

Optical Induction in Chiral Crystals. I. The Crystal and Molecular Structures of 4,4'-Dimethylchalcone

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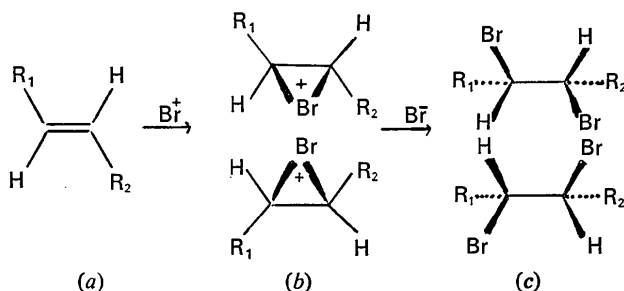
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The structure of 4,4'-dimethylchalcone (4,4'-dimethylbenzylideneacetophenone, $C_{17}H_{16}O$) has been determined from three-dimensional diffractometer data by direct methods. The crystals are orthorhombic, space group $P2_12_12_1$, with $a=15.2464$, $b=5.9059$, $c=14.6283$ Å, $Z=4$. The structure was refined by least-squares calculations to $R=0.045$. The molecule is distorted from planarity, the angle between the planes of the two phenyl rings being 48.6° . This molecular conformation is believed to control the formation of an optically active product in the bromination reaction of a single crystal of the title compound.

Introduction

Penzien & Schmidt (1969a) have shown that gas/solid bromination of a single crystal of 4,4'-dimethylchalcone (I, Fig. 1) which crystallizes in a chiral space group ($P2_12_12_1$) yields one of the two possible enantiomeric dibromides in excess, thus achieving an asymmetric synthesis starting with optically inactive molecules. The bromination reaction is believed to involve the following steps ($R_1=p$ -tolyl, $R_2=p$ -toluoyl):



It is obvious that crystal chirality is a necessary condition. However, it is not at all clear whether chirality of the environment *per se* is also a sufficient condition for optical induction, since another chalcone derivative, 4-methoxychalcone ($R_1=4$ -methoxyphenyl, $R_2=$ benzoyl) which also crystallizes in a chiral space group ($P2_1$), yields no optically active product when treated with bromine under the same conditions (Penzien & Schmidt, 1969b). The different behaviour of the two compounds may be attributed to a difference in the degree of *prochirality* conformation. By *prochirality* we mean the existence of a chiral symmetry element in the solid state which is non-detectable in the dispersed phase owing to fast racemization or reversion to the more symmetrical shape. According to these definitions the degree of *prochirality* in 4-methoxychalcone is rather small owing to the fact that the molecular

conformation in the solid is nearly planar (Rabinovich & Schmidt, 1970).

On the other hand if *prochirality* is not required, then specificity of the reaction [front-side *versus* rear-side attack of the double bond (a) leading to the chiral bromonium ion (b)] may be controlled by anisotropy of bromine diffusion into the crystal. A study of the molecular conformation and packing arrangement was needed to answer these questions.

Experimental

Crystals of (I) were grown by slow evaporation of ethyl acetate solution. Accurate cell dimensions (Table 1) were derived by a least-squares procedure based on high-order reflexions ($2\theta > 140^\circ$) measured on a General Electric goniostat with Cu $K\alpha$ radiation.

Table 1. Crystal data

4,4'-Dimethylchalcone, $C_{17}H_{16}O$, m.p. $132^\circ C$

Orthorhombic, $P2_12_12_1$	M.W. 236, $U=1317.2$ Å ³
$a=15.2464 \pm 0.0003$ Å	$D_x=1.19$ g cm ⁻³ for $Z=4$
$b=5.9059 \pm 0.0005$	$D_m=1.20$ g cm ⁻³
$c=14.6283 \pm 0.0005$	$\mu(Cu K\alpha)=6.0$ cm ⁻¹

Three-dimensional diffraction data ($2\theta \leq 160^\circ$, one octant only) were collected manually from a nearly equidimensional crystal mounted along [010], on the General Electric goniostat by the stationary-counter stationary-crystal technique at room temperature ($25^\circ C$) with Ni-filtered Cu $K\alpha$ radiation. The intensities were corrected for Lorentz, polarization and absorption effects. The weighting factors $w(hkl)$ and assignment of 'unobserved' reflexions were derived by a procedure previously described (Filippakis, Leiserowitz & Schmidt, 1967).

