C(1)–C(6)–C(7)	180 (1)	−177 (1)	−178 (1)	−178 (1)
C(1)–C(2)–C(3)–Cl(1)	−177 (1)	−179 (1)	180 (1)	−180 (1)
Cl(1)–C(3)–C(4)–C(5)	177 (1)	180 (1)	−179 (1)	179 (1)
C(4)–C(5)–C(6)–C(7)	−179 (1)	177 (1)	178 (1)	178 (1)
C(1)–C(6)–C(7)–O(1)	−29 (1)	−27 (1)	−38 (1)	−32 (1)
C(1)–C(6)–C(7)–C(8)	−164 (1)	−162 (1)	−172 (1)	−164 (1)
C(1)–C(6)–C(7)–C(10)	95 (1)	99 (1)	88 (1)	96 (1)
C(5)–C(6)–C(7)–O(1)	150 (1)	154 (1)	146 (1)	149 (1)
C(5)–C(6)–C(7)–C(8)	16 (1)	19 (1)	12 (1)	17 (1)
C(5)–C(6)–C(7)–C(10)	−85 (1)	−81 (1)	−88 (1)	−83 (1)
O(1)–C(7)–C(8)–C(9)	132 (1)	131 (1)	136 (1)	136 (1)
C(6)–C(7)–C(8)–C(9)	−98 (1)	−99 (1)	−95 (1)	−94 (1)
C(10)–C(7)–C(8)–C(9)	18 (1)	18 (1)	21 (1)	20 (1)
O(1)–C(7)–C(10)–C(9)	−138 (1)	−136 (1)	−140 (1)	−138 (1)
O(1)–C(7)–C(10)–C(11)	98 (1)	101 (1)	97 (1)	98 (1)
C(6)–C(7)–C(10)–C(9)	101 (1)	100 (1)	96 (1)	96 (1)
C(6)–C(7)–C(10)–C(11)	−23 (1)	−24 (1)	−26 (1)	−29 (1)
C(8)–C(7)–C(10)–C(9)	−19 (1)	−18 (1)	−21 (1)	−21 (1)
C(8)–C(7)–C(10)–C(11)	−142 (1)	−141 (1)	−144 (1)	−145 (1)
C(7)–C(8)–C(9)–C(10)	−19 (1)	−18 (1)	−21 (1)	−21 (1)
C(7)–C(8)–C(9)–C(16)	−142 (1)	−140 (1)	−142 (1)	−146 (1)
C(8)–C(9)–C(10)–C(7)	18 (1)	18 (1)	21 (1)	20 (1)
C(8)–C(9)–C(10)–C(11)	141 (1)	140 (1)	143 (1)	143 (1)
C(16)–C(9) C(10) C(7)	137 (1)	137 (1)	139 (1)	143 (1)
C(16)–C(9)–C(10)–C(11)	−100 (1)	−101 (1)	−99 (1)	−94 (1)
C(8)–C(9)–C(16)–C(15)	176 (1)	176 (1)	175 (1)	−174 (1)
C(10)–C(9)–C(16)–C(15)	71 (1)	72 (1)	73 (1)	79 (1)
C(7)–C(10)–C(11)–C(12)	160 (1)	161 (1)	166 (1)	−171 (1)
C(9)–C(10)–C(11)–C(12)	54 (1)	56 (1)	61 (1)	83 (1)
C(10)–C(11)–C(12)–C(13)	11 (3)	0 (3)	−4 (4)	−63 (2)

Table 2 (*cont.*)

	A	*B′**	*C*	*D*
C(11)–C(12)–C(13)–C(14)	5 (4)	17 (4)	15 (4)	75 (4)
C(12)–C(13)–C(14)–C(15)	−81 (2)	−85 (2)	−79 (2)	−95 (4)
C(13)–C(14)–C(15)–C(16)	95 (2)	92 (2)	100 (1)	81 (4)
C(14)–C(15)–C(16)–C(9)	−61 (2)	−60 (2)	−68 (1)	−64 (2)

	O···O (Å)	O···H (Å)	H–O (Å)	O···H–O (°)
O(1)*A*···H–O(1)*C*	2·73 (1)	1·9 (1)	0·9 (1)	145 (9)
O(1)*C*···H–O(1)*B*	2·72 (1)	1·9 (1)	0·8 (1)	163 (10)
O(1)*B*···H–O(1)*D*	2·74 (1)	1·5 (1)	1·4 (1)	151 (6)
O(1)*D*···H–O(1)*A*	2·76 (1)	2·1 (1)	0·8 (1)	149 (10)

