décomposé en une translation t: distance t de son barycentre (ω) par rapport au plan BCD, et d'une rotation d'angle θ autour d'un axe passant par ω et parallèle à la trace de l'intersection des deux plans A et BCD. D'après ces paramètres, la molécule de BF1 est la plus plane. Les déformations enregistrées pour BF2 et BF3 se limitent à un déplacement du cycle A : $t = 0,225$ et $0,356$ Å respectivement, les valeurs de θ restent faibles : 3,32 et 4,41°. La distorsion s'accentue avec la molécule de BF4: $\theta = 9,3°$ et $t = 0,133$ Å.

Il semblerait toutefois que la présence d'une liaison hydrogène entre O(4) et O(17) (BF4) ou d'un proche contact de van der Waals entre O(4) et HC(17) occasionne sinon une bonne planéité, du moins une faible distorsion moléculaire. En effet, la molécule de BF5 où n'existe pas une telle interaction s'éloigne très sensiblement de la planéité: $\theta = 24,5°$ et $t = 0,241$ Å.

Plus la liaison C(2)—C(11) est courte, c'est à dire plus le caractère de double liaison est renforcé, plus réduit est θ (BF1, BF2 et BF3). Un allongement de C(2)—C(11) correspond à une valeur plus élevée de θ (BF4 et BF5: 1,480 Å). Ces remarques confirment l'effet sur la planéité de la conjugaison entre les deux parties de la molécule.

L'influence de la proximité de H(3) et H(12) sur la planéité (Rossi et al., 1980) n'est pas évidente, puisque les distances correspondantes ne sont pas corrélées aux valeurs de θ et de t.

Nota

Cette étude sur les dérivés des flavones a été initiée à la demande de P. Queval qui en a effectué les synthèses et testé les propriétés biologiques. Malheureusement, la maladie dont il cherchait à démontrer les mécanismes, l'a emporté. Ce travail est donc publié en sa mémoire, sans qu'il ait pu lui-même profiter de ces résultats.

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Structure of a Cyclization Photoproduct* of 1-(4-Chlorophenyl)-2-cyclohexylethanone

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Abstract. The material studied is a solid-state photoproduct (23%) in the Norrish type II reaction of 1-(4-chlorophenyl)-2-cyclohexylethanone. $C_{14}H_{17}ClO$, $M_r = 236.74$, monoclinic, $C2/c$, $a = 19.611$ (9), $b = 17.485$ (4), $c = 16.996$ (7) Å, $\beta = 119.59$ (3)°, $V = 5068$ (4) Å^3, $Z = 16$ (two molecules per asymmetric unit), $D_x = 1.241$ g cm^{-3}, λ(Mo $K\alpha_1$) = 0.70930 Å, $\mu = 2.76$ cm^{-1}, $F(000) = 2016$, $T = 295$ K, $R = 0.063$ for 1744 observed reflections. In each of the two molecules the cyclobutanol ring is *trans*-fused to the cyclohexane ring, and the hydroxyl group is *cis* to the nearest bridgehead H atom. On the basis of the above structure, the other cyclization photoproducts have been established as the *trans*-fused-*trans*-OH isomer (30%), and *cis*-fused-*trans*/*cis*-OH isomers (3%/4%). Furthermore, from the known conformation of the reactant, the photochemical results are explained.

Introduction. The present cyrstallographic investigation has been undertaken as part of a study on the Norrish type II reaction (Ariel, Ramamurthy,

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* (1α,6β)-7α-(4-Chlorophenyl)bicyclo[4.2.0]octan-7β-ol.

