New steroid α,β-unsaturated ketones as chiral components of induced cholesteric liquid crystal systems*

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New (*E*)-16-arylidene derivatives of 3β-hydroxyandrost-5-en-17-one and their acetates containing different substituents in the arylidene fragment were synthesized. The ability of the synthesized chiral compounds to induce helical supramolecular ordering (their helical twisting power) upon the introduction into the nematic liquid crystal (LC) 4-cyano-4′-pentylbiphenyl (5CB) and into multicomponent mixtures E63 and LC-1289 characterized by a wide mesophase interval. The dependence of the helical twisting power of the studied chiral additives (CAd) on their molecular structure was analyzed. The highest helical twisting power (44.6—67.1 μm^{-1}) was revealed for the synthesized acetates. It was found that the composites based on LC-1289 and E63 containing the studied CAd in very low concentrations (≤10—11 mol.%) have selective light reflection in the visible spectral region. The helical twisting power of the studied α,β-unsaturated ketones is determined by the combined influence of the anisotropy of polarizability of CAd molecules and specific features of their molecular shape.

Key words: 3β-hydroxy-5-androsten-17-one (*E*)-16-arylidene derivatives, steric structure, liquid crystals, chiral additives, helical twisting power, selective light reflection.

It is known that chiral compounds based on natural steroid structures (numerous cholesterol esters with aliphatic and aromatic carboxylic acids) exhibit the mesomorphic properties, forming the cholesteric (Chol) and Chol and/or smectic A* (SmA*) mesophases.[1,2] At the same time, steroid compounds (both mesogenic and possessing no intrinsic mesomorphic properties), being introduced to the nematic mesophase, can induce the formation of a helical supramolecular structure (see, *e.g.*, Ref. 3). In materials science of liquid crystals (LC), the chiral compounds with this ability were named chiral additives (CAd). The helical twisting power (β) is a quantitative characteristic of the efficiency of the CAd effect in the LC systems.[4,5] In the most part of cholesterol esters this ability is manifested in the intrinsic mesophase, providing the formation of the supramolecular helix, whose pitch corresponds to selective light reflection in the visible spectral region.[2] Particular cholesterol esters CholOCOAlk (Alk = $C_{15}H_{31}$ and $C_{16}H_{33}$) were studied[3] as chiral additives to nematic 4-*n*-butoxyphenyl 4-*n*-hexyloxybenzoate (LC ZLI 1792, Merck, Germany). When these CAd are introduced into the nematic LC, their helical twisting power by the absolute value does not exceed 15 μm^{-1}. The low helical twisting power ($|\beta_{mol}| = 4.4\ \mu m^{-1}$) was revealed for cholesterol nonanoate in the nematic systems ZLI-4792 and MLC-6260 (Merck). The $|\beta_{mol}|$ value of the cholesterol derivatives containing the difluoroxymethylene bridging group in the same LC systems is still lower (<0.05 μm^{-1}).[6]

The strong helical twisting power of the steroid compounds with the unusual molecular shape was reported.[7] Molecules of compounds of this type, namely, diastereomeric dimeric steroid derivatives of 2,6,9-trioxabicyclo[3.3.1]nonanes, contain the angular quasi-planes.** In one of the studied diastereoisomers (with the concave surface, *concave*) these quasi-planes form an angle of 65°, and in the second (planar) diastereoisomer this angle is 165°. It was shown that the sizes and orientation of the

* Dedicated to Professor S. V. Tsukerman (1909—1985) on his 100th birthday.

** Molecular fragments of the nearly planar structure arranged at a certain angle to each other are implied.

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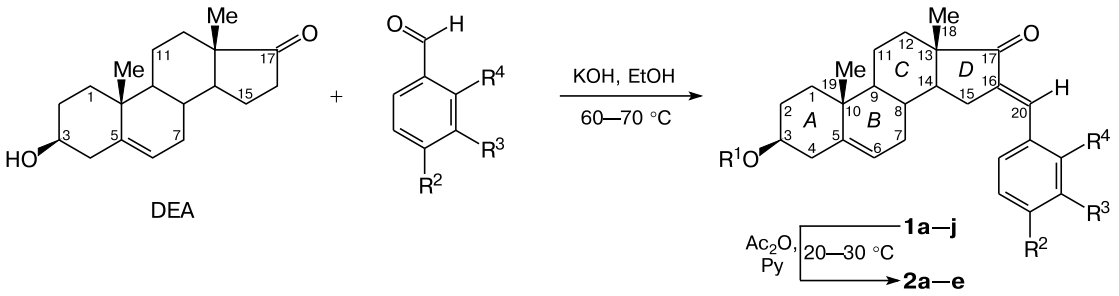
Scheme 1



DEA is dehydroepiandrosterone; R^1 = H (**1**), Ac (**2**); substituents R^1—R^4 for all compounds studied are given in Table 1.

quasi-planes affect considerably the helical twisting power of the chiral compounds. It was also found that an increase in the size of the 3β-substituent enhances the twisting effect of the compounds (3-H < 3-Me < 3-OBz).

At the same time, the studies of various non-steroid CAd (see, *e.g.*, Refs 5 and 8—14), including those containing the enone fragments,[5,8—10,13] made it possible to formulate some structural criteria that determine the ability of chiral compounds to efficiently induce the helical supramolecular ordering upon the introduction into the nematic LC. It was revealed that an important role belongs to the presence in CAd molecules of a highly polarized π-electronic system, including that fixed by the saturated cycle of the *s-cis*-enone group or its enhydrazone analog >C=C—C=N—N< (see Refs 8, 10, 12, 13, and 15). Nevertheless, the role of various structural features of chiral molecules as factors determining their helical twisting power in mesophases is studied incompletely. There are contradictory data on the influence of orientation of the alkyl substituent (for example, the Me group at the chiral center[8,10,13]) on the twisting effect of the additives.

In order to study the factors affecting the helical twisting power of the CAd, we synthesized new chiral α,β-unsaturated ketones, *viz.*, 16-arylidene derivatives of 3-hydroxyandrost-5-en-17-one (**1a—j**) and their acetates (**2a—e**) (Scheme 1, Table 1). The synthesized compounds were studied as potential twisting additives to the LC systems.

Interest in these compounds is due to a combination in their molecules of the structural carrier of chirality (steroid androstene skeleton) and the arylidene group with the *s-cis*-enone fragment (fixed five-membered ring). It can be expected that the study of compounds with this structure would allow one to extend concepts about the influence of the steric structure of molecules of these CAd on their helical twisting power in the mesophases. It is of special interest to compare the effect of the size and geometry of the aliphatic cycle fixing the configuration of the cinnamoyl motive (the six-membered ring in the structures based on 3*R*-methylcyclohexanone[9,10,12,13] and *p*-menthan-3-ones[5,8] and the five-membered ring in unsaturated ketones studied in the present work). It is also important to obtain information on the influence of the orientation of methyl substituents relative to the basal plane of the steroid ring on the efficiency of twisting in the mesophase. The positive influence of the Me group in the axial position on the twisting properties of the CAd was observed for α,β-unsaturated ketones and *p*-menthan-3-one and *p*-menth-4-en-3-one derivatives.[5,8] At the same time, the high helical twisting power of *Z*-isomers of 3*R*-methylcyclohexanone arylidene derivatives,[16] which exist in the "chair" conformation and containing the methyl substituent in the equatorial position, was found.[17]

It can be expected that an information on the influence of the molecular polarizability of chiral additives would be provided by the comparison of the helical twist-

Table 1. Helical twisting power (β_{mol}) of CAd **1** and **2** in the nematic matrix 5CB

