Molecular structure and conformational analysis of chiral (−)-3-(4-bromobenzylidene)-1-isopropyl-2-methoxy-4-methylcyclohexene

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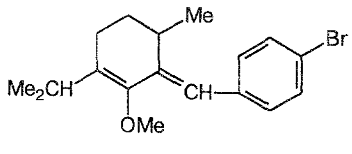
(−)-3-(4-Bromobenzylidene)-1-isopropyl-2-methoxy-4-methylcyclohexene, capable of inducing spiral supramolecular ordering when introduced to nematic and some smectic mesophases, has been studied by an X-ray structural analysis. The crystals are orthorhombic; at 20 °C a = 6.055(1), b = 13.282(3), c = 20.734(4) Å, V = 1668(1) Å^3, d_{calc} = 1.380 g cm^{-3}, space group $P2_12_12_1$, Z = 4. The cyclohexene ring has a conformation intermediate between a sofa and a half-chair. The methyl and methoxyl groups are in a *syn* orientation with respect to the mean plane of the cycle. The angle between the plane of the aryl substituent and the exocyclic double bond is 33°. The observed distortions of bond angles at unsaturated carbon atoms are typical of derivatives of benzylidenecyclohexene. Molecular mechanics calculations demonstrated that the conformation observed in the crystalline state is not the most favorable, and this conformation is stabilized through intermolecular interactions upon stacking in crystals. It was shown that the relative orientation of the methyl and methoxyl groups as well as the orientation of the aryl substituent substantially affect the conformation of the cyclohexene ring.

Key words: molecular structure, conformational analysis, crystal structure, X-ray structural analysis, molecular mechanics, (−)-3-(4-bromobenzylidene)-1-isopropyl-2-methoxy-4-methylcyclohexene.

Studies of molecular structures of the products of chemical modification of chiral cyclic ketone, (−)-menthone,[1–6] are important both for organic stereochemistry and in connection with the ability of these compounds to induce spiral supramolecular ordering when they are introduced to nematic and some smectic mesophases.[7,8] A quantitative characteristic of this effect, the twisting ability, substantially depends on the spatial molecular structure of chiral compounds[7,9,10]; however, the character of this relationship is still not clearly understood. Some regularities of the effect of the structure of chiral additives on the properties of liquid-crystalline systems were established based on the results of systematic studies of a series of (1*R*,4*R*)-2-arylidenementhan-3-ones.[7,10] The study of diastereisomeric *C*-alkylated derivatives of chiral additives of this type and of the products of *O*-alkylation of the corresponding enol forms containing an arylbutadiene fragment in an *s-trans* conformation, which is fixed by the cycle, is of importance for further elucidation of these regularities.

The aim of this work is to study the molecular and crystal structure of chiral (−)-3-(4-bromobenzylidene)-1-isopropyl-2-methoxy-4-methylcyclohexene (**1**) by an X-ray structural analysis and molecular mechanics.



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Compound **1** is a product of methylation of the enol form of (−)-2-(4-bromobenzylidene)-(−)-menthan-3-one (**2**), which is obtained by the reaction of (−)-menthone with 4-bromobenzaldehyde in a superbasic DMSO—KOH medium, with dimethyl sulfate.[10] The methylating reagent used and reaction conditions should favor *O*-methylation of enols.[11] The structure of the methylation product obtained for the first time was

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† Deceased.

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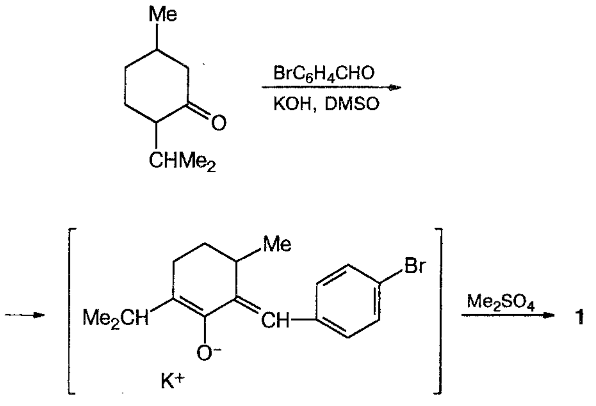

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Table 1. Bond lengths in the structure of **1**

