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Structural Study of Two Isomeric (2-Phenyl-3-chromanyl)methanols

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Abstract

The crystal structures of *trans* and *cis*-diphenyl(2-phenyl-3-chromanyl)methanol, $C_{28}H_{24}O_2$, M_r = 392·49, have been determined from three-dimensional X-ray diffraction data. The crystals are respectively orthorhombic, *Pbca*, with a = 9·970 (17), b = 18·787 (21), c = 22·445 (23) Å, V = 4204·1 Å^3, Z = 8, D_m = 1·24 (2), D_x = 1·28 Mg m^{-3}, Cu $K\alpha$, λ = 1·5418 Å, μ = 6·07 cm^{-1}, $F(000)$ = 1664, T = 294 (2) K, and monoclinic, $P2_1/c$ with a = 10·768 (17), b = 16·197 (19), c = 12·038 (18) Å, β = 91·26 (11)°, V = 2099·02 Å^3, Z = 4, D_m = 1·24 (2), D_x = 1·27 Mg m^{-3}, Mo $K\alpha$, λ = 0·7107 Å, μ = 0·82 cm^{-1}, $F(000)$ = 832, T = 294 (2) K. Both structures were solved by direct methods and refined by full-matrix least squares with anisotropic thermal parameters for the heavy atoms and isotropic thermal coefficients for the hydrogen atoms. The residual R factors are respectively 6 and 4·8% for the observed structure factors having intensities higher than $3\sigma(I)$. A least-squares analysis of the rigid-body motion of the molecules shows that the *cis*-diphenyl(2-phenyl-3-chromanyl)methanol molecule is more rigid than the *trans* one. In the *trans* compound the dihydropyran ring adopts a slightly distorted half-chair conformation bearing its substituents in axial position, whereas in the *cis* one a sofa conformation is preferred in which all its atoms except C(3) are in the same plane. Furthermore the structure reveals the presence of a weak hydrogen bond between the hydroxyl group and the heterocyclic oxygen atom [O···H 2·09 (6), O···O 2·86 (7) Å] in the *trans* substance; on the other hand, a strong OH···π bond is observed in the *cis* molecule, which involves the alcohol hydroxyl and the 2-phenyl group, and contributes to the rigidity of the whole molecule.

Introduction

In a monosubstituted six-membered ring, usually a substituent prefers the equatorial position of a chair conformation (Eliel, Allinger, Angyal & Morrison, 1966). In heterocyclic compounds, the axial position may be favoured when an anomeric effect operates as in 2-halo, 2-alkoxy or 2-acyloxytetrahydropyrans (Lemieux, Kullnig, Bernstein & Schneider, 1958; Booth & Ouellette, 1966; Anderson & Sepp, 1967, 1968).

In the absence of polar effects, the preferred conformation for a vicinally *trans* disubstituted ring is the diequatorially substituted chair (*e-e* conformation). For instance, *trans*-1,2-dimethylcyclohexane exists 99% in the diequatorial conformation (Eliel, 1962).

But, if steric hindrance between the two substituents becomes too high, one can expect that the diaxially substituted chair (*a-a* conformation) would be favoured over the diequatorial conformation. Such a diaxially substituted chair has been reported in the case of *trans*-dimethyl 2,2′-(1,2-cyclohexylene)bis(2-methylpropanoate) (compound I). X-ray structure determination has shown that this derivative presents a chair conformation bearing the substituents in axial positions

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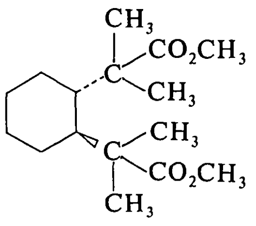
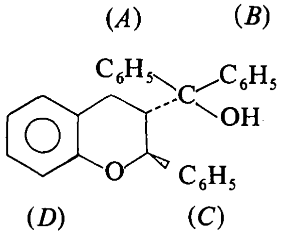
(van Koningsveld, 1973). But in this case the chair is distorted by a flattening which lowers the torsion angle in the substituted part of the ring to 37·4° (instead of 58° in cyclohexane) so that the substituents are in fact lying in altered axial positions, their dihedral angle amounting only to 134·5°.

We have undertaken a structural study of a dihydropyran derivative for which we were expecting a more perfectly diaxial disposition for bulky vicinal substituents. The compound studied is *trans*-diphenyl-(2-phenyl-3-chromanyl)methanol (compound II) for which a preliminary study in solution had shown that it would exist as a diaxially substituted ring (Sliwa & Sliwa, 1976).

The above assumptions are confirmed by the molecular structure of *trans*-diphenyl(2-phenyl-3-chromanyl)methanol. For comparison the structure determination of the *cis* isomer, which reveals some interesting characteristics, is also reported. This X-ray structure determination has been partially described in addition to the IR and NMR study in a preceding paper (Baert, Fouret, Sliwa & Sliwa, 1980).