CAd	R^1	R^2	R^3	R^4	$\beta_{mol}/\mu m^{-1}$
1a	H	OMe	OMe	H	−38.7±1.0
1b	H	OMe	H	OMe	−34.4±1.7
1c	H	H	OMe	OMe	−33.6±1.2
1d	H	OMe	CH_2OMe	H	−34.2±0.9
1e	H	$OCHF_2$	OEt	H	−32.2±1.1
1f	H	$OCHF_2$	OMe	H	−29.0±1.1
1g[a]	H	$OCHF_2$	OMe	H	−6.2±0.3
1h	H	Ph	H	H	6.1±0.8[b]
1i	H	OMe	OMe	OMe	−20.3±0.3
1j	H	OC_9H_{19}	H	H	5.6±0.5[b]
2a	Ac	OMe	OMe	H	−60.8±1.9
2b	Ac	H	OMe	OMe	−60.9±1.6
2c	Ac	OMe	CH_2OMe	H	−67.1±0.7
2d	Ac	OMe	OMe	OMe	−44.6±0.5
2e	Ac	$OCHF_2$	OMe	H	−48.1±0.5
CholA[c]					−11.8±0.4

[a] Compound **1g** contains no double bonds in the steroid skeleton.
[b] The sign of β was not determined.
[c] Cholesterol acetate.

ing power of the compounds with the double bond in cyclohexane ring *B* of the steroid skeleton and without it. Finally, the variation of the character of substituents and their positions in the benzene ring changing the shape of the additive molecules would make it possible to monitor the effect of this very important factor on the properties of the LC systems including the CAd under study.

The helical twisting power of CAd **1** and **2** was studied in solutions of nematic 4-cyano-4´-pentylbiphenyl (5CB) at relatively low concentrations (0.01—0.02 mole fractions) with the purpose of revealing the fundamental regularities of the influence of the molecular structure on the efficiency of the twisting effect of CAd. In addition, in the case of the CAd with the maximum $|\beta_{mol}|$ values, the search for possibilities of preparation of LC compositions selectively reflecting light in the visible spectral region at moderate concentrations (~10 mol.%) of additives is practically significant. For this study we chose the multicomponent mixtures LC E63 (Merck) and LC-1289 (Moscow Scientific Industrial Joint Enterprise "NIOPIK") characterized by a wide temperature mesomorphic interval.

According to the existing concepts (see, *e.g.*, Refs 5, 8, 10, and 11), the most important molecular factors determining the efficiency of formation of the supramolecular helix in the mesophase upon the introduction of the CAd are the molecular polarizability (its anisotropy and chirality) and the shape of the additive molecules. The theoretical simulation in the framework of the semiempirical AM1 method[18] was performed to elucidate the molecular shape of the CAd of the studied type. It was shown for a series of chiral carbocyclic compounds (see, *e.g.*, Ref. 17) that the simulation results are adequate to the experimental data.

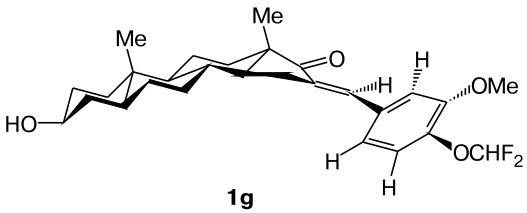
Results and Discussion

Synthesis and identification of 3β-hydroxyandrost-5-en-17-one 16-arylidene derivatives. New α,β-unsaturated ketones **1** containing the hydroxy substituent at the 3β-carbon atom were synthesized by the condensation of 3β-hydroxyandrost-5-en-17-one (DEA) with aromatic aldehydes in an alkaline medium by analogy to the earlier described procedure[19] (see Scheme 1). The corresponding 3β-acetoxy derivatives **2** were synthesized by the acetylation of hydroxy compounds **1** with acetic anhydride in pyridine.

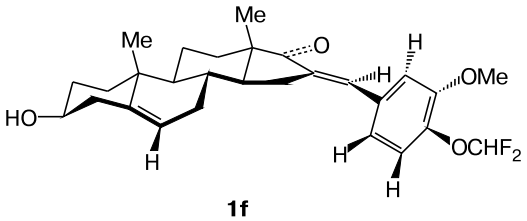
The individual character of the synthesized compounds and their composition were confirmed by the results of HPLC and mass spectrometry. Their structure follows from the ^{1}H NMR and IR spectra. The structures of the obtained compounds contain the arylidene group, which is manifested by the presence in the ^{1}H NMR spectra of multiplets of aromatic protons at 6.46—7.77 ppm corresponding to the character of substitution in the benzene ring. The characteristic singlet signal of the arylidene proton $=CH_\beta$ (δ 7.37—7.82) is also identified in this region. In addition, the spectrum of each synthesized compound exhibits signals belonging to the corresponding substituents R^2, R^3, or R^4 in the benzene ring.

The signals of the protons OH, MeCOO, H(3), H(4), H(6), H(14), and H(15) and the groups 18-Me and 19-Me were identified on the basis of analysis of their multiplicity and comparison with the literature data for similar compounds.[20] The modification of the cyclopentane ring by the cinnamoyl fragment insignificantly affects the signals of other protons of the steroid skeleton of the compounds under study.

Steric structures of androst-5-en-17-one 16-arylidene derivatives. Specific features of the steric structure of the studied 16-arylidene derivatives were characterized on the basis of the results of their AM1 simulation and ^{1}H NMR spectra. The results of simulation of structure **1g** of the 5α-androstane series compared to the corresponding Δ^5-derivative **1f** indicate the substantial difference in the conformations of their rings *B*. In the case of compound **1g** with the saturated skeleton including rings *A*—*C*, all the three cycles have the "chair" conformation with approximately the same ensocyclic torsion angles (φ = 55.0—58.3°) close to those in the unsubstituted cyclohexane molecule, namely, 55.9° (see Ref. 21) and 54.5° (see Ref. 22), and lying almost in one plane.



1g



1f

According to the simulation results, if the molecules of the studied compounds contain the C(5)=C(6) double bond, six-membered cycle *B* takes the "half-chair" conformation with the substantially flattened fragment C(10)C(5)C(6)C(7) (structure **1f**). The appreciable change in the geometry compared to saturated structure **1g** follows from the simulation results for ring *A* as well (decrease in the torsion angles in the region adjacent to the cyclohexene fragment). The presence of the C(5)=C(6) double bond affects the geometry of cycle *C* to relatively

lesser extent. In addition, the change in the geometry of ring *B* induces a noticeable turn of cycle *C* relative to cycle *A* (by 12—14°) in structure **1f**. This imparts somewhat twisted shape to the system of rings of the steroid skeleton, which makes a certain contribution to its chirality. A similar situation is observed in the structure of the estrone 16-benzylidene derivative (according to the results of our simulation, the turn angle of cycle *C* relative to benzene ring *A* is 8°). The results of the X-ray diffraction study of this compound indicate some turn of ring *C* relative to cycle *A*.[23]

As a whole, the steric structure of the fragment of the CAd under study, including the cyclohexane (*A* and *C*) and cyclohexene (*B*) rings in the consecutive *trans—trans*-fusion, and the equatorial 3β-orientation of the hydroxy group are analogous to those for cholesterol and its esters (see, *e.g.*, X-ray diffraction data[24]). This three-ring system along with annelated five-membered ring *D* has the anisotropic quasi-plate shape with the angular methyl groups 18-Me and 19-Me. The presence of the highly polarized double bond C(5)=C(6) in this fragment undoubtedly favors the dispersion attraction between the CAd and surrounding molecules of the nematic solvent.

The cinnamoyl group in the studied CAd has the *E*-configuration according to the NOESY results for ketone **1i**. The multiplet of *ortho*-protons with the center at δ 7.6 is characterized by the correlation peak with the signals of protons at the C(15) atom, which makes it possible to assign the compounds studied to *E*-isomers. No higher-field signal of the arylidene proton, which is characteristic of the *Z*-isomers and appears usually at 6.3—6.5 ppm,[17,25,26] is observed in the spectra of these compounds. Evidently, according to the earlier established regularities (see, *e.g.*, Ref. 17), the *Z*-isomers of the studied α,β-unsaturated ketones are characterized by considerably higher energies due to the substantial steric strain between the O atom of the carbonyl group and the aryl group.