Structure determination and refinement

The structure was solved by a computer program for direct phase determination (Kaufman & Leiserowitz,

Table 2. Fractional coordinates and vibration tensor components (\AA^2) of the heavy atoms and their *e.s.d.*'s

All values are multiplied by 10^4 . The anisotropic temperature factor is of the form: $\exp[-2\pi^2(h_1a^1)(h_2a^2)(h_3a^3)U^{ij}]$, where h_i and a^j , $i=1,2,3$ are reflexion indices and reciprocal unit-cell edges respectively.

	<i>x</i>	<i>y</i>	<i>z</i>	U^{11}	U^{22}	U^{33}	U^{12}	U^{23}	U^{13}
C(1)	-982 (2)	2773 (5)	1196 (2)	505 (14)	505 (14)	514 (14)	15 (12)	-18 (13)	-78 (13)
C(2)	-1017 (2)	674 (5)	1616 (2)	472 (14)	532 (15)	606 (16)	-64 (13)	8 (14)	15 (13)
C(3)	-284 (2)	-686 (5)	1661 (2)	524 (14)	436 (13)	555 (15)	-52 (12)	20 (13)	30 (13)
C(4)	521 (2)	26 (4)	1294 (2)	481 (13)	435 (13)	467 (13)	-69 (12)	-54 (12)	10 (11)
C(5)	557 (2)	2168 (4)	896 (2)	517 (14)	438 (13)	553 (15)	-52 (12)	-22 (13)	72 (13)
C(6)	-182 (2)	3482 (5)	837 (2)	615 (15)	411 (12)	529 (15)	-60 (13)	22 (13)	15 (14)
C(7)	1272 (2)	-1528 (5)	1320 (2)	492 (13)	469 (14)	532 (15)	-30 (13)	-23 (13)	30 (12)
C(8)	2109 (2)	-1024 (5)	1171 (2)	505 (15)	459 (14)	629 (17)	24 (12)	22 (14)	14 (13)
C(9)	2782 (2)	-2832 (5)	1170 (2)	574 (16)	456 (14)	685 (18)	-8 (12)	-27 (15)	3 (14)
O(10)	2572 (2)	-4843 (4)	1141 (2)	603 (12)	474 (11)	1490 (26)	-47 (10)	-50 (16)	-14 (15)
C(11)	3727 (2)	-2190 (4)	1213 (2)	506 (13)	415 (13)	522 (14)	-3 (11)	-8 (12)	-3 (12)
C(12)	4354 (2)	-3756 (5)	938 (2)	584 (16)	442 (14)	581 (16)	34 (13)	-64 (13)	-26 (13)
C(13)	5237 (2)	-3238 (5)	993 (2)	574 (15)	539 (15)	541 (16)	87 (14)	-36 (13)	19 (13)
C(14)	5517 (2)	-1166 (5)	1331 (2)	538 (14)	573 (16)	519 (15)	-9 (14)	49 (14)	-7 (13)
C(15)	4895 (2)	388 (5)	1617 (2)	585 (15)	462 (14)	609 (17)	-74 (13)	-48 (14)	-27 (14)
C(16)	4004 (2)	-101 (5)	1545 (2)	565 (15)	425 (13)	612 (16)	28 (13)	-68 (14)	29 (14)
C(17)	-1787 (2)	4248 (7)	1129 (3)	590 (20)	737 (23)	956 (30)	63 (19)	104 (23)	-54 (20)
C(26)	6449 (2)	-631 (9)	1383 (3)	558 (19)	929 (29)	885 (29)	-76 (19)	56 (27)	-37 (20)