Bond	*d*/Å	Bond	*d*/Å
Br(1)—C(15)	1.89(1)	C(5)—C(6)	1.50(1)
O(1)—C(2)	1.41(1)	C(7)—C(8)	1.52(2)
O(1)—C(10)	1.46(1)	C(7)—C(9)	1.51(2)
C(1)—C(2)	1.33(1)	C(11)—C(12)	1.48(1)
C(1)—C(6)	1.52(1)	C(12)—C(13)	1.37(1)
C(1)—C(7)	1.51(1)	C(12)—C(17)	1.40(2)
C(2)—C(3)	1.44(1)	C(13)—C(14)	1.40(1)
C(3)—C(4)	1.49(1)	C(14)—C(15)	1.38(2)
C(3)—C(11)	1.33(1)	C(15)—C(16)	1.37(2)
C(4)—C(5)	1.54(1)	C(16)—C(17)	1.37(1)
C(4)—C(18)	1.54(2)		

Table 2. Bond angles in the structure of **1**

Angle	φ/deg	Angle	φ/deg
C(2)—O(1)—C(10)	112.3(8)	C(1)—C(7)—C(8)	110.7(9)
C(2)—C(1)—C(6)	117.9(8)	C(1)—C(7)—C(9)	112.4(9)
C(2)—C(1)—C(7)	122.7(8)	C(8)—C(7)—C(9)	108.9(8)
C(6)—C(1)—C(7)	119.3(7)	C(3)—C(11)—C(12)	131.6(9)
O(1)—C(2)—C(1)	117.8(8)	C(11)—C(12)—C(13)	119.6(9)
O(1)—C(2)—C(3)	114.9(7)	C(11)—C(12)—C(17)	123.8(8)
C(1)—C(2)—C(3)	127.2(8)	C(13)—C(12)—C(17)	116.5(8)
C(2)—C(3)—C(4)	114.4(7)	C(12)—C(13)—C(14)	124.2(10)
C(2)—C(3)—C(11)	121.1(9)	C(13)—C(14)—C(15)	116.8(10)
C(4)—C(3)—C(11)	124.3(8)	Br(1)—C(15)—C(14)	119.4(8)
C(3)—C(4)—C(5)	110.5(8)	Br(1)—C(15)—C(16)	119.9(8)
C(3)—C(4)—C(18)	110.8(8)	C(14)—C(15)—C(16)	120.8(9)
C(5)—C(4)—C(18)	111.5(8)	C(15)—C(16)—C(17)	121.1(10)
C(4)—C(5)—C(6)	110.3(7)	C(12)—C(17)—C(16)	120.5(9)
C(1)—C(6)—C(5)	113.9(7)		

confirmed by the X-ray structural study (Fig. 1, Tables 1—3). The chiral center of this compound, as in the case of (−)-menthone[12] or 2-arylidenementhanones,[1] has an *R* configuration, *i.e.*, this center is not affected in the course of alkylation.

The conformation of the cyclohexene ring in molecule **1** may be characterized as an intermediate between a sofa and a half-chair; the puckering parameters[13] are as follows: s = 0.73, θ = 40.6°, and ψ = 20.3°. This is also evidenced by the values of φ_1—φ_6 torsion angles in the cycle (see Table 3) and the character of deviations of the atoms from the mean P_1—P_3 planes (Table 4).

The methyl group at the C(4) atom has a pseudoaxial orientation (the φ_7 torsion angle); the isopropyl substituent at the C(1) atom has a conformation with a *syn*-periplanar arrangement of the hydrogen atom at the C(7) atom and the C(1)=C(2) double bond (the φ_8 torsion angle). This mutual arrangement of the C—H and C=C bonds is typical of alkyl-substituted unsaturated compounds.[14] The methoxyl group at the C(2) atom is oriented perpendicular to the C(1)=C(2) bond (the φ_9 torsion angle) and is attached to the cyclohexene ring in a *syn* orientation with respect to the methyl