Table 1. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^3$)
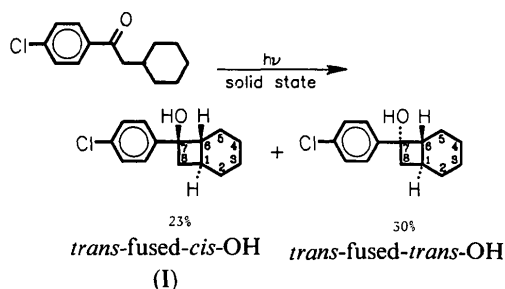
	Molecule A				Molecule B			
	x	y	z	U_{eq}*	x	y	z	U_{eq}*
Cl(1)	8819 (1)	1720 (1)	2379 (1)	80	8839 (1)	3752 (1)	2447 (1)	100
O(1)	9722 (3)	1087 (3)	6568 (3)	55	9989 (3)	7338 (3)	3295 (3)	68
C(1)	8743 (3)	1698 (3)	4665 (4)	45	9765 (4)	5769 (4)	3484 (4)	62
C(2)	8692 (3)	1934 (3)	3860 (4)	49	9676 (4)	4997 (4)	3300 (4)	69
C(3)	8838 (3)	1409 (4)	3361 (4)	51	8950 (5)	4731 (4)	2676 (5)	61
C(4)	9028 (3)	661 (4)	3642 (4)	57	8326 (4)	5212 (4)	2253 (4)	68
C(5)	9070 (3)	432 (3)	4444 (4)	48	8427 (4)	5987 (4)	2449 (4)	57
C(6)	8932 (3)	950 (3)	4968 (4)	41	9153 (4)	6278 (3)	3068 (4)	44
C(7)	9027 (4)	741 (3)	5892 (4)	43	9297 (4)	7116 (3)	3331 (4)	46
C(8)	8933 (4)	− 122 (3)	6049 (4)	53	8579 (4)	7662 (3)	2896 (4)	70
C(9)	8051 (4)	30 (3)	5644 (4)	49	8469 (4)	7490 (4)	3714 (4)	60
C(10)	8273 (3)	846 (3)	5964 (4)	44	9328 (3)	7320 (3)	4229 (4)	47
C(11)	7568 (4)	1386 (3)	5477 (4)	54	9541 (4)	6830 (4)	5065 (4)	57
C(12)	6935 (4)	1078 (4)	5687 (5)	66	9306 (4)	7321 (5)	5644 (5)	82
C(13)	6752 (4)	219 (4)	5472 (5)	73	8475 (4)	7615 (5)	5141 (5)	88
C(14)	7479 (4)	− 301 (4)	5925 (5)	62	8232 (4)	8032 (4)	4246 (5)	80

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

Scheffer & Trotter, 1983), the light-induced cleavage and/or cyclization of organic carbonyl compounds possessing favorably oriented γ-H atoms.

A series of crystal structure determinations of α-cycloalkylacetophenones (Ariel & Trotter, 1985, 1986a, 1986b; Evans & Trotter, 1988) has established the geometric requirements for the Norrish type II reaction. Recently, the crystal structure of the minor cyclization photoproduct of 1-(4-chlorophenyl)-2-cyclooctylethanone has been determined (Ariel, Garcia-Garibay, Scheffer & Trotter, 1989), to establish the configuration of the ring junction in the cyclization products, and to provide more understanding of the mechanism of the solid-state Norrish type II reaction. The structural information available for the reactant and the photoproduct allowed construction of the detailed molecular pathway in the cyclization reaction. 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 major trans-fused-trans-OH photoproduct, which was formed in a marginal excess (65%).

1-(4-Chlorophenyl)-2-cyclohexylethanone undergoes Norrish type II reaction upon irradiation in solution and in the solid state (Omkaram, 1986; Ariel, Evans, Garcia-Garibay, Harkness, Omkaram, Scheffer & Trotter, 1988).

trans-fused-cis-OH   trans-fused-trans-OH
(I)

The solution and solid-state photoreaction results are similar: 60% cyclization products and 40% cleavage products. There is 30% of the trans-ring junction, trans-OH, and 23% of the trans-ring junction, cis-OH cyclization products, the latter (I) being the material of which crystals were obtained for the present crystal analysis. The cis-ring junction, trans/cis-OH materials are the minor cyclization products, only 7% in the solid state (6% in solution).*

We report here the crystal structure of compound (I), and utilize the structural data to rationalize the photochemical results.