* Molecule *B′* is the (symmetry-related) enantiomorph of *B*, for direct comparison with the torsion angles of *A*, *C* and *D*. Molecules *A*, *B*, *C* and *D* form an H-bonded tetramer.

folded conformations, with bond torsion angles of about 20°, normal sp^3–sp^3 bonds ranging from 1·52 (1) to 1·58 (2) Å, mean 1·54 Å, close to the value expected for *n*-alkanes of 1·533 Å (Bartell & Kohl, 1963), and intraannular bond angles of 87 (1)–90 (1)°, mean 88°. The hydroxyl group is *cis* to the nearest bridgehead H atom, H(10). The torsion angle H(10)–C(10)–C(7)–O(1) is −13, 10, −14, −12° for molecules *A*, *B*, *C* and *D*, respectively.

The individual values of some of the bond lengths and bond angles in each of the cyclooctyl rings are uncertain due to disorder of the outer atoms C(12)–C(15), indicated by the large apparent temperature factors (Table 1), and by the apparent short C–C distances and large C–C–C angles (Table 2). No attempt was made to resolve this disorder, since the lack of high-order data and the correlation between parameters would probably preclude accurate determination of atomic positions. The disorder did not obscure structural details in other regions of the four independent molecules, but prevented detailed conformational analysis of the cyclooctyl rings.

The four independent molecules of compound (I) are hydrogen bonded to form a tetramer, O(1)*A*···H–O(1)*C*···H–O(1)*B*···H–O(1)*D*···H–O(1)*A*··· (Fig. 2). This presence of a 3:1 ratio of enantiomers in the tetramer is probably the reason for the (rare) occurrence of four independent molecules in the asymmetric unit; other ratios (*e.g.* 2:2 or 4:0) could presumably

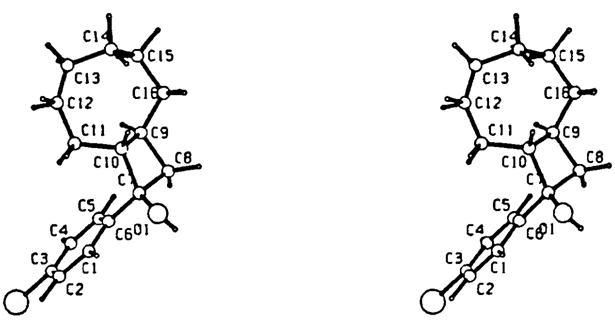

Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) stereoview of molecule *B* of compound (I) with crystallographic atom numbering.

have been accommodated in other space groups with fewer than four crystallographically independent molecules.

1-(4-Chlorophenyl)-2-cyclooctylethanone undergoes Norrish type II reaction upon irradiation in solution and in the solid state (Harkness, 1986; Ariel, Evans, Garcia-Garibay, Harkness, Omkaram, Scheffer & Trotter, 1988). The molecule has an equatorial H atom on C(10) which is suitably oriented for abstraction by the carbonyl O atom (Evans & Trotter, 1988). The photoreaction results mainly in cyclization products (about 75% in solution, and 82% in the solid state). The main solid-state product is the *trans*-ring junction, *trans*-OH cyclobutanol (65%); the minor *trans*-ring junction, *cis*-OH product (12%) is the material for which crystals were obtained for the present crystal analysis. Rationalization of these photochemical results can be obtained from a study of the orientations of the radical *p*-orbitals in the postulated biradical intermediate (Fig. 3 and Table 3). Bond formation *via* overlap of lobe *a* with lobe *b* (and *b'*) would result in *cis*-ring junction, *cis*- (and *trans*-) OH products; overlap of *a'* with *b* (and *b'*) would result in *trans*-ring junction, *trans*- (and *cis*-) OH products.* Qualitative examination (Fig. 3) indicates that lobes *a'* and *b* are in closest proximity, and hence bonding *via a'/b* overlap

* There is a minor error in Evans & Trotter (1988), which states that *a'/b'* overlap produces the *trans*-OH isomer.