In the studied compounds, the *s-cis*-enone group is fixed by five-membered ring *D*. This exocyclic enone group is only somewhat twisted relative to the ordinary bond C(16)—C(17): according to the simulation results, the torsion angle O=C(17)—C(16)=C(20) (φ_{en}) is 4—10° (Table 2). Nevertheless, this twisting can be very important for inducing the helical supramolecular structure in the mesophase due to its stereospecific character: the sign of this torsion angle (plus) is unambiguously determined by the configuration of the rigid steroid skeleton and remains unchanged upon the variation of substituents R^2, R^3, and R^4 in the aryl group.

The steric structure of the arylidene fragment of the studied compounds is characterized, on the one hand, by the degree of acoplanarity of the benzene ring and double bond (torsion angle φ_{Ar}, see Table 2), and on the other hand, by steric strain between the H atoms in the *ortho*-position of this ring and at the C(15) atom. In the general case, according to the simulation results, for the *ortho*- and *meta*-substituted compounds the rotation of the aromatic ring gives four alternative rotamers differed by values of the torsion angle φ_{Ar}. These structures differ from each other, on the one hand, by the remote or approached arrangement of substituents R^3 and R^4 relative to the steroid skeleton (Fig. 1, *a* and *b* or Fig. 1, *c* and *d*, respectively) and, on the other hand, by their arrangement "above" (see Fig. 1, *a*, *d*) or "under" the skeleton (see Fig. 1, *b*, *c*). The mutual transformations of these rotamers affect the random molecular shape of the CAd and its anisometry depending on the number of size of the *ortho*- and *para*-substituents.

Table 2. Energy characteristics (ΔE/kcal mol^{-1}) and selected torsion angles (φ_{en}, φ_{Ar}/deg) for probable conformers of compounds **1** and **2** according to the AM1 calculations

CAd	ΔE	φ_{en}	φ_{Ar}
1a	0.81	7.0	51.6
	0	3.5	−33.6
1b	0.88	10.3	48.9
	0	3.7	−29.9
	2.01	6.7	62.2
	2.06	8.9	−54.6
1c	0.55	10.2	51.3
	0	3.0	−35.2
	1.68	5.7	65.0
	1.16	8.7	−57.4
1d	0.74	7.8	51.1
	0	4.0	−31.7
1i	0.70	9.8	46.4
	0	4.7	−27.8
	1.90	6.6	62.6
	1.63	8.8	−56.3
2a	0.78	8.5	52.8
	0	4.0	−32.0
2b	0.55	10.3	50.7
	0	4.2	−31.7
	1.67	5.8	65.1
	0.98	8.9	−59.2
2c	0.73	8.2	51.1
	0	4.5	−29.9
2d	0.69	9.8	47.6
	0	4.2	−29.0
	1.92	6.4	62.7
	1.65	8.7	−56.1
2e	0.68	8.1	54.4
	0	4.7	−30.0

By analogy to some other chiral α,β-unsaturated ketones (see, *e.g.*, Ref. 27), for the compounds with R^4 = H, using CAd **1a**, **1d**, **1f** and **2a**, **2c**, **2e** (see Table 2) as examples, we consider two main types of rotamers at the arylidene group: with the negative value of the torsion angle φ_{Ar} (type **A**) and with the positive φ_{Ar} value (type **B**). The rotamers of the first type in which the φ_{Ar} angle varies from −33.6° to −29.9° are energetically more favorable. For energetically less favorable rotamers of type **B** the positive φ_{Ar} angle ranges from 51.1° to 56.3°. It is regularly that rotamers **A** have the more flattened enone group (φ_{en} = 3.5—4.7°). Flatter rotamers **A** are energetically more preferential due to more favorable (compared to rotamers **B**) possibilities of double bond conjugation with the aryl group.

The energy differences of the rotamers are more considerable in the presence of the methoxy substituent in the *ortho*-position of the benzene ring (R^4 = OMe) of the studied ketones (see Table 2, compounds **1b**, **1c**, **1i**, **2b**, and **2d**). It is characteristic that the rotamers with higher

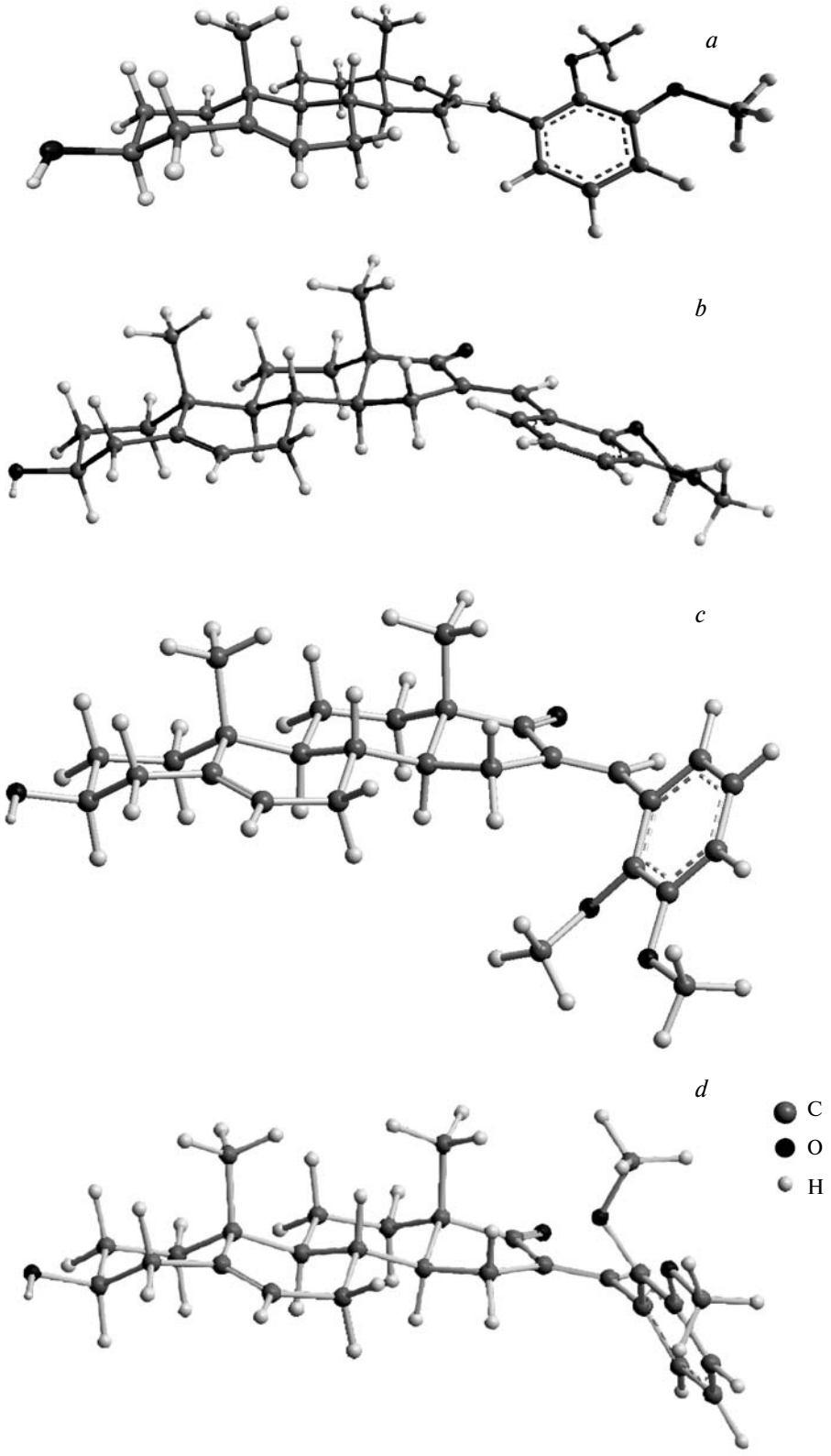


Fig. 1. Steric structures of rotamers of the arylidene fragment of compound **1c**: *a*, methoxy groups are apart and arranged above the steroid skeleton; *b*, methoxy groups are apart and oriented down from the steroid skeleton; *c*, methoxy groups are brought together and oriented down from the steroid skeleton; *d*, methoxy groups are brought together and oriented up from the steroid skeleton.