(I)



(II)

Experimental

Both crystals had a prismatic shape whose dimensions were 0·6 × 0·4 × 0·2 mm for the *trans* and 0·3 × 0·15 × 0·4 mm for the *cis* compound. Intensities were measured by the ω–2θ scan technique on a four-circle diffractometer. The width of the scan was (1·5 + 0·30 tan θ)° for the *trans*, and 1·4° for the *cis*. In both cases the data were corrected for the Lorentz and polarization factor, but not for absorption or extinction.

Each structure has been determined by considering about 1840 reflections with $I \geq 3\sigma(I)$.

Structure determination and refinement

The structures were solved by direct methods using 450 reflections with normalized structure factors $E \geq 1{\cdot}42$ in *MULTAN* (Germain, Main & Woolfson, 1971) for the *trans* molecule; 300 reflexions with normalized structure factors $E \geq 1{\cdot}75$ were sufficient to provide the molecule in the *cis* configuration.

For both structures the H atoms were located from a difference synthesis. The non-H and H atoms were refined anisotropically and isotropically respectively. The refinement of the *trans* molecule converged to an R factor of 6% for all reflections with $I \geq 3\sigma(I)$. For the *cis* molecule $R = 4{\cdot}8\%$ with the same conditions as above.*

The final atomic parameters are listed in Table 1. The scattering factors for the heavy atoms were those of Hanson, Herman, Lea & Skillman (1964), for H those of Stewart, Davidson & Simpson (1965). Unit

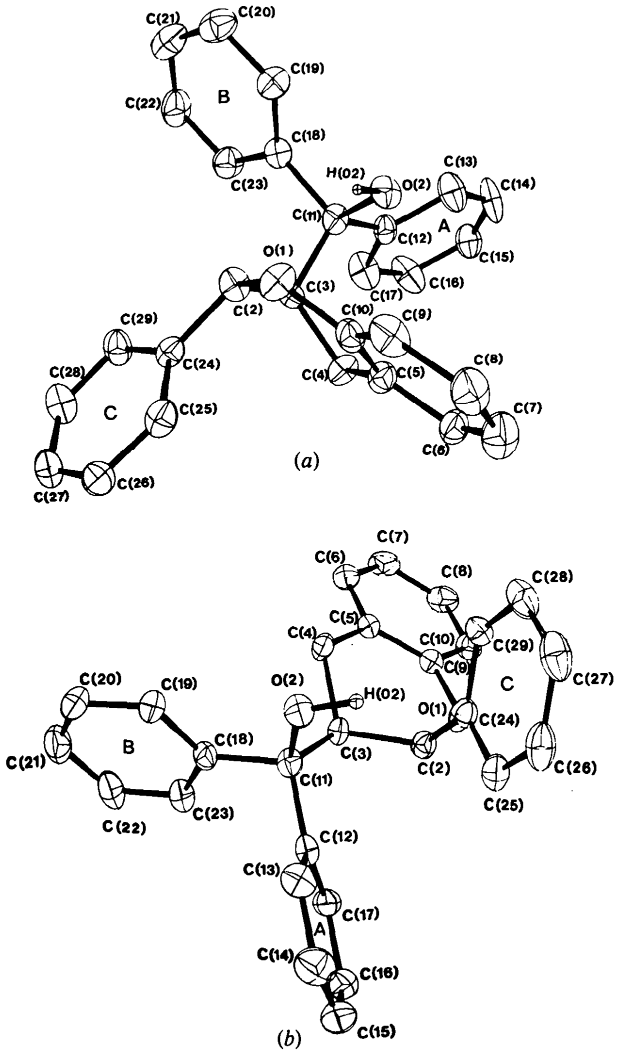


Fig. 1. (*a*) Perspective view of the *trans* molecule; (*b*) perspective view of the *cis* molecule; and key to the numbering of the atoms in the molecules.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38313 (55 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and* B_{eq} *values*

$B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}(\mathbf{a}_i.\mathbf{a}_j)$.