1970), utilizing a modification of the procedure described by Germain & Woolfson (1968). The coordinates of the carbon and oxygen atoms thus determined were refined isotropically in a full-matrix least-squares program. Eventually, all hydrogen atoms, except the six of the methyl groups, were inserted in chemically reasonable positions and the structure was further refined anisotropically for the non-hydrogen atoms and isotropically for the hydrogens. A subsequent difference electron-density map revealed smeared positions of the six methyl hydrogens which were inserted and refined isotropically in the last cycles of refinement. The final agreement values were $R = \sum |kF_o - |F_c|| / \sum kF_o = 0.045$ and $r = \sum w(k^2F_o^2 - |F_c|^2) / \sum w k^4F_o^4 = 0.011$. The scattering factors used were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon and oxygen, and McWeeny (1951) for hydrogen. Standard deviations of all parameters were estimated by the usual least-squares procedure, the number of observations and the number of parameters being 1500 and 227 respectively. Final values of the fractional coordinates, thermal parameters and their estimated standard deviations are listed in Tables 2 and 3.*

Results and discussion

Bond lengths and angles

Fig. 2 shows the experimental bond lengths and angles uncorrected for curvilinear thermal motion. The r.m.s. values of the estimated standard deviations in bond lengths and bond angles are 0.004 \AA and 0.25° respectively. The former compares well with that obtained from the 'bond-scatter' $(\sum (r_i - \bar{r})^2 / (n-1))^{1/2} =$

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30554 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Hydrogen atom parameters and their *e.s.d.*'s ($\times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U^2 (\text{\AA}^2)$
H(18)	-159 (2)	11 (5)	189 (2)	23 (7)
H(19)	-29 (2)	-212 (5)	201 (2)	32 (8)
H(20)	113 (2)	277 (5)	65 (2)	34 (8)
H(21)	-18 (2)	504 (5)	54 (2)	25 (7)
H(22)	115 (2)	-326 (5)	145 (2)	30 (8)
H(23)	229 (2)	53 (5)	104 (2)	42 (10)
H(24)	414 (2)	-521 (5)	66 (2)	40 (9)
H(25)	565 (2)	-442 (5)	79 (2)	40 (9)
H(27)	508 (2)	187 (6)	188 (2)	46 (9)
H(28)	359 (2)	98 (5)	177 (2)	30 (8)
H(29)	-225 (2)	358 (8)	77 (3)	82 (14)
H(30)	-207 (2)	436 (8)	175 (3)	93 (15)
H(31)	-168 (2)	563 (7)	79 (3)	75 (14)
H(32)	685 (3)	-186 (8)	172 (3)	132 (17)
H(33)	672 (2)	-18 (8)	86 (3)	96 (17)
H(34)	657 (2)	24 (8)	185 (3)	78 (17)

0.006 \AA) of the 12 aromatic bonds which have an average $\bar{r} = 1.389 \text{ \AA}$.

The aromatic bond angles show no significant deviations from 120° except at the substituted atoms, where smaller values are observed. Similar values have been observed in other methyl-substituted phenyl rings, *e.g.*, *p*-methylchalcone (Rabinovich, 1974), 2,3-dimethylbenzoic acid (Smith, Florencio & García-Blanco, 1971), *p*-cresol (Bois, 1970), 1,1-di-*p*-tolyl-

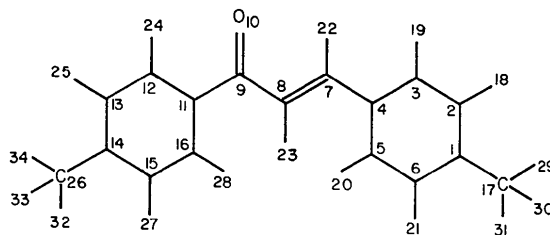


Fig. 1. 4,4'-Dimethylchalcone (I). Chemical formula and numbering of atoms.