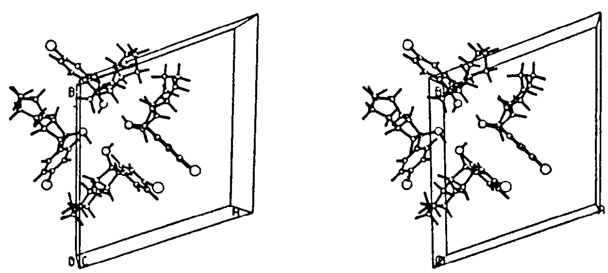

Fig. 2. *PLUTO* stereoview of the packing arrangement of compound (I).

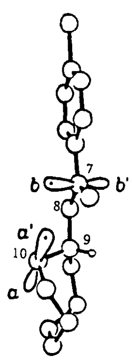

Fig. 3. The orientations of the radical *p*-orbitals in the postulated biradical intermediate (Evans & Trotter, 1988).

Table 3. *Biradical geometry for* 1-(4-*chlorophenyl*)-2-*cyclooctylethanone* (*see Fig.* 3) (*Evans & Trotter,* 1988)

Starting material				Photoproduct		
p-Orbital lobes		φ_1*	φ_2†	Ring junction	OH‡	ratio (%)
a	*b*	+135	−83	*cis*	*cis*	5
a	*b'*	+135	+97	*cis*	*trans*	
a'	*b*	−45	−83	*trans*	*trans*	65
a'	*b'*	−45	+97	*trans*	*cis*	12

* φ_1 = C(8)—C(9)—C(10)—p_ν.
† φ_2 = C(9)—C(8)—C(7)—p_{CO}.
‡ With respect to adjacent C(10) H atom.

should occur with least atomic motion in a topochemically controlled reaction in the solid state, giving the *trans*-ring junction, *trans*-OH material, which is the major (65%) photoproduct. A more quantitative understanding follows from an examination of the torsion angles between the central C(8)—C(9) bond and the *p*-orbital lobes on C(10) [C(8)—C(9)—C(10)—p_ν] and C(7) [C(9)—C(8)—C(7)—p_{CO}] (Table 3). Both these angles have to change to C(8)—C(9)—C(10)—C(7) and C(9)—C(8)—C(7)—C(10) torsion angles of about −20° (for molecule *B*, Table 2), and these movements are most easily achieved from the −45° (8—9—10—p_ν) and −83° (9—8—7—p_{CO}) angles of the *a'/b* lobes (Table 3).

Reaction pathway

These ideas can be further developed to trace the whole reaction pathway in the solid-state photochemical transformation of 1-(4-chlorophenyl)-2-cyclooctylethanone to the major *trans*-OH photoproduct. The detailed crystal and molecular structure of the reactant is available (Evans & Trotter, 1988), and the molecular structure of the *trans*-OH photoproduct can be derived from the structure of the *cis*-OH compound (I) by interchanging the OH and aryl substituents (except for the exact orientation of the aryl ring). The proposed reaction mechanism involves abstraction of a C(10) H atom by the carbonyl O atom, with the resulting biradical giving the cyclization product by formation of a C(7)···C(10) bond; this requires a reduction of the C(7)···C(10) non-bonded distance of 3·14 (3) Å to a bonded C(7)—C(10) length of 1·57 (1) Å (Table 2), which can be achieved with minimum atomic movement of about 1·6 Å.

The proposed detailed pathway can be analysed (Ariel, Askari, Scheffer, Trotter & Wireko, 1987) in terms of the following motions:

(i) Transfer of H(10) to O(1) [with increase in the C—O bond length* and change of hybridization at C(10) from sp^3 to sp^2†].

* The increase in C—O bond length is allowed for when minimizing the molecular energy of the photoproduct [step (iii)].

† Initial sp^3 hybridization at C(10) probably changes to sp^2 in the biradical, but in the photoproduct C(10) again becomes four-coordinate.