	trans					*cis*			
	x	*y*	*z*	B_{eq} (Å^2)		*x*	*y*	*z*	B_{eq} (Å^2)
O(1)	4030 (5)	9429 (2)	4727 (2)	5·5 (4)	C(8)	8654 (6)	10830 (4)	−4042 (5)	4·4 (2)
O(2)	5497 (5)	8465 (3)	3981 (2)	5·2 (1)	C(26)	9601 (6)	7631 (5)	832 (6)	4·8 (2)
C(2)	3992 (8)	9817 (4)	4173 (3)	4·4 (2)	C(14)	6251 (7)	5736 (4)	−429 (6)	5·3 (2)
C(3)	3814 (7)	9320 (3)	3625 (3)	3·7 (2)	C(23)	3677 (6)	8487 (4)	−642 (6)	4·5 (2)
C(4)	2555 (8)	8865 (4)	3719 (3)	4·4 (2)	C(16)	6655 (6)	5882 (4)	−2356 (6)	4·5 (2)
C(5)	2494 (8)	8541 (4)	4334 (3)	4·6 (2)	C(27)	9810 (6)	8351 (6)	1412 (5)	5·2 (2)
C(6)	1725 (9)	7941 (4)	4450 (4)	5·8 (3)	C(4)	6401 (5)	9481 (3)	−1750 (5)	3·2 (1)
C(7)	1718 (11)	7631 (5)	5014 (4)	7·8 (3)	C(22)	2412 (6)	8624 (4)	−931 (7)	5·7 (2)
C(8)	2444 (11)	7933 (5)	5466 (4)	7·7 (3)	C(28)	9433 (6)	9101 (5)	965 (6)	4·9 (2)
C(9)	3195 (9)	8540 (5)	5373 (3)	6·1 (3)	C(20)	2737 (6)	8137 (5)	−2787 (6)	5·1 (2)
C(10)	3199 (8)	8841 (4)	4800 (3)	4·7 (2)	C(6)	6836 (5)	10754 (4)	−2921 (5)	3·9 (1)
C(11)	5118 (8)	8907 (4)	3491 (3)	4·2 (2)	C(15)	6584 (6)	5400 (4)	−1447 (7)	5·4 (2)
C(12)	4962 (8)	8405 (4)	2952 (3)	4·4 (2)	C(13)	6009 (6)	6575 (4)	−357 (5)	4·0 (1)
C(13)	5602 (10)	7757 (4)	2951 (4)	7·8 (3)	O(1)	8760 (3)	8897 (3)	−2563 (3)	3·8 (1)
C(14)	5514 (12)	7292 (4)	2468 (5)	8·3 (2)	O(2)	6022 (4)	8257 (3)	−27 (3)	3·5 (1)
C(15)	4752 (12)	7473 (5)	1999 (4)	6·7 (2)	C(5)	7199 (5)	9982 (3)	−2523 (5)	3·0 (1)
C(16)	4164 (11)	8097 (5)	1981 (4)	8·2 (3)	C(11)	5841 (5)	8016 (4)	−1163 (4)	2·8 (1)
C(17)	4254 (10)	8512 (4)	2447 (3)	6·6 (3)	C(2)	8061 (5)	8370 (4)	−1828 (4)	2·8 (1)
C(18)	6269 (8)	9441 (4)	3381 (3)	4·7 (2)	C(18)	4456 (5)	8173 (4)	−1454 (5)	3·2 (1)
C(19)	7378 (9)	9477 (4)	3741 (3)	5·2 (2)	C(17)	6421 (6)	6728 (4)	−2288 (5)	3·5 (1)
C(20)	8357 (9)	9988 (5)	3657 (5)	6·9 (3)	C(29)	8874 (6)	9121 (4)	−96 (5)	3·6 (1)
C(21)	8253 (10)	10471 (5)	3214 (4)	7·3 (3)	C(9)	9044 (6)	10074 (4)	−3646 (5)	3·6 (1)
C(22)	7198 (10)	10451 (5)	2851 (4)	7·1 (3)	C(10)	8312 (5)	9650 (4)	−2899 (5)	3·0 (1)
C(23)	6201 (9)	9941 (4)	2916 (4)	6·0 (2)	C(3)	6652 (5)	8563 (3)	−1929 (5)	2·6 (1)
C(24)	2897 (7)	10390 (4)	4192 (3)	4·4 (2)	C(24)	8660 (5)	8389 (4)	−692 (5)	2·9 (1)
C(25)	2929 (9)	10914 (4)	3752 (3)	4·3 (2)	C(19)	3978 (5)	7994 (4)	−2499 (5)	3·7 (1)
C(26)	1974 (10)	11437 (5)	3746 (4)	7·1 (3)	C(21)	1963 (6)	8458 (5)	−1986 (7)	5·7 (2)
C(27)	1009 (10)	11473 (5)	4172 (5)	7·5 (3)	C(12)	6109 (5)	7084 (4)	−1288 (5)	2·7 (1)
C(28)	967 (9)	10964 (5)	4594 (5)	7·4 (3)	C(7)	7545 (6)	11183 (4)	−3684 (6)	4·5 (2)
C(29)	1915 (9)	10430 (4)	4618 (3)	5·8 (2)	C(25)	9040 (5)	7645 (4)	−212 (5)	3·8 (1)

weights were used throughout. The absolute values of peaks and troughs in the final difference synthesis did not exceed 0·2 e Å^{-3}. Figs. 1(*a*) and (*b*) give projections of the molecules, and the numbering of the atoms.