ethylene (Casalone, Gavezzotti, Mariani, Mugnoli & Simonetta, 1970) and *p*-toluoylacetophenone enol (Kato, 1971). The deviation from the expected value of 120° is consistent with observations by Carter, McPhail & Sim (1966) and Hope (1969) that aromatic substitution by electron-donating groups leads to an internal angle smaller than 120° on the substituted carbon, whereas electron-withdrawing groups have the opposite effect. The average length of the two single C-CH₃ bonds (1.511 Å) is in agreement with the values found in other molecules (Smith *et al.*, 1971; Takwale & Pant, 1971; Bois, 1970; Kato, 1971).

The bond lengths and angles of the central enone system are similar to those observed in other chalcone derivatives, with similar conformations of the enone system but different substituents at the *para* positions (Table 4). The prominent feature of this bond-length analysis is the shortening of the C-C single bond (3) compared with (5) and (7), which results from its rela-

tively good conjugation with the $\begin{array}{c} \diagup \\ \text{C}=\text{C} \\ \diagdown \end{array}$ double bond and the aromatic ring. The difference in the lengths of bonds (5) and (7) is not significant. The bond angles which deviate significantly from 120° are (3,4), (2,3) and (7,9). The corresponding averaged values (127.7, 122.8 and

122.6) are typical of such '*cis*-hindered' systems where the relaxation of the $1 \cdots 6$ interaction of the hydrogens (marked by a dotted line in the figure of Table 4) is achieved partly by the opening of the related bond angles. Similar bond lengths and angles were observed in other compounds containing an enone system adjacent to an aromatic ring, *e.g.*, *p*-chlorocinnamide (Rabinovich, 1969), *trans*- β -2-furylacrylamide (Leiserowitz & Rabinovich, 1969), *trans*-1,2-dibenzoyl and ditoluoyl ethylene (Bart & Schmidt, 1971), and *cis*-1,2-dibenzoyl ethylene (Rabinovich, Schmidt & Shakked, 1970).

Thermal motion analysis

Rigid-body motion analysis of the vibration tensors of the non-hydrogen atoms was carried out by means of a computer program (Shmueli, 1972) based on the method of Schomaker & Trueblood (1968). The results are summarized in Table 5. As might be expected for such a flexible molecule, the agreement between the observed and calculated U^{ij} is rather poor, [compare the r.m.s. of ΔU^{ij} (0.0065 Å²) with the mean value (0.0016 Å²) of $\sigma(U^{ij})$]. The principal axes of translation and libration are nearly parallel to the principal axes of inertia. The translational vibrations are nearly isotropic with the largest vibration (0.23 Å) along the