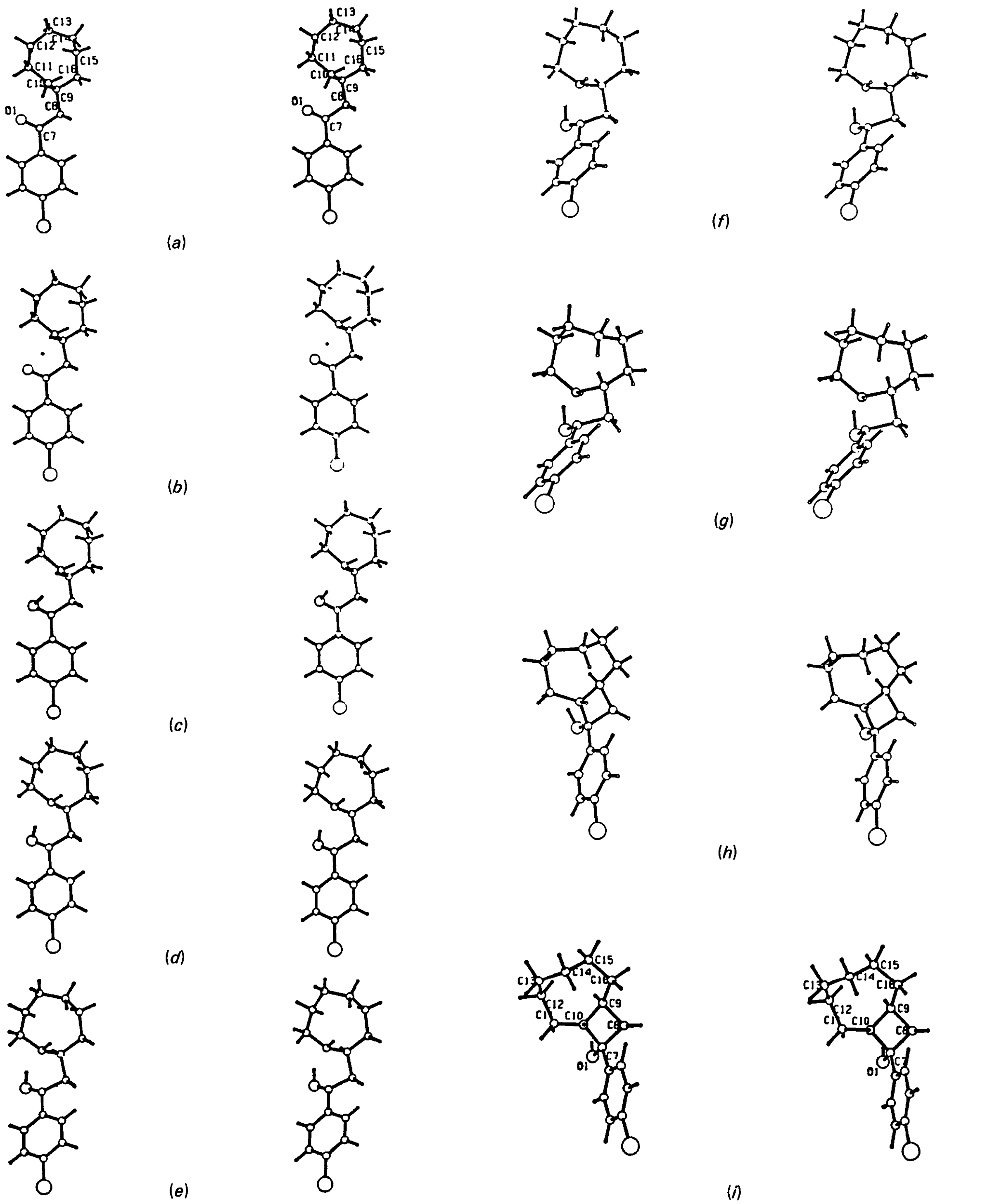

Fig. 4. Reaction pathway. Step (i), transfer of H(10*B*) (Evans & Trotter, 1988) to O(1) to form a biradical: (*a*) starting material, (*b*) half-way through H transfer, (*c*) biradical [change of hybridization at C(10), from sp^3 to sp^2, is ignored – see text]. Step (ii), stepwise reduction of the C(7)···C(10) distance of 3·14 (3) Å (Evans & Trotter, 1988) to a final bonded distance of 1·57 (1) Å (Fig. 1) *via* rotation about C(8)—C(9) of 50°, rotation about C(8)—C(7) of 80°, reduction of C(7)—C(8)—C(9) and C(8)—C(9)—C(10) valency angles to 90°, and pyramidalization at C(7): (*d*) 20% of motions applied [C(7)···C(10) = 2·87 Å], (*e*) 40% (2·57 Å), (*f*) 60% (2·26 Å), (*g*) 80% (1·95 Å), (*h*) 100% (1·64 Å). Step (iii): (*i*) *MMP*2 minimization of the energy of the simulated photoproduct [(*h*), 100%] results in minor adjustments of the conformation. During energy minimization the Cl atom is replaced with an H atom, because of insufficient energy parameters; that H atom, of the minimized conformation, is replaced with a Cl atom to represent the minimized simulated photoproduct in (*i*).