Thermal-vibration analysis

In the *trans* isomer (see Table 4) all the intramolecular distances of the phenyl rings that are far from the centre of the molecule are shorter than the standard values. It was expected that these discrepancies were caused by thermal agitation, and a least-squares analysis of the rigid-body motion of the molecule was carried out (Schomaker & Trueblood, 1968).

Two rigid-body models were used, comprising different groups of atoms: one consisting of all non-hydrogen atoms, and the other in which the molecule was divided into four fragments consisting of three phenyl rings and the chroman group (Table 3). A comparison of the thermal-vibration analysis of the two molecules is given in Table 2. The results show that the eigenvalues of **T** represent a more anisotropic translation of the whole molecule in the *trans* compound than in the *cis* one. The rotational motion in the two cases is quite negligible and the fit of the calculated U_{ij} terms to those observed is better for the molecule of

Table 2. *Rigid-body vibration parameters for all the heavy atoms of the cis and trans molecules*

		trans			*cis*	
T (Å^2) $\times 10^{-4}$	657 (29)	21 (24)	−85 (27)	307 (16)	24 (14)	54 (15)
		538 (29)	39 (24)		376 (16)	−8 (16)
			378 (29)			382 (20)
L (rad^2) $\times 10^{-4}$	32 (3)	−7 (2)	−14 (1)	22 (2)	16 (2)	−2 (1)
		28 (4)	29 (3)		23 (2)	0 (2)
			8 (2)			12 (2)
S (Å rad) $\times 10^{-4}$	17 (8)	−23 (5)	−1 (5)	8 (5)	−21 (3)	6 (3)
	−21 (5)	−24 (10)	15 (5)	−4 (3)	−1 (5)	11 (3)
	12 (5)	16 (5)	7 (120)	9 (3)	0 (2)	6 (72)
R.m.s. ($U^o - U^c$) (Å^2)		0·0114			0·0069	
E.s.d. U_{ij}^{obs} (Å^2)		0·0121			0·0073	

Table 3. *Rigid-body vibration parameters for the heavy atoms of the phenyl rings A, B, C with an adjacent atom*

	Fragment *A*			Fragment *B*			Fragment *C*		
T (Å^2) × 10^{-4}	613 (59)	−34 (53)	−9 (48)	664 (51)	−0 (46)	7 (56)	725 (49)	−10 (41)	45 (51)
		625 (48)	114 (40)		644 (57)	86 (56)		671 (48)	42 (50)
			407 (43)			391 (65)			363 (59)
L (rad^2) × 10^{-4}	49 (14)	−12 (17)	−7 (20)	96 (44)	49 (30)	−55 (19)	84 (38)	−78 (28)	−13 (18)
		234 (34)	282 (24)		75 (40)	−10 (21)		190 (38)	19 (18)
			444 (40)			79 (19)			69 (16)
S (Å rad) × 10^{-4}	13 (57)	−86 (24)	0 (22)	−39 (66)	98 (47)	11 (57)	9 (58)	−55 (38)	57 (50)
	36 (46)	13 (73)	−59 (33)	25 (40)	56 (65)	23 (54)	−9 (39)	−22 (57)	−99 (50)
	−77 (51)	38 (46)	−26 (59)	63 (28)	−72 (33)	−17 (68)	80 (29)	81 (28)	13 (61)
R.m.s. $(U^o - U^c)$ (Å^2)		0·0043			0·0049			0·0044	
E.s.d. U_{ij}^{obs} (Å^2)		0·0060			0·0068			0·0061	

Table 4. *Bond lengths corrected for molecular vibrations* (Å)

	trans		*cis*
	Uncorrected	Corrected	
O(1)–C(2)	1·441 (8)		1·452 (7)
O(1)–C(10)	1·391 (9)		1·371 (7)
O(2)–C(11)	1·429 (8)		1·431 (6)
C(2)–C(3)	1·554 (9)		1·551 (7)
C(3)–C(4)	1·533 (10)		1·528 (8)
C(3)–C(11)	1·543 (10)		1·560 (8)
C(4)–C(5)	1·509 (10)		1·516 (8)
C(5)–C(6)	1·387 (10)		1·392 (8)
C(5)–C(10)	1·378 (10)		1·397 (8)
C(6)–C(7)	1·391 (13)		1·393 (9)
C(7)–C(8)	1·370 (14)		1·401 (10)
C(8)–C(9)	1·379 (13)		1·376 (9)
C(9)–C(10)	1·405 (10)		1·391 (8)
C(11)–C(12)	1·540 (9)	1·547	1·545 (8)
C(11)–C(18)	1·544 (10)	1·552	1·546 (8)
C(12)–C(13)	1·373 (11)	1·408	1·398 (8)
C(12)–C(17)	1·372 (11)	1·406	1·383 (8)
C(13)–C(14)	1·395 (12)	1·401	1·388 (10)
C(14)–C(15)	1·320 (14)	1·355	1·395 (11)
C(15)–C(16)	1·329 (13)	1·365	1·348 (11)
C(16)–C(17)	1·376 (12)	1·383	1·396 (9)
C(18)–C(19)	1·371 (11)	1·384	1·380 (9)
C(18)–C(23)	1·406 (11)	1·417	1·397 (9)
C(19)–C(20)	1·381 (13)	1·388	1·393 (9)
C(20)–C(21)	1·349 (14)	1·360	1·389 (11)
C(21)–C(22)	1·331 (14)	1·345	1·375 (12)
C(22)–C(23)	1·388 (13)	1·395	1·416 (9)
C(2)–C(24)	1·534 (10)	1·543	1·500 (8)
C(24)–C(25)	1·394 (10)	1·410	1·394 (9)
C(25)–C(26)	1·368 (13)	1·376	1·385 (9)
C(26)–C(27)	1·358 (14)	1·375	1·376 (11)
C(27)–C(28)	1·347 (14)	1·362	1·387 (11)
C(28)–C(29)	1·379 (13)	1·387	1·401 (9)
C(29)–C(24)	1·371 (11)	1·387	1·403 (9)