both positive and negative φ_{Ar} angles ($|\varphi_{Ar}| = 45—55°$) possess higher energies compared to those of the energetically more favorable (by 1.5—2.0 kcal mol^{-1}) rotamers. Therefore, the fraction of these rotamers in an equilibrium system is smaller and, in some cases, negligible (for instance, for compound **1b**). As follows from the simulation results, the lower-energy rotamers correspond to the situation when the methoxy group of R^4 is apart from the main skeleton (see Fig. 1, *a*, *b*). In these rotamers, the transverse molecular axis is "displaced" relative to the fundamental molecular axis of the steroid skeleton and forms with the latter an obtuse angle (125°—130° according to the simulation results). This orientation of the *ortho*-methoxy group (and similar for *meta*-substituent R^3) increases the anisotropy of the CAd molecules and the anisotropy of their polarizability, which exerts the most appreciable effect in the case of 3β-acetoxy-substituted compounds **2**.

The rotameric state of trimethoxy-substituted arylidene derivatives **1i** and **2d** (see table 2) does not substantially differ from that for the dimethoxy derivatives containing *o*-MeO group.

The rotamers at the arylidene group are sterically hindered due to the shortened nonvalent contact $H_o\cdots H(15)$ (2.14—2.23 Å). Nevertheless, in the experimental ^{1}H NMR spectra of the compounds both with R^4 = OMe and unsubstituted in the *ortho*-position, the retarded rotation of the benzene ring is not observed, at least at temperatures close to ambient.

It is doubtless that the rotamer differences for the arylidene group of the studied unsaturated ketones contribute to the degree of anisotropy of these chiral molecules, *i.e.*, determine their random molecular shape to a substantial extent.

Structure and helical twisting power of the unsaturated ketones under study. All studied compounds **1** and **2** induce the left cholesteric helix in the mesophase 5CB (the β values are negative, see Table 1). This direction of induced twisting in the mesophase correlates with the above mentioned stereospecific character of twisting of the enone group in the CAd molecules, namely, with the positive sign of the torsion angle φ_{en}, which is unambiguously determined by the configuration of the rigid steroid skeleton. This feature of the structure of the studied molecules defines, most likely, the steric peculiarities of their intermolecular dispersion interaction with the surrounding molecules of the nematic and, finally, defines the direction of twisting (sign) of the induced cholesteric helix. It should be mentioned that the same sign of the corresponding torsion angle was obtained for the efficient CAd of the series of left-twisting 2-arylidene-*p*-menthan-3-ones using simulation and by the data of X-ray diffraction experiments.[5]

A similar ratio between the intramolecular twisting of the π-system of the CAd and the direction of induced supramolecular twisting in the mesophase was revealed for a wide series of biaryl structures with the helical nature of chirality.[28—31]

The absolute values of the helical twisting power (β) for compounds **1** and **2** (see Table 1) vary in the very wide range: from very low values (CAd **1g**, **1h**, and **1j**) to the values higher more than an order of magnitude (**2a—c**).

When analyzing the relationship between the helical twisting power of the CAd and their steric structure, we based our considerations, as in the earlier studies,[13,16,17] on the concepts on the decisive influence on the properties of the induced cholesteric mesophases of the balance of the forces of anisotropic intermolecular attraction and specific steric repulsion between the molecules of the CAd and nematic solvent. The former factor is defined by the characteristics of molecular polarizability of the CAd, first of all, by its anisotropy (anisotropic component of the dispersion attraction between molecules of the components). As for the specific steric repulsion in nematic—CAd systems, it is determined (when the same nematic is used) by the molecular shape of the CAd.

Compared to cholesterol esters, the very high helical twisting power of the most part of the synthesized compounds containing the 3β-hydroxy substituents (**1a—1f**) and first of all the 3β-acetoxy substituents (**2a—e**, see Table 1) are the result of the replacement of the isooctyl radical by the conjugated cinnamoyl group O=C—C=C—Ar and related polarization and steric features of the molecules. Undoubtedly, this group substantially enhances the polarizability of molecules, including its important component along the fundamental molecular axis.

The polarizability of the steroid skeleton of the studied CAd and efficiency of their intermolecular dispersion interaction with the nematic depend to a considerable extent on the presence of the C(5)=C(6) double bond. The absence of this double bond in molecule **1g** decreases substantially the dispersion component of intermolecular attraction in the nematic—CAd system and, as a consequence, sharply decreases the helical twisting power of CAd **1g** compared to that of compound **1f**. However, it should be noted that cholesterol ester molecules also contain the C(5)=C(6) double bond and, nevertheless, they exhibit very weak twisting properties (for the β values for cholesterol acetate obtained by us using the method similar to that used in the studies of CAd **1** and **2**, see Table 1). Obviously, in the case of cholesterol acetate, the polarizability effect mainly caused by the C(5)=C(6) bond is insufficient to provide the necessary dispersion attraction between molecules of CAd and nematic 5CB. In the systems under study, this attraction is achieved due to the combined effect of the easily polarized double bond C(5)=C(6) and arylidene group with readily polarized alkyloxy groups (see Table 1). At the same time, one should take into account a possible influence of the more pronounced chirality of the skeleton of the studied

androstene derivatives due to the above-mentioned features of their geometry compared to CAd **1g**.

An important role of anisotropy of polarizability of the studied CAd in providing a strong helical twisting power is indicated by the fact that the |β| values of CAd **2** containing the acetoxy group at the 3β-carbon atom approximately twofold exceed those for hydroxy analogs **1** (*cf.* the data for compounds **1a** and **2a**, **1c** and **2b**, **1d** and **2c**, **1f** and **2e**). It is poorly probable that this effect is caused by the self-association of the hydroxy-containing CAd due to the formation of intermolecular hydrogen bonds >C=O···HO— and, as a consequence, by some disordering of the additive in the nematic medium.[32] This self-association of CAd is hindered, on the one hand, by the low acidity of the alcoholic hydroxyl and, on the other hand, weak proton-withdrawing properties of the carbonyl group included into the strained aliphatic five-membered cycle.[33] When the β value is measured by the Granjean—Cano method, the CAd concentration is rather low (0.01—0.02 mole fractions), which also decreases the probability of self-association. The intermolecular association of the hydroxy-substituted CAd with the nematic cyano-containing solvent can be considered also poorly probable because of the very weak basic properties of the nitrile group.[34]

It was found that compound **1h** containing the biphenyl substituent possesses a very weak helical twisting power. This fact seems important for understanding of the role of the anisotropy of CAd polarizability during the induction of the supramolecular helix in the mesophase. In the earlier studied CAd series,[8,35,36] including those belonging to the class of α,β-unsaturated ketones,[8,34] the introduction of an additional benzene ring into the conjugated molecular chain is accompanied by a considerable increase in |β|. In the series of 1*R*,4*R*-2-arylidene-*p*-menthan-3-ones, the effect of the biphenyl group exceeds the influence of both the strong electron-donating dimethylamino group and the strong electron-withdrawing nitro group introduced into the benzene ring.[8] It can be assumed that the unexpectedly weak helical twisting power of the CAd containing the biphenyl group in the series of compounds **1** compared to other known molecular systems is explained by the influence of the molecular shape prevailing on the polarizability effect. For compounds **1** two molecular axes can be considered, which define the shape of the molecules arranged at an angle to each other. This angle depends substantially on the substitution pattern in the phenyl group. In the case of phenyl-substituted CAd **1h**, its value estimated by us by the AM1 simulation is ~105°—107°. This fact along with the presence of the extended transverse biphenyl fragment substantially decreases anisotropy of both the shape and polarizability of molecules and negatively affects the efficiency of inducing the helicoidal structure. A similar situation can be assumed for weakly twisting CAd **1j** containing the extended nonyloxy substituent in the *para*-position of the benzene ring.