Experimental. Colorless crystal from acetonitrile, 0·2 × 0·2 × 0·4 mm, m.p. 385–387 K, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, lattice parameters from setting of 25 reflections with $8 < \theta < 14°$; 3067 reflections measured with $I > 0$, $\theta \le 25°$, $h = -23 \rightarrow 23$, $k = 0 \rightarrow 20$, $l = 0 \rightarrow 20$; $\omega - 2\theta$ scan, ω scan width (0·80 + 0·35tanθ)°, extended 25% on each side for background measurement, horizontal aperture (2·0 + tanθ) mm, vertical aperture 4 mm, Lp correction. Three standard reflections (208, 115, 402) were monitored every hour of exposure time for random intensity fluctuations (2% isotropic decay correction applied), and every 150 reflections for orientation control. Structure was solved by direct methods with MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by block-diagonalized least squares, minimizing $\Sigma w(|F_o| - |F_c|)^2$ using SHELX76 (Sheldrick, 1976). Efforts to locate the hydroxyl H atoms were not successful. O atoms in four neighboring molecules are at distances suitable for hydrogen bonding, but two of the possible hydrogen bonds are across a C_2 axis, and hence probably involve disordered H sites

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* In earlier work (Ariel et al., 1983) it had been assumed that the cyclization products had cis-ring junctions.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°)

	A	B
C(1)—C(2)	1·38 (1)	1·38 (1)
C(2)—C(3)	1·37 (1)	1·37 (1)
C(3)—Cl(1)	1·74 (1)	1·75 (1)
C(3)—C(4)	1·38 (1)	1·36 (1)
C(4)—C(5)	1·38 (1)	1·39 (1)
C(5)—C(6)	1·39 (1)	1·38 (1)
C(1)—C(6)	1·39 (1)	1·38 (1)
C(6)—C(7)	1·53 (1)	1·52 (1)
C(7)—O(1)	1·41 (1)	1·44 (1)
C(7)—C(8)	1·56 (1)	1·55 (1)
C(8)—C(9)	1·54 (1)	1·54 (1)
C(9)—C(10)	1·51 (1)	1·50 (1)
C(10)—C(7)	1·55 (1)	1·54 (1)
C(10)—C(11)	1·53 (1)	1·53 (1)
C(11)—C(12)	1·55 (1)	1·54 (1)
C(12)—C(13)	1·55 (1)	1·51 (1)
C(13)—C(14)	1·54 (1)	1·54 (1)
C(14)—C(9)	1·53 (1)	1·53 (1)
C(2)—C(1)—C(6)	121·6 (5)	122·5 (7)
C(1)—C(2)—C(3)	118·4 (6)	118·3 (7)
C(2)—C(3)—Cl(1)	118·2 (5)	118·2 (6)
C(4)—C(3)—Cl(1)	120·2 (5)	120·5 (6)
C(2)—C(3)—C(4)	121·6 (6)	121·3 (6)
C(3)—C(4)—C(5)	119·3 (6)	119·5 (7)
C(4)—C(5)—C(6)	120·5 (6)	121·0 (7)
C(1)—C(6)—C(5)	118·6 (5)	117·5 (6)
C(1)—C(6)—C(7)	118·8 (5)	119·0 (6)
C(5)—C(6)—C(7)	122·6 (5)	123·5 (6)
C(6)—C(7)—O(1)	108·2 (6)	106·9 (6)
C(8)—C(7)—O(1)	115·1 (5)	117·7 (5)
C(10)—C(7)—O(1)	117·3 (5)	113·6 (5)
C(6)—C(7)—C(8)	116·3 (5)	117·4 (5)
C(6)—C(7)—C(10)	114·4 (5)	115·3 (5)
C(8)—C(7)—C(10)	84·5 (5)	85·0 (5)
C(7)—C(8)—C(9)	87·6 (5)	87·1 (5)
C(8)—C(9)—C(10)	86·6 (5)	86·9 (6)
C(8)—C(9)—C(14)	129·1 (5)	129·2 (6)
C(10)—C(9)—C(14)	111·7 (6)	111·1 (5)
C(7)—C(10)—C(9)	88·7 (5)	89·1 (5)
C(7)—C(10)—C(11)	132·0 (5)	130·6 (5)
C(9)—C(10)—C(11)	111·3 (5)	111·4 (6)
C(10)—C(11)—C(12)	105·9 (5)	104·6 (5)
C(11)—C(12)—C(13)	113·7 (6)	114·1 (6)
C(12)—C(13)—C(14)	114·0 (6)	116·4 (8)
C(9)—C(14)—C(13)	105·1 (5)	104·7 (6)
C(4)—C(5)—C(6)—C(7)	-175·6 (6)	-178·2 (7)
C(1)—C(6)—C(7)—O(1)	-70·4 (7)	49·4 (8)
C(1)—C(6)—C(7)—C(10)	62·3 (8)	-78·0 (8)
C(1)—C(6)—C(7)—C(8)	158·3 (6)	-175·8 (6)
C(5)—C(6)—C(7)—O(1)	105·8 (7)	-133·0 (7)
C(5)—C(6)—C(7)—C(10)	-121·4 (6)	99·7 (7)
C(5)—C(6)—C(7)—C(8)	-25·4 (9)	1·9 (9)
O(1)—C(7)—C(8)—C(9)	143·5 (6)	-139·2 (6)
C(6)—C(7)—C(8)—C(9)	-88·6 (6)	90·9 (6)
C(10)—C(7)—C(8)—C(9)	25·9 (4)	-25·1 (5)
C(7)—C(8)—C(9)—C(10)	-26·6 (5)	25·8 (5)
C(7)—C(8)—C(9)—C(14)	-142·1 (7)	140·8 (7)
C(8)—C(9)—C(10)—C(7)	26·7 (5)	-26·0 (5)
C(14)—C(9)—C(10)—C(7)	157·7 (5)	-157·1 (6)
C(8)—C(9)—C(10)—C(11)	161·9 (5)	-159·8 (5)
C(14)—C(9)—C(10)—C(11)	-67·1 (7)	69·0 (7)
O(1)—C(7)—C(10)—C(9)	-141·8 (6)	143·9 (6)
O(1)—C(7)—C(10)—C(11)	100·3 (8)	-98·2 (8)
C(6)—C(7)—C(10)—C(9)	90·0 (6)	-92·2 (6)
C(6)—C(7)—C(10)—C(11)	-28·0 (9)	25·7 (9)
C(8)—C(7)—C(10)—C(9)	-26·4 (5)	25·8 (5)
C(8)—C(7)—C(10)—C(11)	-144·3 (7)	143·7 (7)
C(7)—C(10)—C(11)—C(12)	167·2 (6)	-169·3 (6)
C(9)—C(10)—C(11)—C(12)	58·6 (7)	-61·0 (7)
C(10)—C(11)—C(12)—C(13)	-52·3 (7)	52·1 (8)
C(11)—C(12)—C(13)—C(14)	53·9 (8)	-51·9 (1·0)
C(12)—C(13)—C(14)—C(9)	-54·0 (8)	50·9 (9)
C(10)—C(9)—C(14)—C(13)	60·4 (7)	-58·2 (7)
C(8)—C(9)—C(14)—C(13)	164·4 (6)	-162·2 (7)