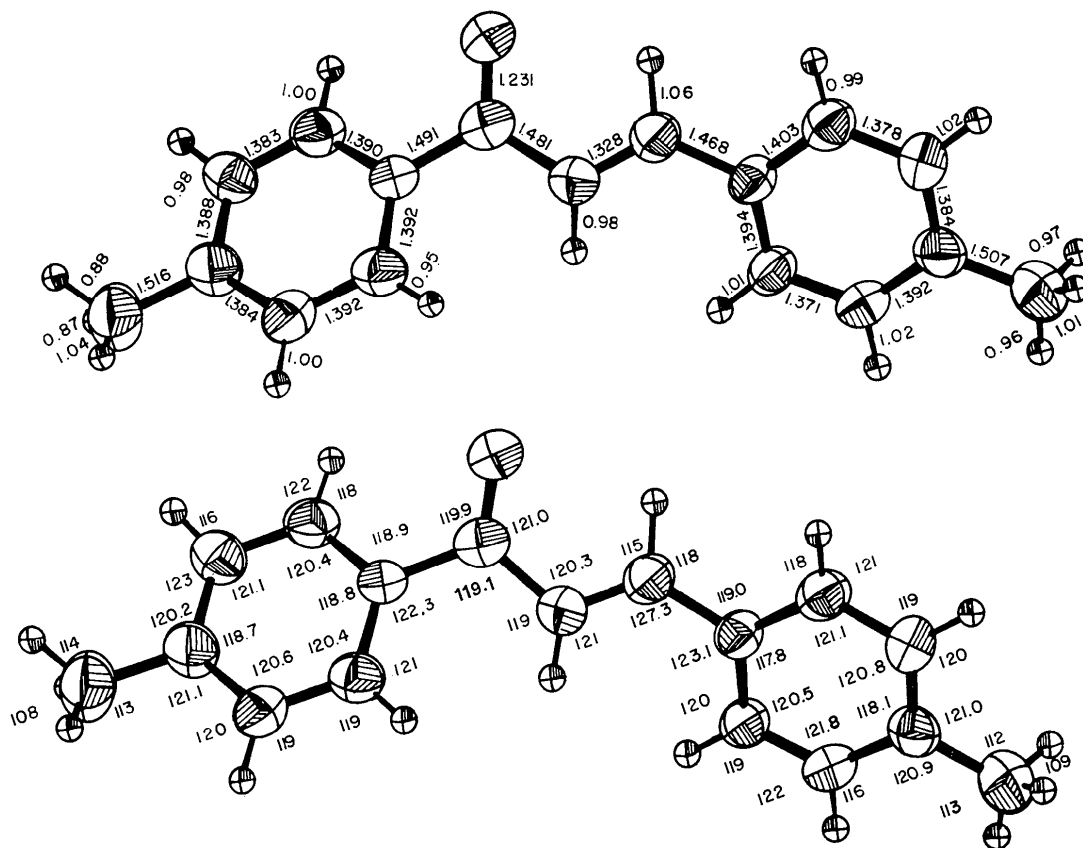
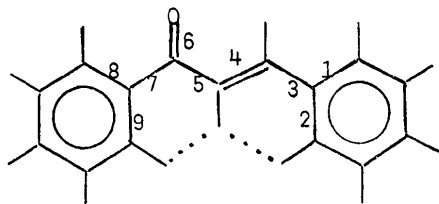


Fig. 2. Bond lengths (Å) and angles ($^\circ$). The thermal ellipsoids are drawn at 50% probability level (Johnson, 1965). The view is along the *c* axis.

Table 4. Bond lengths (Å) and angles (°) of chalcone derivatives

The last entry of each line gives the averaged value with its 'bond scatter'.



Bond	I ¹	II ²	III ³	IV ⁴	V ⁵	Average
(3)	1.468	1.465	1.464	1.456	1.441	1.459 (10)
(4)	1.328	1.333	1.319	1.332	1.327	1.328 (6)
(5)	1.481	1.490	1.478	1.484	1.468	1.480 (8)
(6)	1.231	1.228	1.204	1.243	1.220	1.225 (10)
(7)	1.491	1.468	1.499	1.498	1.491	1.489 (12)

Angle

(1, 3)	119.0	120.1	118.4	119.8	119.0	119.3 (7)
(2, 3)	123.1	122.8	123.5	121.9	122.9	122.8 (6)
(3, 4)	127.2	127.2	127.6	128.0	128.5	127.7 (6)
(4, 5)	120.3	122.0	120.4	119.2	121.2	120.6 (10)
(5, 6)	121.0	119.8	121.1	122.6	121.6	121.2 (10)
(5, 7)	119.1	119.3	118.5	117.6	119.1	118.7 (7)
(6, 7)	119.9	120.9	120.4	119.8	119.3	120.1 (6)
(7, 8)	118.9	118.7	117.6	117.3	118.9	118.3 (8)
(7, 9)	122.2	123.7	123.4	122.1	121.4	122.6 (10)