An analysis of the relationship between the helical twisting power of CAd **1** and **2** and the character of substitution in their benzene ring suggests that strong twisting is favored by the presence of the alkoxy substituent R^3 in the *meta*-position combined with the methoxy group R^4 and 3β-acetoxy group (CAd **2a—c**, see Table 1).

In both series of **1** and **2**, the trimethoxy-substituted CAd exhibit a lower helical twisting power than the substituted CAd (*cf.* the data for compounds **1i** and **1a—c**, **2d** and **2a**,**b**). This can be a consequence of the randomly stronger (in the first case) turn out of the aryl group relative to its axis, which decreases the molecular anisometry (effect of changing the molecular shape) and anisotropy of polarizability (polarization effect).

The replacement of the methoxy group in molecules of CAd **1a**, as well as of acetate **2a**, by the difluoromethoxy group is accompanied by the noticeable decrease in |β| (*cf.* the data for compounds **1a** and **1f**, **2a** and **2e**). This is possibly reasoned by the electron-acceptor effect of the $OCHF_2$ group characterized by the constant $\delta_p = 0.18$,[37] due to which the electron density on the benzene rings of CAd **1f** and **2e** is lower than that in molecules of the methoxy-substituted analogs. The corresponding decrease in the contribution to the polarizability of the arylidene fragment and studied molecular systems as a whole can weaken the dispersion attraction between molecules of **1f** (or **2e**) and the nematic solvent compared to that in the case of CAd **1a** (or **2a**).

The experimental data suggest that the geometry of the saturated cycle that fixes the *s-cis*-enone group (cyclopentane ring *D*) in the molecular systems under study exerts no decisive effect on the helical twisting power of the CAd. Note for comparison that although the 3*R*,6*R*-3-methyl-6-isopropylcyclohexanone (*p*-menthanone) 2-arylidene derivatives containing the *s-cis*-enone group fixed by the cyclohexane ring exhibit a weaker twisting effect than acetates **2**, they can be attributed, nevertheless, to well twisting CAd. For the *p*-methoxy-substituted compound of this series in 5CB, $|\beta_{mol}| = 27.8 \pm 0.4\ \mu m^{-1}$,[38] while $|\beta_{mol}|$ increases to $40.1 \pm 2.4\ \mu m^{-1}$ upon the introduction of an additional benzene ring to the arylidene fragment.[15]

LC systems selectively reflecting light in the visible spectral region. The typical spectral characteristics for the LC systems selectively reflecting light are presented in Fig. 2. This property is most pronounced for the composites based on liquid crystals E63 and LC-1289 containing CAd **2a—c** with the high helical twisting power. The results of measurements in LC-1289 with the known molar composition are most appropriate for the establishment of the correlation of this property with the molecular structure of the CAd. Therefore, the spectral characteristics and the data on the helical twisting power in this nematic correlate in Table 3 with the molar and weight concentrations

of the CAd, whereas those in E63 correlate with the weight concentrations only. It is seen from the data in Table 3 that the studied CAd **2a**,**b** in LC-1289 exhibit selective light reflection in the visible green range (λ_{max} = 511—525 nm) at the concentrations 5.8—6.2 mol.% (9.5—10.3 wt.%). Selective light reflection of the LC composition including compound **2b** (5.6 mol.%, 9.7 wt.%) is somewhat shifted to the short-wavelength region, which corresponds to the higher helical twisting power of this CAd. The $|\beta_{mol}|$ values of the studied steroid α,β-unsaturated ketones **2a—c** noticeably exceed the corresponding value for the known CAd, *viz.*, 2-(4-phenylbenzylidene)-*p*-menthan-3-one (PBM). Possibly, this difference is caused by the fact that the quasi-plate fragment of the studied molecules including four aliphatic rings contains two angular Me groups. This structural feature of compounds **1** and **2** along with the presence of the cinnamoyl fragment provides the balance of forces of dispersion attraction and specific steric repulsion favorable for helix ordering.

Thus, the study of the new type of chiral α,β-unsaturated ketones made it possible to create the series of LC composites capable of selective light reflection in the visible spectral region from the red to blue-green color.

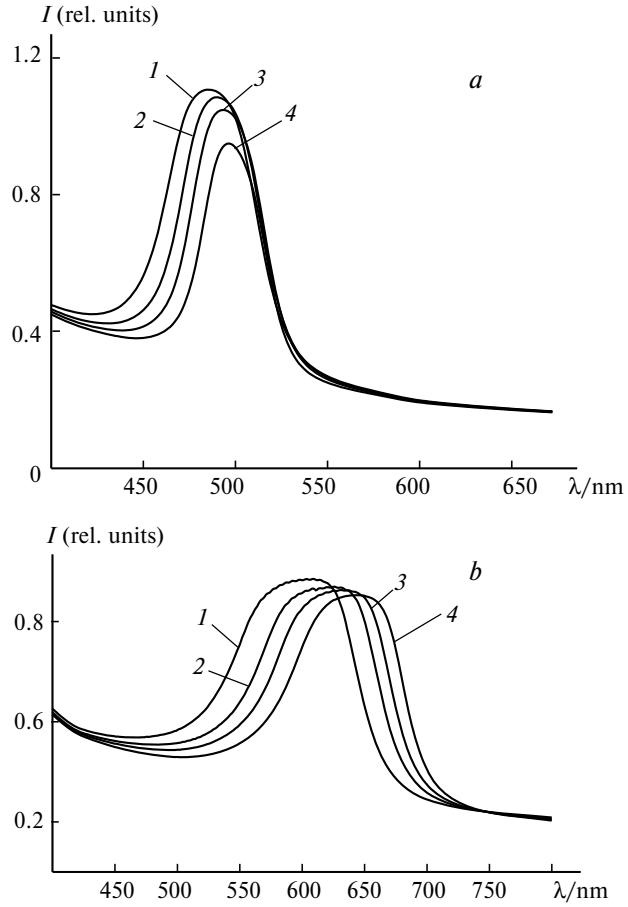


Fig. 2. Selective light reflection spectra of chiral nematic mixtures: *a*, LC-1289—**2c** (5.9 mol.%) at T = 28.5 (*1*), 37.5 (*2*), 40.5 (*3*), and 44.5 °C (*4*); *b*, E63—**2f** (9.9 wt.%) at T = 28.5 (*1*), 36.5 (*2*), 41.5 (*3*), and 47 °C (*4*).

Table 3. Characteristics of LC composites nematic—CAd capable of selective light reflection in the visible spectral region

CAd	C (wt.%) [C (mol.%)]	T_i /°C	T_{red} /K	λ_{max}/nm (color) at 298 K	P /μm	β (T_{red})
			Nematic LC-1289*			
2a	9.5 [5.8]	47	40.6	525 (green)	0.364	47.4 (28.9)
2b	9.7 [5.9]	47	40.6	482 (greenish-blue)	0.328	51.7 (31.5)
2c	10.3 [6.2]	45.5	39	511 (green)	0.356	45.3 (27.2)
PBM	8.6 [7.7]	57.5	50.9	571 (yellowish-green)	0.365	35.6 (31.7)
			Nematic E63**			
1e	13.1	54	47.5	660 (red)	0.432	17.7
2a	9.1	75.5	68.5	498 (greenish-blue)	0.360	30.6
2b	7.2	71	64	681 (red)	0.460	30.1
2b	8	71	64	618 (red)	0.422	29.3
2c	9.9	86	79	509 (green)	0.376	27.0
2e	9.9	79	72	580 (yellow)	0.429	23.5
PBM	12.2	50	43.5	530 (green)	0.329	24.9

* The composition of LC-1289: 38% 4-cyano-4′-*n*-pentyl-, 8% 4-cyano-4′-*n*-propoxy-, and 15% 4-cyano-4′-*n*-octylbiphenyls, 30% 4-ethoxyphenyl 4-*n*-butylcyclohexanecarboxylate, 9% 4-cyanodiphenyl *trans*-4-butylcyclohexanecarboxylate. LC-1289 is characterized by the following phase transitions: Cryst (−20) → N (62) → Iso (Cryst, N, and Iso are the crystalline, nematic, and isotropic phases, respectively). Here and for nematic E63 the temperatures (°C) of the phase transitions Cryst → N and N → Iso are given in parentheses.