the *cis* compound. We also notice from Table 4 that the bond lengths of the *cis* molecule are in good agreement with the standard values. Consequently, it seems that the *trans* structure is far from being rigid. The independent librations of the different fragments *A*, *B*, *C* recoil on the agitation of the whole molecule, and explain the significant values of **T** and the misfit of the calculated and observed U_{ij} terms.

These results are also in agreement with the partial correction of the bond lengths according to the formula of Busing & Levy (1964).

The discrepancies we observed (Table 2) in the thermal motion of the molecules of these two compounds are certainly related to the configuration (*cis* or *trans*) of the molecule and to the nature and strength of the intramolecular hydrogen bond.

In the *trans* molecule the O—H···O hydrogen bond [2·09 (6) Å, $\Delta\nu = 34$ cm^{-1} in IR] is rather weak, and cannot restrict the fragments *A* and *B*, relative to the chroman group. Furthermore, the phenyl ring (*C*) is able to rotate freely around the C(2)–C(24) bond.

On the other hand, the relatively strong O—H···π bond [2·36 (4) Å] between H(O2) and C(24) ($\Delta\nu$ = 50 cm^{-1} in IR) stabilizes the phenyl ring (*C*) making the freedom of the two other groups *A* and *B* less important.

The root-mean-square differences between the observed U_{ij} terms and those calculated from the derived **T**, **L** and **S** for the three phenyls *A*, *B*, *C*, with the adjacent atom taken as origin, are respectively 0·0043, 0·0049, 0·0044 Å^2 (Table 3). The bond lengths corrected for the effects of molecular vibrations (Busing & Levy, 1964), reported in Table 4, are in better agreement with the standard values, and Table 3 shows that the phenyl ring *A* has more librational motion than the other two; in fact it is the farthest fragment from the chroman group.

Results and discussion

Molecular geometry

The geometry of the *trans* molecule can be inferred from Figs. 1(*a*) and 2(*a*). The bond lengths uncorrected and corrected for the effect of molecular librations are reported in Table 4. Bond angles are listed in Table 5. The IR and NMR results have been fully confirmed by the X-ray diffraction study which shows only a slight distortion from the perfectly *trans* diaxial position of the two substituents [Fig. 2(*a*), bond C(2)–C(3)]. The observed value [162 (0·5)°] for the dihedral angle of the two substituents must be compared not with the 180° value for a perfect chair, but with the 173° value