(ii) Reduction of C(7)···C(10) from 3·14 (3) Å to a final bonded distance of 1·57 (1) Å; the motion can be analysed as:

(*a*) rotation of 50° about C(8)—C(9) (change of torsion angle from +70° to +20°),

(*b*) rotation of 80° about C(8)—C(7),

(*c*) reduction of the C(7)—C(8)—C(9) and C(8)—C(9)—C(10) valency angles to 90°.

(*d*) pyramidalization at C(7) and C(10).*

(iii) Minor adjustments of the resulting photoproduct conformation and dimensions to minimize the molecular energy.

The reaction pathway was constructed (Fig. 4) by transferring the H atom [step (i) above, Figs. 4(*a*), (*b*), (*c*)], followed by C(7)···C(10) distance reduction [step (ii), with all the motions applied concurrently; intermediate steps at 20, 40, 60, 80, 100% of the motions are shown in Figs. 4(*d*), (*e*), (*f*), (*g*), (*h*)]. A local computer program was designed to perform the various motions. Final *MMP*2 adjustment of the energy of the photoproduct molecule (Allinger & Flanagan, 1983) resulted in minor changes of molecular dimensions [C(7)—C(10) changed from 1·64 to 1·55 Å; C(7)—O(1) changed from 1·21 to 1·41 Å] (Fig. 4*i*).

The topochemical implications of the reaction were determined by examining intermolecular interactions developed between the reacting molecule and the surrounding unreacting molecules in the lattice of the reactant (Fig. 5). Movement of C(10) towards C(7) produces unfavourable C···H intermolecular contacts, which, in the absence of any overall movement of the reacting molecule, become as short as 0·970 Å (Fig. 5*b*). These short contacts can probably be relieved by a movement of the whole reacting molecule, or by changes in the conformations of the ring system or aryl substituent. The possible movements are too complex to allow a definitive description of this process. The reaction does appear to be a topochemically favourable one, since *trans*-fused-*trans*-OH photoproduct is produced with a remarkable excess.

* See footnote † on page 15.

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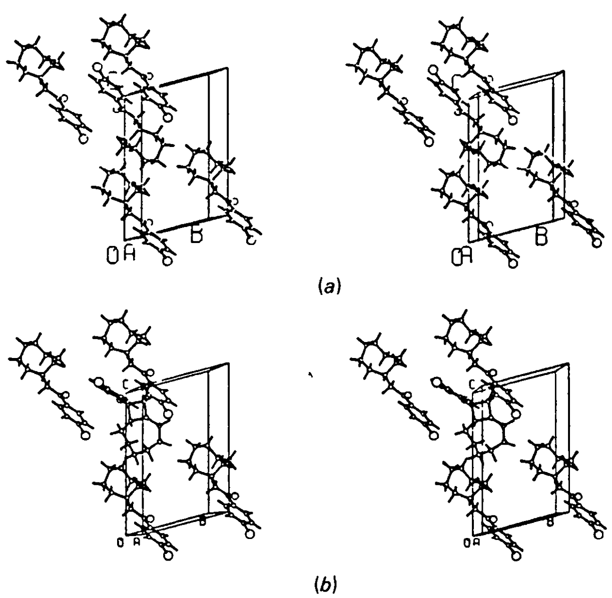

Fig. 5. Stereoview of the lattice of the reactant before (*a*) (Evans & Trotter, 1988) and after (*b*) the reaction. (*b*) Centre – minimized simulated photoproduct (Fig. 4*i*) occupying a lattice position of the reactant. Shortest intermolecular C···H contact = 0·970 Å [C(1)reactant(*x*, *y*, 1+*z*)···H(8a)100%(1−*x*, −*y*, 1−*z*)]. There are ten other intermolecular contacts < 2 Å (two C···H and eight H···H).

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