** The nematic E63 includes diphenyl and terphenyl cyano derivatives and has the phase transitions: Cryst (8) → N (83) → Iso. the exact content of the components LC E63 is unknown.

In addition, the studies of the synthesized compounds extended the concepts about the structural factors affecting the helical twisting power in the mesophase. As discussed above, these factors are the presence of the polarized double bond in the steroid skeleton, the presence of the polarized arylidene fragment containing the alkoxy substituents, whose positions in the benzene ring substantially affect the molecular shape (its anisotropic characteristics), and the presence of the acetoxy group and related

increase in the molecular anisometry and anisotropy of polarizability. The quasi-plate shape of the steroid skeleton is also important, and its substantial influence is enhanced (compared to that of cholesterol esters) by the action of a combination of other aforementioned structural peculiarities of the CAd under study.

It is most likely that the angular methyl groups affect the stereospecific repulsion between molecules of the additive and nematic, although it is impossible to separate the contribution of this type of interaction, because necessary authentic compounds for comparison are lacking.

It should be mentioned that the effect of each particular factor taken separately can be insufficient for providing the high efficiency of twisting typical of the most part of the studied CAd. However, their combined effect makes it possible to achieve good results.

Experimental

^{1}H NMR spectra were recorded on Varian Mercury VX-200 (200 MHz) and Bruker DRX-500 (500.13 MHz) spectrometers in $CDCl_3$ and DMSO-d_6. Chemical shifts are given relative to Me_4Si.

The completeness of the reaction was monitored by TLC on Silufol UV-254 plates in a chloroform—methanol (3 : 1) system, developing with iodine vapors or UV irradiation. Quantitative chromatographic analysis was carried out on a Bischoff high-performance liquid chromatograph with a UV detector ($\lambda = 254$ nm), using a column 2.0S250 mm packed with Prontosil 120-5-C18-H (5 μm), MeCH—H_2O (87 : 13) as eluent, and a flow rate of 0.25 mL min^{-1}. According to the HPLC data, the content of the major substance was at least 96%. Mass spectra with direct inlet were measured on a Varian 1200L GC-MS instrument (the energy of ionizing electrons was 70 eV), and the m/z values for $I > 10\%$ are presented.

IR spectra were recorded in KBr pellets on a Specord IR-85 instrument. Specific rotation was determined on a Perkin—Elmer-343 polarimeter in chloroform and expressed in (deg mL) (g dm)$^{-1}$, and the solution concentration was expressed in g (100 mL)$^{-1}$. Melting points were measured on a Boetius heating stage in the polarized light and were not corrected; the double values possibly indicate liquid-crystalline transformations.

Substituted benzaldehydes were commercially available (Aldrich) and used as received. Dehydroepiandrosterone (DEA) (Acros) was additionally recrystallized from methanol and, according to the HPLC data, it contained at least 98% of the major substance.

3-β-Hydroxy-16*E*-arylideneandrost-5-en-17-ones 1 (general procedure). The corresponding benzaldehyde (1.92 mmol) and KOH (0.1 g) were added to a solution of DEA (0.50 g, 1.73 mmol) in alcohol (10 mL). The reaction mixture was refluxed for 3 h. A precipitate of the product was filtered off and crystallized from methanol (15 mL).

16*E*-(3,4-Dimethoxybenzylidene)-3-β-hydroxyandrost-5-en-17-one (1a). The yield was 0.48 g (72%), m.p. 192—193 °C (from MeOH) (*cf.* Ref. 39: m.p. 270—272 °C; *cf.* Ref. 40: m.p. 150—153 °C), $[\alpha]_D^{20}$ −13.5 (*c* 1.0, $CHCl_3$). Found (%): C, 77.10; H, 8.42. $C_{28}H_{36}O_4$. Calculated (%): C, 77.03; H, 8.31. IR (KBr), ν/cm^{-1}: 3536 (OH); 1716 (C=O); 1620 (C=C). ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 7.39 (br.s, 1 H, $=CH_\beta$); 7.18 (d, 1 H, $J = 8.5$ Hz); 7.07 (br.s, 1 H); 6.92 (d, 1 H, $J = 8.5$ Hz); 5.40 (dd, 1 H, C(6)H, $J = 4.4$, 2.0 Hz); 3.93 (s, 3 H); 3.92 (s, 3 H); 3.54 (m, 1 H, C(3)H); 2.89 (dd, 1 H, $J = 15.9$, 5.8 Hz); 2.43 (td, 1 H, $J = 14.1$, 2.7 Hz); 2.36—2.17 (m, 3 H); 1.10—1.67 (m, 6 H); 1.62—1.34 (m, 5 H); 1.15—1.05 (m, 2 H); 1.08 (s, 3 H); 0.99 (m, 3 H). MS, m/z (I_{rel} (%)): 436 [M]$^+$ (100), 213 (10), 177 (14), 176 (58), 161 (12), 151 (22), 105 (14), 91 (18).

16*E*-(2,4-Dimethoxybenzylidene)-3-β-hydroxyandrost-5-en-17-one (1b). The yield was 40%, m.p. 175—179 °C (from MeOH), $[\alpha]_D^{20}$ +34.9 (*c* 1.0, $CHCl_3$). Found (%): C, 77.15; H, 8.47. $C_{28}H_{36}O_4$. Calculated (%): C, 77.03; H, 8.31. IR (KBr), ν/cm^{-1}: 3432 (OH); 1712 (C=O); 1625 sh (C=C). ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 7.82 (br.s, 1 H, $=CH_\beta$); 7.47 (d, 4 H, $J = 8.5$ Hz); 6.53 (dd, 1 H, $J = 8.5$, 2.2 Hz); 6.46 (d, 1 H, $J = 2.2$ Hz); 5.39 (dd, 1 H, C(6)H, $J = 4.4$, 2.0 Hz); 3.85 (s, 6 H); 3.53 (m, 1 H, C(3)H); 2.78 (dd, 1 H, $J = 15.9$, 6.5 Hz); 2.40 (td, 1 H, $J = 14.1$, 2.7 Hz); 2.35—2.15 (m, 3 H); 1.99—1.75 (m, 4 H); 1.73—1.48 (m, 5 H); 1.42—1.30 (m, 2 H); 1.13—1.01 (m, 2 H); 1.07 (s, 3 H); 0.98 (m, 3 H). MS, m/z (I_{rel} (%)): 436 [M]$^+$ (71), 406 (33), 405 (100), 177 (17), 176 (32), 161 (49), 151 (30).

16*E*-(2,3-Dimethoxybenzylidene)-3-β-hydroxyandrost-5-en-17-one (1c). The yield was 80%, m.p. 158—160 °C (from MeOH), $[\alpha]_D^{20}$ +8.8 (*c* 1.0, $CHCl_3$). Found (%): C, 77.23; H, 8.38. $C_{28}H_{36}O_4$. Calculated (%): C, 77.03; H, 8.31. IR (KBr), ν/cm^{-1}: 3420 (OH); 1712 (C=O); 1624 (C=C). ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 7.78 (br.s, 1 H, $=CH_\beta$); 7.13 (d, 4 H, $J = 8.5$ Hz); 7.09 (t, 1 H, $J = 8.5$ Hz); 6.94 (d, 1 H, $J = 8.5$ Hz); 5.38 (dd, 1 H, C(6)H, $J = 4.4$, 2.0 Hz); 3.88 (s, 3 H); 3.84 (s, 3 H); 3.53 (m, 1 H, C(3)H); 2.80 (dd, 1 H, $J = 15.9$, 6.5 Hz); 2.41 (td, 1 H, $J = 14.1$, 2.7 Hz); 2.34—2.14 (m, 3 H); 1.99 (dm, 1 H, $J = 12.8$ Hz); 1.89—1.48 (m, 8 H); 1.43—1.30 (m, 2 H); 1.13—1.02 (m, 2 H); 1.07 (s, 3 H); 0.99 (m, 3 H). MS, m/z (I_{rel} (%)): 436 [M]$^+$ (12), 407 (12), 406 (68), 405 (100), 161 (59), 105 (10), 91 (14).