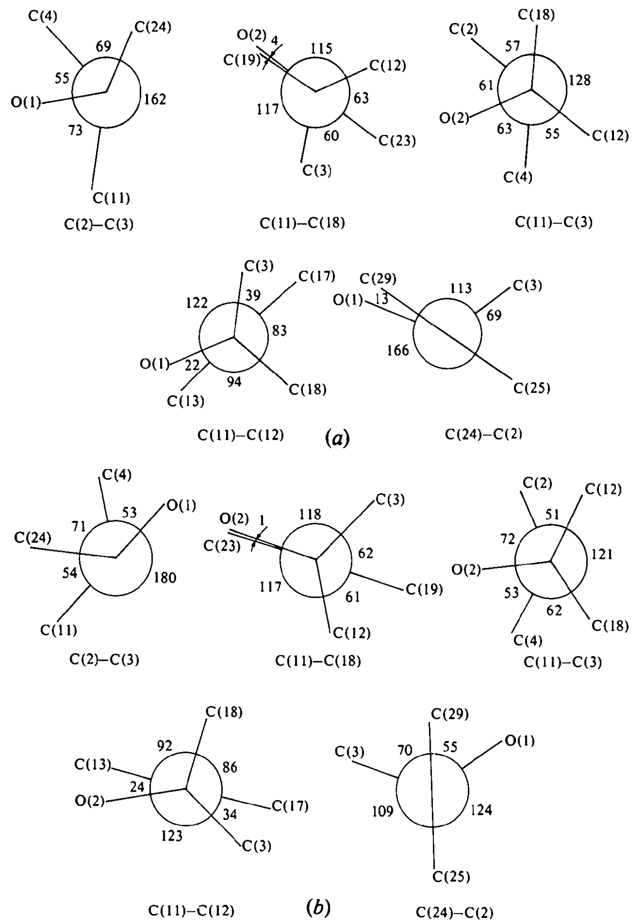


Fig. 2. Newman projection along some interesting bonds: (*a*) *trans* molecule; (*b*) *cis* molecule. Angles in ° ($\bar{\sigma} = 0{\cdot}5$°).

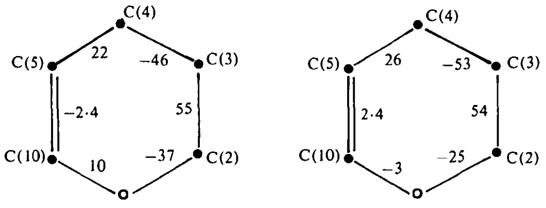
Table 5. *Bond angles* (°)

	trans	*cis*
C(2)–O(1)–C(10)	119·1 (5)	121·3 (4)
O(1)–C(2)–C(3)	112·6 (5)	110·7 (4)
O(1)–C(2)–C(24)	110·4 (6)	108·9 (4)
C(3)–C(2)–C(24)	111·1 (6)	117·9 (4)
C(2)–C(3)–C(4)	108·5 (5)	111·2 (4)
C(2)–C(3)–C(11)	111·0 (5)	113·5 (4)
C(4)–C(3)–C(11)	116·0 (5)	111·5 (4)
C(3)–C(4)–C(5)	112·6 (6)	109·3 (5)
C(4)–C(5)–C(6)	121·4 (7)	122·2 (5)
C(4)–C(5)–C(10)	120·5 (6)	119·7 (5)
C(6)–C(5)–C(10)	118·1 (7)	118·0 (5)
C(5)–C(6)–C(7)	120·9 (8)	121·4 (6)
C(6)–C(7)–C(8)	119·8 (9)	118·9 (6)
C(7)–C(8)–C(9)	121·1 (9)	120·8 (6)
C(8)–C(9)–C(10)	118·2 (8)	119·3 (6)
O(1)–C(10)–C(5)	122·6 (7)	123·1 (5)
O(1)–C(10)–C(9)	115·3 (6)	115·4 (5)
C(5)–C(10)–C(9)	121·9 (7)	121·5 (5)
O(2)–C(11)–C(3)	111·4 (5)	110·1 (4)
O(2)–C(11)–C(12)	105·9 (5)	109·8 (4)
O(2)–C(11)–C(18)	107·6 (5)	106·4 (4)
C(3)–C(11)–C(12)	111·9 (5)	112·9 (4)
C(3)–C(11)–C(18)	109·4 (5)	108·8 (4)
C(12)–C(11)–C(18)	110·4 (6)	108·7 (4)
C(11)–C(12)–C(13)	119·7 (7)	118·7 (5)
C(11)–C(12)–C(17)	124·1 (6)	122·8 (5)
C(13)–C(12)–C(17)	116·2 (7)	118·5 (5)
C(12)–C(13)–C(14)	121·7 (8)	120·6 (6)
C(13)–C(14)–C(15)	119·5 (9)	119·3 (6)
C(14)–C(15)–C(16)	120·5 (9)	120·5 (7)
C(15)–C(16)–C(17)	121·1 (9)	120·5 (6)
C(12)–C(17)–C(16)	120·9 (8)	120·5 (6)
C(11)–C(18)–C(19)	122·6 (7)	120·7 (5)
C(11)–C(18)–C(23)	120·9 (6)	119·5 (5)
C(19)–C(18)–C(23)	116·3 (7)	119·8 (6)
C(18)–C(19)–C(20)	121·7 (8)	121·9 (6)
C(19)–C(20)–C(21)	120·7 (9)	118·5 (7)
C(20)–C(21)–C(22)	119·5 (9)	120·7 (7)
C(21)–C(22)–C(23)	121·5 (9)	120·9 (7)
C(18)–C(23)–C(22)	120·1 (8)	118·3 (6)
C(2)–C(24)–C(25)	117·3 (6)	118·4 (5)
C(2)–C(24)–C(29)	124·5 (6)	123·1 (5)
C(25)–C(24)–C(29)	118·1 (7)	118·4 (5)
C(24)–C(25)–C(26)	119·8 (8)	120·6 (6)
C(25)–C(26)–C(27)	121·5 (9)	120·7 (6)
C(26)–C(27)–C(28)	118·8 (9)	120·2 (7)
C(27)–C(28)–C(29)	121·4 (9)	119·4 (6)
C(24)–C(29)–C(28)	120·2 (8)	120·6 (6)

which is actually the angle between vicinal axial bonds in the slightly flattened chair of cyclohexane (Bucourt, 1974).