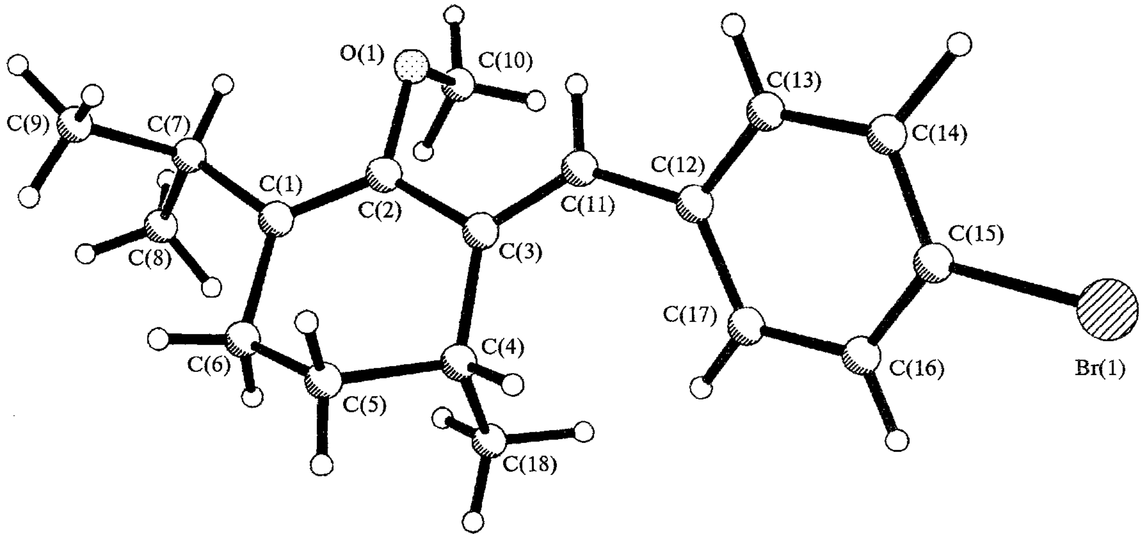


Fig. 1. Structure of molecule **1**.

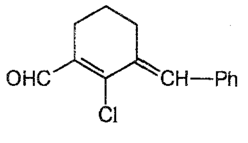
Table 3. Selected torsion angles in the structure of **1**

Torsion angle		φ/deg
C(1)C(2)C(3)C(4)	(φ_1)	6(2)
C(2)C(3)C(4)C(5)	(φ_2)	−38(1)
C(3)C(4)C(5)C(6)	(φ_3)	59(1)
C(4)C(5)C(6)C(1)	(φ_4)	−47(1)
C(5)C(6)C(1)C(2)	(φ_5)	16(1)
C(6)C(1)C(2)C(3)	(φ_6)	6(2)
C(2)C(3)C(4)C(18)	(φ_7)	86(1)
H(7)C(7)C(1)C(2)	(φ_8)	2(1)
C(1)C(2)O(1)C(10)	(φ_9)	−89(1)
C(1)C(2)C(3)C(11)	(φ_{10})	−168(1)
C(3)C(11)C(12)C(17)	(φ_{11})	33(2)

group at the C(4) atom (see deviations of the C(10) and C(18) atoms from the mean P_1—P_3 planes, Table 4).

The conjugated arylbutadiene system in molecule **1** is nonplanar (the φ_{10} and φ_{11} torsion angles), which is, apparently, determined by shortened intramolecular contacts H(18a)...H(17) 2.03(2) Å (the sum of the van der Waals radii is 2.32 Å [15]), H(17)...H(4) 2.20(2) Å, H(17)...C(4) 2.68(2) Å (2.87 Å), and C(17)...C(4) 3.21(2) Å (3.42 Å). Apparently, these shortened contacts determine the increased values of the bond angles about the sp^2 carbon atoms of the diene fragment: C(1)—C(2)—C(3) 127.2(8)°, C(4)—C(3)—C(11) 124.3(8)°, and C(3)—C(11)—C(12) 131.6(8)° (see Table 2).

Analogous deformations of bond angles are also typical of other benzylidenecyclohexenes with two substituents at the double bond (for example, **3** [16]). These deformations were also found in the structures of *E*-2-benzylidene-6-benzylcyclohexanone (**4**) [17] and different arylidene derivatives of diastereoisomeric *p*-menthan-3-ones (**5a,b**).[1,4,5]



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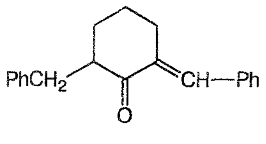

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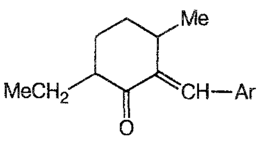
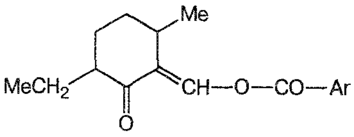