(or a lowering of symmetry to *Cc*). A difference map showed several peaks, but in locations which were not sufficiently unambiguous to allow positive placement of (possibly half-occupied) H sites. All

other H atoms were placed in calculated positions, and their temperature factors were refined isotropically. 329 parameters consisting of 102 positional parameters, 192 anisotropic temperature factors, 34 isotropic temperature fractors and a scale factor. Convergence at $R = 0.063$, $wR = 0.055$ for 1744 observed reflections for which $F \geq 3\sigma(F)$, where $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$, S = scan count, B = time-averaged background count. $R = 0.137$, $wR = 0.071$ for all data, $w = 1/\sigma^2(F)$, $(\Delta/\sigma)_{max} = 0.3$, highest $\Delta\rho$ peak in final difference synthesis = 0.32 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 two independent molecules have a similar configuration, with the four-membered and the six-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) = 150, − 149° for molecules A and B, respectively [molecules A and B in Table 1 have opposite chirality, but the material is racemic (space group C2/c), so that both enantiomers of the two independent molecules are present in the crystal]. The four-membered cyclobutanol rings have the usual folded conformations, with bond torsion angles of about 25°, normal sp^3—sp^3 bonds ranging from 1·50 (1) to 1·56 (1) Å (mean 1·54 Å), close to the value expected for *n*-alkanes, of 1·533 Å (Bartell & Kohl, 1963), and intra-annular bond angles of 84·5 (5)–89·1 (5)° (mean 86·9°). The cyclohexane rings have chair conformations, with bond torsion angles in the range 50·9 (9)–69·0 (7)° (mean
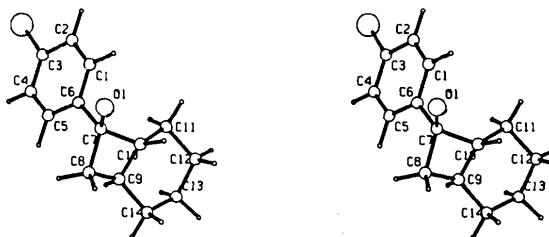
Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) stereoview of molecule B of compound (I) with crystallographic atom numbering.