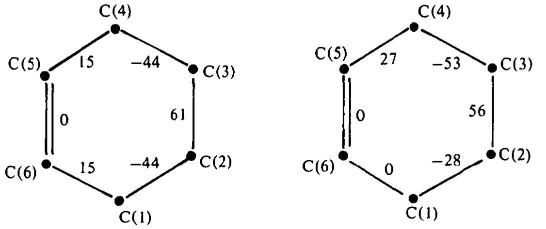
This unusual conformation for a vicinally *trans* disubstituted ring (when anomeric or polar effects are absent) can be explained by reduction of the synaxial interactions as compared to cyclohexane derivatives and by destabilization of the alternative diequatorial conformation owing to steric overcrowding of bulky substituents. Furthermore, the crystallographic study determines the nature of the intramolecular hydrogen bond O(2)–H(O2)···O(1) [2·09 (6) Å] occurring in the *trans* isomer; despite its low IR $\Delta\nu_{\rm OH}$ value (34 cm^{-1}) it is an OH···O bond that involves the heterocyclic ether oxygen atom and the alcohol hydrogen. Comparison with the usual length of hydrogen bonds of the OH···O type, *ca* 1·7 Å (Hamilton & Ibers, 1968), shows that this is indeed a 'weak' hydrogen bond. The torsion angles which are given in Fig. 3 show that the conformation of the dihydropyran is intermediate between a half-chair and a sofa, but is closer to the half-chair [the sofa is defined as a conformation in which all the atoms of the ring except one are in the same plane (Philbin & Wheeler, 1958)].

The configuration of the *cis* molecule can be deduced from Figs. 1(*b*) and 2(*b*). The torsion angles which are given in Fig. 3 show that the dihydropyran ring is much closer to a sofa than a half-chair conformation, since all its atoms except C(3) lie nearly in the same plane. This C(3) sofa conformation provides a more remote position from the benzo group for the 2-phenyl substituent which stands in an axial position without lengthening of the C(2)–C(24) bond [1·500 (8) Å compared to 1·543 (10) Å in the *trans* isomer]. The bulkier 3-substituent lies in equatorial position attached to the chroman ring by a bond which is longer than usual [1·560 (8) Å]. This lengthening must be related to



Experimental
trans

Experimental
cis



Half-chair

Sofa

Fig. 3. Observed ring torsional angles and, below, calculated torsional angles (Bucourt & Hainaut, 1965) (°) for two forms of the cyclohexene ring ($\bar{\sigma} = 0{\cdot}5°$).

the buttressing effect exerted by the 2-phenyl group since the dihedral angle between the two substituents is reduced to 54 (0·5)° as a consequence of intramolecular hydrogen bonding. The crystallographic study determines the nature of the intramolecular hydrogen bond O(2)–H(O2)$\cdots\pi$, 2·36 (4) Å being the distance between H(O2) and C(24), the nearest atom belonging to the phenyl ring (*C*). The distance from H(O2) to the barycentre of the phenyl ring is 2·65 (4) Å while the van der Waals contact distance would be 3·0 Å. Concerning the length of this hydrogen bond one can notice a greater contraction from the van der Waals contact distance in the *cis* than in the *trans* isomer. This result, which shows that this OH$\cdots\pi$ bond is stronger than the OH$\cdots$O hydrogen bond found in the *trans* molecule, in accordance with the previous IR study, confirms the above assumptions, namely that the diaxial conformation of the *trans* isomer is due to the steric hindrance that its bulky substituents would experience in the alternative diequatorial conformation, and not to the stabilizing effect of its OH$\cdots$O hydrogen bonding.

Molecular packing

No intermolecular distances are less than the sum of the van der Waals radii of the involved atoms in both structures. Figs. 4(*a*) and (*b*) show some contacts between one molecule and its nearest neighbours, where we notice the value of 3·13 (1) Å between the ether oxygen atoms of the two molecules related by the inversion centre, for the *trans* isomer. There is no such direct van der Waals contact between the ether oxygen atoms in the *cis* molecule; on the other hand the distances between O(2) and the nearest carbon atoms are almost identical in the two structures.