5a: 1*R*, 4*S*
5b: 1*R*, 4*R*

A comparison of the geometrical structures of **1**, **3**—**5** demonstrates that the observed deformations of bond angles result from nonbonded interactions between the aryl group of the benzylidene fragment and the α-hydrogen of the cyclohexane ring. In molecules **6a,b**, in which the aryl group is separated from the exocyclic double bond by an ester bridge, deformations of this type are virtually absent.[2,3]



6a: 1*R*, 4*S*
6b: 1*R*, 4*R*

The above-mentioned unfavorable nonbonded interactions cause a pseudo-axial orientation of the methyl group at the C(4) atom. Molecular mechanics calculations (Table 5) demonstrate that the energy of the most stable conformer of compound **1** with a pseudo-axial orientation of this substituent is 1.09 kcal mol^{-1} lower

Table 4. Deviations of atoms (Å) from the calculated mean P_1—P_3 planes in the crystal (X-ray structural analysis) and in the energetically most favorable conformers A and B (based on the results of calculations)

Atom	X-ray structural analysis			Conformer A			Conformer B		
	P_1	P_2	P_3	P_1	P_2	P_3	P_1	P_2	P_3
C(1)	−0.01*	0.02*	0.07*	0.01*	0.02*	0.01*	−0.02*	0.00*	0.03*
C(2)	−0.03*	−0.02*	0.00*	−0.02*	−0.02*	−0.02*	0.04*	0.00*	0.03*
C(3)	−0.02*	0.01*	−0.07*	0.01*	0.01*	0.01*	−0.04*	0.00*	−0.06*
C(4)	0.01*	0.26	0.07*	−0.01*	−0.01	0.00*	0.02*	0.18	0.03*
C(5)	−0.81	−0.47	−0.64	−0.67	−0.66	−0.65	−0.72	−0.51	0.03
C(6)	−0.27	−0.01*	−0.07*	−0.02	−0.01*	−0.01*	−0.15	0.00*	0.03*
C(7)	0.09	0.02	0.19	0.09	0.10	0.09	0.08	0.02	0.03
C(10)	1.65	1.32	1.48	−1.27	−1.27	−1.28	1.46	1.25	0.03
C(11)	−0.22	−0.29	−0.38	0.13	0.11	0.12	−0.07	−0.10	0.03
C(18)	1.47	1.78	1.56	1.42	1.42	1.43	1.48	1.68	0.03
O(1)	0.23	−0.02	0.10	−0.04	−0.04	−0.05	0.18	0.02	0.03

* Atoms through which the mean planes pass.

Table 5. Relative stability and selected geometric parameters of conformers of compound **1**

Conformer	ΔE /kcal mol^{-1}	Torsion angles /deg			Puckering parameters		
		φ_9	φ_{11}	φ_8	s	θ /deg	ψ /deg
A	0	94.9	−58.1	7.4	0.71	42.9	0.03
B	0.39	−95.1	−57.3	4.3	0.72	35.3	14.3
C	0.63	−100.5	35.4	5.4	0.75	36.6	27.1
D	1.54	86.5	29.0	5.2	0.73	41.5	16.9
E	1.90	−112.0	−53.8	−170.2	0.76	34.4	21.3
F	2.40	100.1	−54.8	145.9	0.71	45.6	0.3
G	2.43	−100.4	−55.9	−145.9	0.75	33.7	23.8
H	3.39	106.5	−53.6	−138.0	0.71	45.4	4.0
I	1.09	−97.9	−46.3	−6.9	0.73	52.7	20.3
J	2.09	88.8	−46.3	−2.1	0.73	43.6	18.0

Note. In conformers A—H, the methyl group at the C(4) atom has a pseudo-axial orientation; in conformers I and J, this group has a pseudo-equatorial orientation.

than that of the analogous conformer with a pseudo-equatorial orientation of the methyl group. An axial or pseudo-axial orientation of the methyl group was established also for the structures of **5** and **6**.[1,4–6]

Of note is a substantial increase in the endocyclic bond angle at the C(2) atom (see Table 2), which cannot be directly associated with the above-mentioned nonbonded interactions between atoms of the substituent at the C(3) and C(4) atoms. This deformation of the cycle may be caused by the fact that a decrease in unfavorable nonbonded interactions H(11)...O(1) 2.30(2) Å (the sum of the van der Waals radii is 2.45 Å [15]) and O(1)...H(7) (2.34(2) Å) is achieved in this case.