$57.5°$) and valency angles 104.6 (5)–116.4 (8)° (mean $110.3°$), similar to the ideal chair conformation with $111.5°$ valency angles (torsion angle 55°; Boucourt & Hainaut, 1965). 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 $-7, 9°$ for molecules *A* and *B*, respectively. It is noteworthy that the only difference in conformation between molecules *A* and *B* is 20° in the torsion angles around the C(6)—C(7) bond, caused by a different rotation of the aryl group in the two independent molecules.

Two *A* and two *B* molecules are arranged around a C_2 axis, with four possible hydrogen bonds, O···O $= 2.72$ (1) and 2.80 (1) (across the C_2 axis), and 2.80 (1) ($\times 2$) Å.*

The molecule has an equatorial H atom on C(10) which is suitably oriented for abstraction by carbonyl oxygen (Ariel & Trotter, 1985). Rationalization of the photochemical results (see *Introduction*) can be obtained from a study of the orientations of the radical *p*-orbitals in the postulated biradical intermediate (Fig. 2). Bond formation *via* overlap of these *p*-orbitals would result in the photoproducts shown in Table 3 (*i.e.* overlap of lobe *a* with lobe *b* would give *cis*-ring junction, *cis*-OH product, *etc.*). Qualitative examination (Fig. 2) indicates that orbitals p_γ (a/a') and p_{CO} (b/b') are approximately normal to each other, and hence all four modes of bonding might be possible. A more quantitative understanding follows from an examination of the two torsion angles between the central C(8)—C(9) bond and the *p*-orbital lobes on C(7) and C(10) (Table 3). Both these angles have to change to bond torsion angles of about $-25°$ in the photoproduct (Table 2), and these movements are most easily achieved from the $-92°$ (8—9—10—p_γ) and $-95°$ (9—8—7—p_{CO}) angles of the a'/b lobes, to give
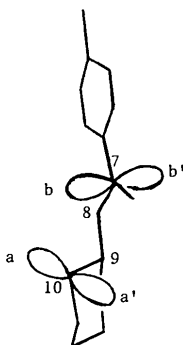
* See previous footnote.

Fig. 2. The orientations of the radical *p*-orbitals in the postulated biradical intermediate.

Table 3. *Biradical geometry for* 1-(4-*chlorophenyl*)-2-*cyclohexylethanone* (*see Fig.* 2)

Starting material			Photoproduct		
p orbital lobes	φ_1*	φ_2†	Ring junction	OH‡	Ratio (%)
a *b*	$+88$	-95	*cis*	*cis*	4
a *b'*	$+88$	$+85$	*cis*	*trans*	3
a' *b*	-92	-95	*trans*	*trans*	30
a' *b'*	-92	$+85$	*trans*	*cis*	23

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

the *trans*-ring junction, *trans*-OH product (30%). The next most favorable route is interaction of a'/b' lobes, to give the next most abundant *trans*-ring junction, *cis*-OH photoproduct (23%); this route involves minimum change (-92 to $-25°$) in the 8—9—10—p_γ torsion angle [which is the more difficult angle to change, since the C(9)—C(10) bond is part of the cyclohexyl ring], but a larger change ($+85$ to $-25°$) in the 9—8—7—p_{CO} angle.

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