(1) 4,4'-Dimethylchalcone (present analysis). (2) 4-Methoxychalcone (Rabinovich & Schmidt, 1970). (3) Chalcone (Rabinovich, 1970). (4) 4'-Bromochalcone (Rabinovich, Schmidt & Shakked, 1973). (5) 4-Methylchalcone (Rabinovich, 1974).

longest molecular axis. The librational motion is highly anisotropic with the largest libration (6.95°) again about the long axis of the molecule.

Table 5. Results of rigid-body motion analysis

The eigenvectors of L and T are referred to the molecular system of inertia I (in terms of the corresponding direction cosines $\times 10^4$). The eigenvectors of I are referred to the reciprocal vectors a^* , b^* and c^* . Components of the origin shifts $\varrho(\varrho_1, \varrho_2, \varrho_3)$, referred to the molecular centroid are given in Å units.

Eigenvalues	Eigenvectors
308 (at. wt. Å ²)	14.761 1.477 0.074
3318	I 3.812 -5.717 0.233
3572	0.136 -0.083 -14.626
(6.95°)*	-9997 -207 -95
(1.70)	L -158 3273 9448
(1.20)	-165 9447 -3276
(0.23 Å)	-9995 326 11
(0.20)	T -152 -4369 -8994
(0.18)	-288 -8989 4371

$$\varrho(-0.37, 0.23, -0.03)$$

$$[\sum(\Delta U^{ij})^2 / (6n - s)]^{1/2} = 0.0065 \text{ Å}^2, (n = 18 \text{ and } s = 20)$$

* The corresponding r.m.s. amplitudes are given in parentheses.

Molecular packing

Fig. 3 shows a stereoscopic view of the packing arrangement along [010], drawn by the computer pro-

gram ORTEP (Johnson, 1965). The molecules are arranged in layers parallel to (001), the spacing between the layers being nearly uniform (3.7 Å). All molecules in any one layer are identically oriented as they are related by translations along [100] and [010], whereas molecules belonging to different layers are related by the screw axes. The molecular contacts are mainly of the type H...H and C...H.

Several experiments have been carried out in order to establish the various processes involved in gas/solid bromination. Buckles, Hausman & Wheeler (1950) claimed that the reaction of solids with bromine takes place on the surface of the crystal; Labes, Blakeslee & Bloor (1965) observed charge-transfer complexes of bromine with aromatic hydrocarbons prior to bromination; Hadjoudis, Kariv & Schmidt (1972) suggested that the difference between rates of addition to the double bond in polymorphic forms or in closely related

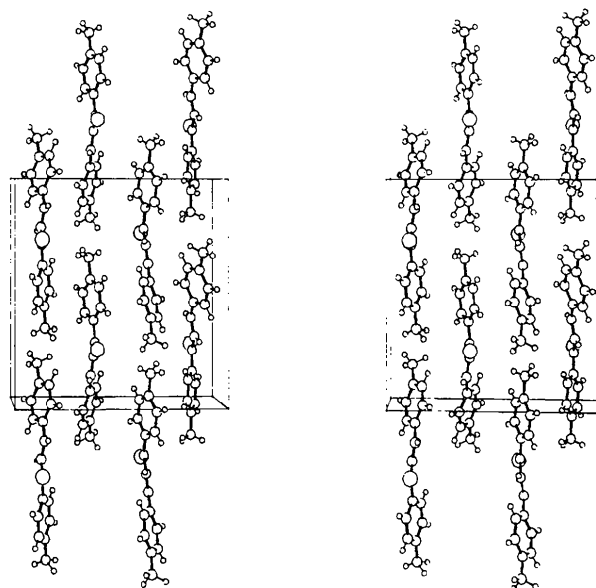


Fig. 3. Stereoscopic view of the packing arrangement along the b axis. The origin of the unit cell is in the top left-hand corner with the a axis vertical and c axis horizontal.