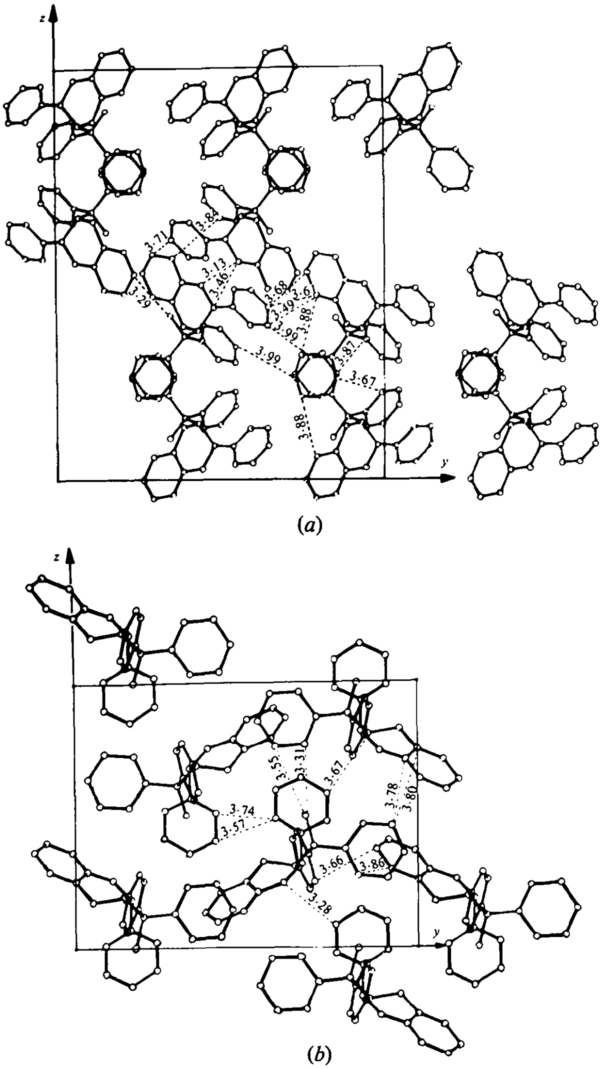


Fig. 4. Projections along **a**, with the shortest intermolecular distances (Å): (*a*) *trans* molecule ($\bar{\sigma} = 0{\cdot}011$ Å); (*b*) *cis* molecule ($\bar{\sigma} = 0{\cdot}009$ Å).

The shortest molecular distance between two carbon atoms is 3·57 (1) Å (Fig. 4*b*), the van der Waals contact distance being 3·6 Å. Some van der Waals contacts have been included on the projections; they demonstrate very weak intermolecular interactions between the molecules, especially in the *trans* structure.

As was expected by the NMR and IR study (δOH and νOH were independent of the concentration), there is no intermolecular hydrogen bond. The stability of the structure is assured by van der Waals forces.

Conclusion

The geometry of *trans*-diphenyl(2-phenyl-3-chromanyl)methanol (II) appears to be the more diaxial for a vicinally disubstituted six-membered ring, in the absence of polar effects. Comparison with the molecular structure of *trans*-dimethyl 2,2′-(1,2-cyclohexylene)bis(2-methylpropanoate) (I) previously reported shows that in our compound the dihedral angle between the substituents is close to the value of 173° found in cyclohexane for vicinal axial C—H bonds [162 (0·5)° in II instead of 134·5 (0·5)° in I]. Furthermore, the flattening in the substituted part of the ring [endocyclic torsion angle of 55 (0·5)°] is far less pronounced than in I [37·4 (5)°] and very close to that of cyclohexane itself (56°).

This X-ray structure determination shows also that the chroman ring of the *cis* isomer adopts a C(3) sofa conformation bearing the 2-phenyl substituent in axial position and the bulkier 3-substituent in an equatorial one. These two substituents are brought closer by a rather strong hydrogen bond of the $\mathrm{OH}\cdots\pi$ type which contributes to the rigidity of the whole molecule.

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An X-ray Crystallographic Study on the Geometry of the C—$\bar{\mathrm{N}}$—O Group and the [1,5] Sigmatropic Rearrangement from C-Nitroso Compounds to Oximes

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Abstract

Single-crystal X-ray analyses of *N*-(4-chlorophenyl)-3-methylamino-2-nitroso-2-butenamide (I) and 5,5-dimethyl-2-nitroso-3-phenylamino-2-cyclohexen-1-one (II) show that in both compounds the —N=O groups are implied in conjugated double-bond systems and their geometries are intermediate between those of oximes and C-nitroso derivatives and very close to those observed in isonitroso $>$C=N—O$^-$ ions. The comparison of bond distances and angles of the C—$\bar{\mathrm{N}}$—O group with those of several C-nitroso compounds and oximes allows the extrapolation of the geometry of the transition state of an asymmetric [1,5] sigmatropic rearrangement describing the interconversion from nitrosovinylamine to iminoxime. The present conclusions are compared with the results of theoretical *ab initio* calculations obtained by other

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