3-β-Hydroxy-16*E*-(4-methoxy-3-methoxymethylbenzylidene)-androst-5-en-17-one (1d). The yield was 89%, m.p. 94—97 °C (from MeOH), $[\alpha]_D^{20}$ −19.9 (*c* 1.0, $CHCl_3$). Found (%): C, 77.18; H, 8.28. $C_{29}H_{38}O_4$. Calculated (%): C, 77.29; H, 8.49. IR (KBr), ν/cm^{-1}: 3492 (OH); 1716 (C=O); 1624 (C=C). ^{1}H NMR (DMSO-d_6, 200 MHz), δ: 7.54 (d, 1 H, $J = 8.8$ Hz); 7.53 (br.s, 1 H, $=CH_\beta$); 7.23 (br.s, 1 H); 7.06 (d, 1 H, $J = 8.8$ Hz); 5.30 (d, 1 H, C(6)H, $J = 4.0$ Hz); 4.40 (s, 2 H); 3.82 (s, 3 H); 3.34 (m, 1 H, C(3)H); 3.31 (s, 3 H); 2.75 (dd, 1 H, $J = 17.0$, 7.0 Hz); 2.14 (m, 3 H); 1.9—1.2 (m, 11 H); 1.0—1.09 (m, 2 H); 0.98 (s, 3 H); 0.86 (s, 3 H). MS, m/z (I_{rel} (%)): 450 [M]$^+$ (100), 213 (15), 190 (31), 159 (17), 135 (15), 91 (11).

16*E*-(4-Difluoromethoxy-3-ethoxybenzylidene)-3-β-hydroxy-androst-5-en-17-one (1e). The yield was 90%, m.p. 100—102 °C (from MeOH). Found (%): C, 71.76; H, 7.28. $C_{29}H_{36}F_2O_4$. Calculated (%): C, 71.58; H, 7.46. IR (KBr), ν/cm^{-1}: 3456 (OH); 1716 (C=O); 1628 (C=C). ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 7.37 (br.s, 1 H, $=CH_\beta$); 7.19 (d, 1 H, $J = 8.5$ Hz); 7.13 (d, 1 H, $J = 8.5$ Hz); 7.09 (br.s, 1 H); 6.62 (t, 1 H, $J = 74.8$ Hz); 5.40 (dd, 1 H, C(6)H, $J = 4.3$, 1.9 Hz); 4.12 (q, 2 H); 3.54 (m, 1 H, C(3)H); 2.86 (dd, 1 H, $J = 15.9$, 5.5 Hz); 2.42 (td, 1 H, $J = 13.9$, 2.7 Hz); 2.36—2.16 (m, 3 H); 1.99 (dm, 1 H, $J = 12.8$ Hz); 1.90—1.65 (m, 5 H); 1.63—1.33 (m, 5 H); 1.47 (t, 3 H, $J = 6.9$ Hz); 1.15—1.05 (m, 2 H); 1.08 (s, 3 H); 0.98 (m, 3 H). MS, m/z (I_{rel} (%)): 486 [M]$^+$ (100), 227 (11), 226 (60), 213 (21), 201

(11), 198 (14), 178 (12), 159 (11), 131 (15), 119 (10), 107 (13), 105 (25), 102 (20), 93 (14), 91 (28), 81 (12).

16*E*-(4-Difluoromethoxy-3-methoxybenzylidene)-3-β-hydroxyandrost-5-en-17-one (1f). The yield was 61%, m.p. 118—120 °C (from MeOH). Found (%): C, 71.32; H, 7.07. $C_{28}H_{34}F_2O_4$. Calculated (%): C, 71.17; H, 7.25. IR (KBr), ν/cm^{-1}: 3380 (OH); 1720 (C=O); 1632 (C=C). ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 7.38 (br.s, 1 H, $=CH_\beta$); 7.20 (d, 1 H, *J* = 8.5 Hz); 7.15 (d, 1 H, *J* = 8.5 Hz); 7.10 (br.s, 1 H); 6.59 (t, 1 H, *J* = 74.8 Hz); 5.40 (dd, 1 H, C(6)H, *J* = 4.3, 1.9 Hz); 3.91 (s, 3 H); 3.54 (m, 1 H, C(3)H); 2.87 (dd, 1 H, *J* = 15.8, 5.7 Hz); 2.43 (td, 1 H, *J* = 14.0, 2.6 Hz); 2.36—2.16 (m, 3 H); 2,00—1.66 (m, 6 H); 1.63—1.34 (m, 5 H); 1.15—1.05 (m, 2 H); 1.08 (s, 3 H); 0.99 (m, 3 H). MS, *m/z* (I_{rel} (%)): 472 $[M]^+$ (100), 281 (11), 231 (29), 213 (36), 212 (81), 187 (15).

16*E*-(4-Difluoromethoxy-3-methoxybenzylidene)-3-β-hydroxy-5α-androstan-17-one (1g). For the synthesis of this derivative, epiandrosterone obtained by an earlier described procedure[41] was used instead of DEA. The yield was 85%, m.p. 118—120 °C (from MeOH). Found (%): C, 70.69; H, 7.48. $C_{28}H_{36}F_2O_4$. Calculated (%): C, 70.86; H, 7.65. IR (KBr), ν/cm^{-1}: 3268 (OH); 1720 (C=O); 1632 (C=C). ^{1}H NMR (DMSO-d_6, 200 MHz), δ: 7.38 (br.s, 1 H, $=CH_\beta$); 7.33—7.23 (m, 3 H); 7.13 (t, 1 H, *J* = 74.4 Hz); 4.42 (d, 1 H, *J* =5.0 Hz); 3.88 (s, 3 H); 2.78 (dd, 1 H, *J* = 17.4, 7 Hz); 1.95—0.70 (m, 3 H); 1.8—1.5 (m, 6 H); 1.4—1.0 (m, 10 H); 0.88 (s, 3 H); 0.81 (s, 3 H). MS, *m/z* (I_{rel} (%)): 474 $[M]^+$ (35), 287 (13), 215 (14), 213 (20), 212 (100), 187 (15), 107 (17), 105 (14), 95 (11), 93 (14), 91 (17), 81 (14).

3-β-Hydroxy-16*E*-(4-phenylbenzylidene)androst-5-en-17-one (1h). The yield was 58%, m.p. 244—246 °C (from MeOH). Found (%): C, 84.77; H, 8.14. $C_{32}H_{36}O_2$. Calculated (%): C, 84.91; H, 8.02. IR (KBr), ν/cm^{-1}: 3420 (OH); 1712 (C=O); 1628 (C=C). ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 7.77 (d, 2 H, *J* = 8.5 Hz); 7.72 (d, 4 H, *J* = 8.5 Hz); 7.48 (t, 2 H, *J* = 8.5 Hz); 7.39 (t, 1 H, *J* = 8.5 Hz); 7.34 (s, 1 H, $=CH_\beta$); 5.32 (dd, 1 H, C(6)H, *J* = 4.4, 2.0 Hz); 4.62 (d, 1 H, OH, *J* = 3.7 Hz); 3.27 (m, 1 H, C(3)H); 2.84 (dd, 1 H, *J* = 15.9, 5.8 Hz); 2.55 (t, 1 H, *J* = 14.1 Hz); 2.20—2.09 (m, 3 H); 1.82—1.63 (m, 6 H); 1.50 (qd, 1 H, *J* = 12.7, 3.9 Hz); 1.41—1.28 (m, 3 H); 1.02—0.96 (m, 2 H); 1.01 (s, 3 H); 0.90 (m, 3 H). MS, *m/z* (I_{rel} (%)): 452 $[M]^+$ (65), 261 (14), 231 (14), 229 (11), 213 (25), 193 (23), 192 (100), 191 (39), 178 (16), 167 (41), 165 (17), 145 (11), 131 (13), 119 (12), 115 (14), 107 (14), 105 (28), 95 (11), 93 (18), 91 (41), 81 (22).