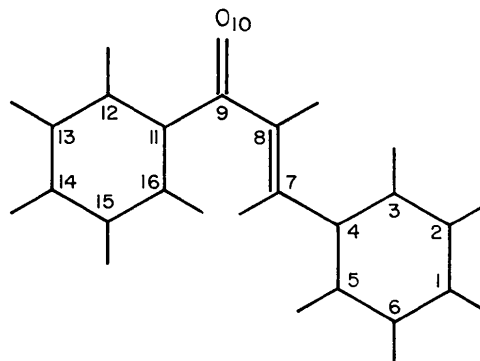


Fig. 4. Transoid conformation of chalcone skeleton.

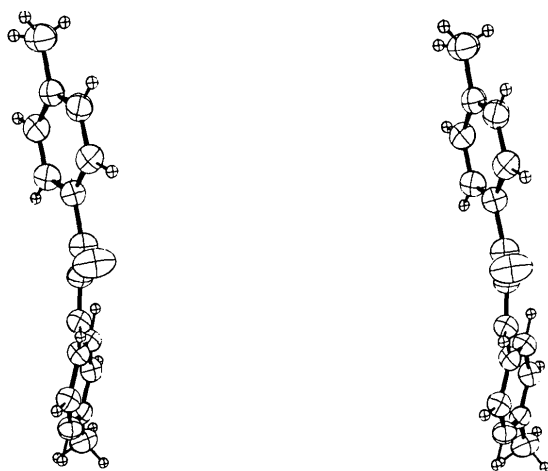


Fig. 5. Stereoscopic view of the molecule seen edge-on along the plane of the ethylenic bond.

compounds of solid α,β -unsaturated acids should be ascribed to differences in rates of diffusion into the crystal, which in turn, depend on the molecular packing. It is obvious from the molecular packing of (I)

that the accessibility of the $\begin{array}{c} \diagup \\ \text{C}=\text{C} \\ \diagdown \end{array}$ double bonds to

the attacking bromine is much less at (100) faces than at (010) and (001) faces. Therefore, the bromination process is probably anisotropic. Anisotropic behaviour of gas/solid reaction which results from the crystal packing has already been observed in the reaction of gaseous ammonia with crystalline benzoic acid derivatives (Miller, Curtin & Paul, 1971; Miller, Curtin & Paul, 1972). Nevertheless, the specificity of the reaction of (I) (leading to an optically active product) is not controlled by any possible anisotropic diffusion process since either molecular face is equally accessible to bromine along any direction, as can be seen from Fig. 3. An examination of the relative ease of access to a double bond shows it is slightly less impeded by neighbouring molecules on one side, but the extent of this bias can hardly be large. These observations virtually rule out the possibility that the specificity of the bromination reaction results from the molecular packing.

Molecular conformation

The molecule adopts the *cisoid* conformation in agreement with the majority of observed chalcone structures (Table 4), since this conformation is much more stable than the possible *transoid* conformation (Fig. 4) which is related to the former by a rotation of 180° about the C(8)–C(9) bond. The *transoid* conformation involves very close H...H and C...H contacts which may be relaxed by a large twist about the C(9)–C(11) bond at the expense of the conjugation energy of this system. However, this loss of conjugation energy may be compensated by an attractive inter-

action which may be achieved by a proper substitution at C(16), thus stabilizing the *transoid* conformation as is the case in 3-bromo and 3-chloro-2'-nitrochalcone (Jungk & Schmidt, 1970).

The phenyl rings are planar within 0.01 Å. The molecule as a whole deviates considerably from planarity in contrast to the majority of the analysed chalcone structures. This conformation results from considerable twists about all the single C–C bonds. The torsion angles about the single bonds are listed in Table 6 together with that of 4-methoxychalcone (II) (Rabinovich & Schmidt, 1970). The sense of rotation about the last two bonds in (I) is reversed to that in (II), thus leading to interplanar angles of 48.6° and 9.2° between the two phenyl rings in (I) and (II) respectively. The different chemical behaviour of (I) and (II) may be interpreted in terms of the different conformations.