In the conformation of molecule **1** experimentally observed in the crystal, the benzene ring is noncoplanar with the exocyclic double bond and is rotated so that the H(17) atom in the *ortho* position is located between the substituents at the C(4) atom, *i.e.*, between the methyl group and the hydrogen atom. An analogous orientation of the aryl group is typical also of compounds **3**—**5** and is common for the structures containing the *cis*-β-alkylstyrene fragment.[14]

According to the results of molecular mechanics calculations (see Table 5), the conformation of molecule **1**, which is observed in the crystal, with the above-mentioned puckering parameters is not the most favorable for an "isolated" molecule. Conformer A has the lowest conformational energy; this conformer differs from that observed in the crystal by a mutual orientation of methoxyl and methyl (at the C(4) atom) groups with respect to the cyclohexene ring (the φ_9 angle) as well as by the angle of rotation of the aryl group (the φ_{11} angle). In this conformer, the methoxyl and methyl groups are in an *anti* orientation with respect to the cyclohexene ring, unlike their *syn* orientation in the crystal (see Table 4, deviations of the C(10) and C(18) atoms from the P_1—P_3 planes). The hydrogen atom in one of the *ortho* positions of the benzene ring is located not between the axial methyl group at the C(4) atom and the equatorial H(4) atom as in the crystal, but approaches the H(4) atom from the outward of this fragment. The structure of **1** actually observed in the crystal most closely corresponds to the calculated conformation C (see Tables 3 and 5), the energy of which is 0.63 kcal mol^{-1} higher than that of conformer A. However, the minimum on the potential energy surface, which corresponds to conformation C, is, apparently, shallow, and the conformation of the molecule readily changes to conformer B, which differs by an angle of rotation of the benzene ring (see Table 5).

Apparently, intermolecular interactions are the reason for the stabilization of conformer C in the crystal. In the crystal, molecules **1** form stacks along the X axis (Fig. 2). The energy of the interaction of the basis molecule with two neighboring molecules within the stack calculated by the atom-atom potential method[18] is −5.42 kcal mol^{-1} and with the molecules of adjacent stacks is no more than −3.56 kcal mol^{-1}. This mode of packing in the crystal structure of **1** requires a maximum flattening of molecules, which is realized in conformer C.

According to general stereochemical knowledge, the cyclohexene ring in structures of type **1** may adopt conformations intermediate between a sofa and a half-chair, which differ by the degree of twisting. Possible conformations are very difficult to compare on the basis of torsion angles and deviations of atoms from the mean P_1—P_3 planes. Therefore, we used the puckering parameters s, θ, and ψ,[13] where s is the degree of puckering and θ and ψ are polar angles that characterize the type of conformation of the cycle, to characterize the conformation of the cyclohexene ring. For an ideal sofa conformation, $\theta = 45°$ and $\psi = 0°$; for an ideal half-chair conformation, $\theta = 45°$ and $\psi = 45°$.

The results of conformational analysis by the molecular mechanics method provide evidence that in the energetically most favorable conformer A, the cyclohexene ring has a sofa conformation (see Tables 4 and 5), which is reasonable for structures containing three sp^2 hybridized carbon atoms in the six-membered