Front- and rearside attacks of the $\begin{array}{c} \diagup \\ \text{C}=\text{C} \\ \diagdown \end{array}$ double

bond are equally favourable in the near planar 4-methoxychalcone whereas the marked non-planarity of 4,4'-dimethylchalcone differentiates between the two sides of the molecule as demonstrated by Fig. 5. Clearly, the tilted carbonyl and phenyl groups are blocking access to the double bond from the right, whereas access from the left is easier, thus leading to the observed optically active product.

Table 6. Torsion angles ($^\circ$)

	4,4'-Dimethylchalcone (I)	4-Methoxychalcone (II)
C(5)—C(4)—C(7)—C(8)	–15.8	–9.5
C(4)—C(7)—C(8)—C(9)	176.3	181.8
C(7)—C(8)—C(9)—O(10)	–13.1	2.8
O(10)—C(9)—C(11)—C(12)	–19.8	12.4

Although it may be argued that such examples suffice for the demonstration of the general principle of optical induction, there still exists the important problem of engineering predictable structure types having chiral packing and *prochiral* conformation. Except by the trivial method of the introduction of a chiral group (substituent, complex, etc.), the former has not so far found a solution in principle. However the prediction of molecular conformation in a certain crystal symmetry may be attacked by theoretical methods. An attempt has been made (Warshel, Huller, Rabinovich & Shakked, 1974) to reproduce the structures of 4,4'-dimethylchalcone, 4-methylchalcone (Rabinovich, 1974) and chalcone (Rabinovich, 1970), using the quantum mechanical extension of the consistent force field-scheme (Warshel & Karplus, 1972). An important conclusion which may be drawn from these calculations is that a substitution at the *para* positions of the phenyl rings of a flexible conjugated molecule which does not affect the conformation of the isolated molecule, may be used for achieving a desired conformation in the solid state due to crystal forces.

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Cristallochimie du Sélénium(+IV). I. VSe_2O_6 , une Structure à Trois Chaînes Parallèles $(VO_5)_n^{6n-}$ Indépendantes Pontées par des Groupements $(Se_2O)^{6+}$

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VSe_2O_6 , a new compound prepared by solid-state reaction, crystallizes as pale-green blocks. The unit cell is tetragonal with the dimensions: $a = 11.22$ and $c = 7.86$ Å; the space group is $P4cc$. The structure, determined by Patterson and Fourier methods, has been refined by least-squares procedures to an R of 0.041. The structure contains three independent $(VO_5)_n^{6n-}$ strings of octahedra sharing corners parallel to the [001] direction; the three strings are connected to each other by $(Se_2O)^{6+}$ groups. In the VO_5 octahedra the vanadium atoms are off-centred forming VO^{2+} vanadyl groups. The coordination of selenium(+IV) is 3, the lone pair E forming with the oxygen atoms a tetrahedron. $(Se_2O_5)^{2-}$ groups appear in this structure and their stereochemistry is compared with $(Sn_2F_5)^-$ groups of the double fluoride $NaSn_2F_5$.

Voici quelques années un travail d'ensemble était entrepris au laboratoire sur la cristallochimie des composés oxygénés du tellure(+IV) (Meunier & Galy, 1971; Galy & Meunier, 1971; Meunier, Darriet & Galy, 1972, 1973; Galy, 1972). L'activité stéréochi-

mique de la paire non liée $5s_5$ du tellure(+IV) a été analysée et son influence, au sein des nombreuses phases étudiées, précisée (Andersson, Åström, Galy & Meunier, 1973).

Il paraissait particulièrement intéressant d'étendre