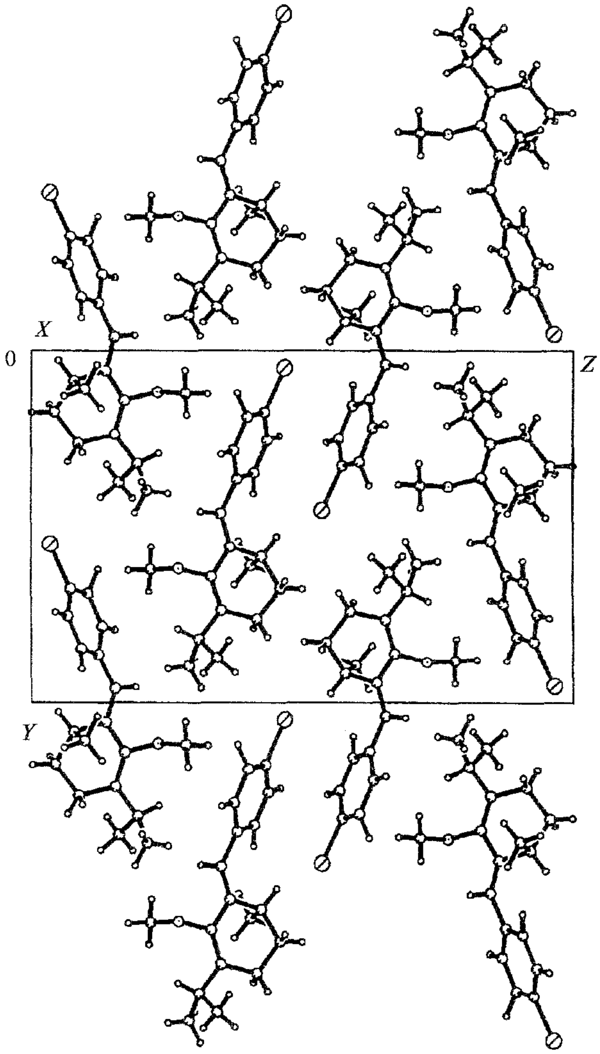


Fig. 2. Crystal packing of molecules **1** (projection onto the Y0Z plane).

cycle. A comparison with other possible conformers makes it possible to establish the factors that determine the occurrence of twisting of an equilibrium conformation of the cycle. The primary and, apparently, the main factor is the presence of nonbonded interactions between methoxyl and methyl groups in the *syn* orientation with respect to the cycle (for example, in conformation B). Another essential factor is the orientation of the benzene ring. When the orientation of this ring is similar to that observed in the crystal, the nonbonded interactions between the hydrogen atom in one of the *ortho* positions and the fragment of the cycle in the α position with respect to the arylidene fragment also cause twisting of the cycle (see the puckering parameters of conformers A, D and B, C, Table 5). A change in the orientation of the isopropyl substituent with respect to the endocyclic double bond have no substantial effect on the equilibrium conformation of the cyclohexene ring and results only in a change in the conformational energy of molecule **1** (see conformers A, F, H and B, E, G, Table 5).

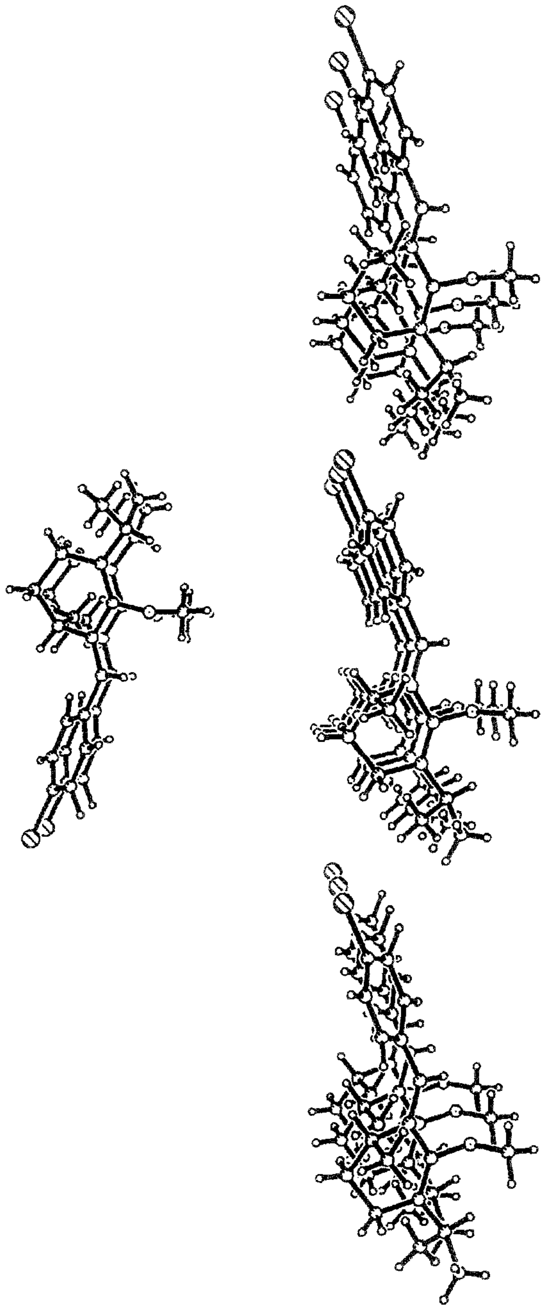


Fig. 3. Overall view of stacks formed by molecules **1** in the crystal.

Experimental

Preparation of (−)-3-(4-bromobenzylidene)-1-isopropyl-2-methoxy-4-methylcyclohexene. Powdered KOH (0.7 g) was added to a solution of (−)-menthone (5 mL) in 5 mL of DMSO at 15—18 °C; the mixture was stirred for 0.5 h, and then a solution of 4-bromobenzaldehyde (5.6 g) in 10 mL of

Table 6. Atomic coordinates of nonhydrogen atoms ($\times 10^4$) in the structure of **1**

Atom	*x*	*y*	*z*
Br(1)	−4959(3)	−478(1)	−350(1)
O(1)	−8658(13)	−6156(4)	−2306(3)
C(1)	−7687(17)	−7357(6)	−1525(4)
C(2)	−7724(17)	−6393(6)	−1701(4)
C(3)	−6779(17)	−5550(6)	−1361(4)
C(4)	−5442(18)	−5832(6)	−785(4)
C(5)	−6516(19)	−6722(6)	−427(4)
C(6)	−6733(19)	−7612(6)	−869(4)
C(7)	−8674(18)	−8187(6)	−1933(5)
C(8)	−6929(22)	−8956(8)	−2112(5)
C(9)	−10563(20)	−8720(9)	−1597(6)
C(10)	−7033(23)	−6185(8)	−2824(4)
C(11)	−7268(17)	−4608(6)	−1525(5)
C(12)	−6650(19)	−3628(6)	−1233(4)
C(13)	−8038(20)	−2818(6)	−1296(4)
C(14)	−7619(22)	−1865(8)	−1037(5)
C(15)	−5634(21)	−1738(7)	−720(5)
C(16)	−4163(18)	−2521(7)	−666(4)
C(17)	−4631(19)	−3451(6)	−919(5)
C(18)	−3036(18)	−6072(7)	−979(5)

DMSO was added dropwise. Then powdered KOH (1.3 g) was added to the mixture, the mixture was stirred for 2 h at 15—18 °C, and dimethyl sulfate (4 mL) was added dropwise. The temperature of the reaction mixture was raised to 30 °C, and the mixture was stirred for 10 min and diluted with 200 mL of a 5 % Na_2CO_3 solution. The solid precipitate was filtered off, washed with water, and recrystallized from 70 mL of MeOH. The product was homogeneous (TLC on Silufol UV-254, benzene); its yield was 5.4 g, m.p. 65—67 °C, $[\alpha]_D^{18}$ −336°. IR (KBr, ν/cm^{-1}): 1620 and 1605 (weak bands, νC=C, νAr). Crystals suitable for X-ray structural analysis were obtained by double recrystallization from MeOH, m.p. 67—68 °C.

X-ray structural study. Crystals of **1** ($C_{18}H_{21}OBr$) are orthorhombic. At 20 °C, a = 6.055(1), b = 13.282(3), c = 20.734(4) Å, V = 1668(1) Å^3, d_{calc} = 1.380 g cm^{-3}, space group $P2_12_12_1$, Z = 4. The unit-cell parameters and intensities of 1148 reflections with $F > 6\sigma(F)$ were measured on an automated four-circle Siemens P3/PC diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique, $2\theta_{max}$ = 60°). An absorption correction was applied with the use of the DIFABS program.

The structure was solved by the direct method with the use of the SHELXTL PLUS program package.[19] Methyl hydrogen atoms were located from the difference electron density synthesis; the remaining hydrogen atoms were calculated geometrically. All hydrogen atoms were refined using a riding model with fixed U_{iso} = 0.08 Å^2. An absolute configuration was determined by refinement of the direct and inverted structures (the difference in the R values was 0.01). The full-matrix least-squares refinement with anisotrpopic temperature factors for nonhydrogen atoms converged to R = 0.065 (R_w = 0.063, s = 2.92). Atomic coordinates of nonhydrogen atoms are listed in Table 6.

The spatial structure of isolated molecule **1** was calculated by the molecular mechanics method[20] with the MMX force field[21] using the PCMODEL program.

The energy of intermolecular interactions in the crystal was estimated by the atom-atom potential method[18] using the NONVPOT program.[22]

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