3-β-Hydroxy-16*E*-(2,3,4-trimethoxybenzylidene)androst-5-en-17-one (1i). The yield was 75%, m.p. 186—188 °C (from MeOH). Found (%): C, 74.49; H, 8.02. $C_{29}H_{38}O_5$. Calculated (%): C, 74.65; H, 8.20. IR (KBr), ν/cm^{-1}: 3492 (OH); 1716 (C=O); 1624 (C=C). ^{1}H NMR ($CDCl_3$, 200 MHz), δ: 7.72 (br.s, 1 H, $=CH_\beta$); 7.27 (d, 1 H, *J* = 8.5 Hz); 6.72 (d, 1 H, *J* = 8.5 Hz); 5.38 (dd, 1 H, C(6)H, *J* = 4.2, 2.1 Hz); 3.91 (s, 3 H); 3.90 (s, 3 H); 3.87 (s, 3 H); 3.53 (m, 1 H, C(3)H); 2.78 (dd, 1 H, *J* = 15.8, 5.6 Hz); 2.39 (td, 1 H, *J* = 14.0, 2.6 Hz); 2.32—1.26 (m, 14 H); 1.16—1.03 (m, 2 H); 1.07 (s, 3 H); 0.97 (m, 3 H). MS, *m/z* (I_{rel} (%)): 466 $[M]^+$ (7), 436 (30), 435 (100), 191 (28), 181 (11).

3-β-Hydroxy-16*E*-(4-nonyloxybenzylidene)androst-5-en-17-one (1j). The yield was 87%, m.p. 98—100 °C (from MeOH). Found (%): C, 81.16; H, 9.59. $C_{35}H_{50}O_3$. Calculated (%): C, 81.03; H, 9.71. IR (KBr), ν/cm^{-1}: 3408 (OH); 1728 (C=O); 1600 (C=C). ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 7.59 (d, 2 H, *J* = 8.5 Hz); 7.27 (br.s, 1 H, $=CH_\beta$); 7.01 (d, 2 H, *J* = 8.0 Hz); 5.33 (m, 1 H, C(6)H); 4.62 (d, 1 H, *J* = 5.0 Hz); 4.00 (t, 2 H, *J* = 5.7 Hz); 3.25 (m, 1 H, C(3)H); 2.77 (dd, 1 H, *J* = 15.8, 5.7 Hz); 2.10—2.20 (m, 3 H); 1.80—1.60 (m, 7 H); 1.50—1.20 (m, 18 H); 1.10—0.90 (m, 2 H); 1.02 (s, 3 H); 0.88 (s, 3 H); 0.86 (t, 3 H, *J* = 7.5 Hz). MS, *m/z* (I_{rel} (%)): 518 $[M]^+$ (100), 520 (10), 519 (44), 518 (100), 327 (10), 258 (17), 233 (21), 231 (19), 213 (40), 211 (10), 201 (11), 133 (21), 132 (40), 131(22), 107 (34), 105 (13), 91 (10).

3-β-Acetoxy-16*E*-(arylidene)androst-5-en-17-ones (general procedure). Acetic anhydride (4 mL, 42.3 mmol) was added to hydroxy derivative **1** (0.68 mmol) in pyridine (2 mL). The reaction mixture was stirred for several hours (TLC monitoring). After the reaction completed, the solution was poured to ice-cold water acidified with HCl. A precipitate of the acetate was filtered off and crystallized from methanol (10 mL).

3-β-Acetoxy-16*E*-(3,4-dimethoxybenzylidene)androst-5-en-17-one (2a). The yield was 0.24 g (91%), m.p. 142—144 °C and 178—180 °C (from MeOH) (*cf.* Ref. 39: m.p. 142—144 °C). Found (%): C, 75.43; H, 8.09. $C_{30}H_{38}O_5$. Calculated (%): C, 75.28; H, 8.00. IR (KBr), ν/cm^{-1}: 1730, 1724, 1708 (C=O); 1624 (C=C). ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 7.39 (br.s, 1 H, $=CH_\beta$); 7.18 (d, 1 H, *J* = 8.5 Hz); 7.07 (br.s, 1 H); 6.92 (d, 1 H, *J* = 8.5 Hz); 5.43 (dd, 1 H, C(6)H, *J* = 4.2, 2.1 Hz); 4.61 (m, 1 H, C(3)H); 3.93 (s, 3 H); 3.91 (s, 3 H); 2.89 (dd, 1 H, *J* = 15.9, 5.7 Hz); 2.43 (td, 1 H, *J* = 14.1, 2.5 Hz); 2.38—2.31 (m, 3 H); 2.18 (dm, 1 H, *J* = 17.0 Hz); 2.04 (s, 3 H); 1.98 (d.m, 1 H, *J* = 12.5 Hz); 1.92—1.53 (m, 8 H); 1.45—1.35 (m, 2 H); 1.20—1.07 (m, 2 H); 1.09 (s, 3 H); 0.98 (m, 3 H). MS, *m/z* (I_{rel} (%)): 478 $[M]^+$ (30), 419 (13), 418 (42), 214 (15), 213 (87), 211 (13), 205 (14), 177 (35), 176 (100), 161 (25), 151 (47), 105 (12).

3-β-Acetoxy-16*E*-(2,3-dimethoxybenzylidene)androst-5-en-17-one (2b). The yield was 82%, m.p. 132—135 °C и 150—152 °C (from MeOH). Found (%): C, 75.12; H, 7.93. $C_{30}H_{38}O_5$. Calculated (%): C, 75.28; H, 8.00. IR (KBr), ν/cm^{-1}: 1731, 1709 (C=O); 1624 (C=C). ^{1}H NMR (DMSO-d_6, 200 MHz), δ: 7.56 (br.s, 1 H, $=CH_\beta$); 7.2—7.1 (m, 3 H); 5.38 (d, 1 H, C(6)H, *J* = 3.4 Hz); 4.44 (m, 1 H, C(3)H); 3.83 (s, 3 H); 3.74 (s, 3 H); 2.73 (dd, 1 H, *J* = 16.2, 5.8 Hz); 2.30 (d, 2 H, *J* = 7.8 Hz); 2.12 (m, 1 H); 1.9—1.3 (m, 11 H); 1.1—1.0 (m, 2 H); 1.03 (s, 3 H); 0.89 (s, 3 H). MS, *m/z* (I_{rel} (%)): 478 $[M]^+$ (4), 448 (21), 447 (57), 388 (27), 387 (100), 161 (23), 91 (13).

3-β-Acetoxy-16*E*-(4-methoxy-3-methoxymethylbenzylidene)-androst-5-en-17-one (2c). The yield was 84%, m.p. 89—92 °C (from MeOH). Found (%): C, 75.49; H, 8.02. $C_{31}H_{40}O_5$. Calculated (%): C, 75.57; H, 8.18. IR (KBr), ν/cm^{-1}: 1732, 1716 (C=O); 1624 (C=C). ^{1}H NMR (DMSO-d_6, 300 MHz), δ: 7.57 (d, 1 H, *J* = 8.1 Hz); 7.55 (br.s, 1 H, $=CH_\beta$); 7.26 (br.s, 1 H); 7.09 (d, 1 H, *J* = 8.1 Hz); 5.41 (d, 1 H, C(6)H, *J* = 4.2 Hz); 4.46 (m, 1 H, C(3)H); 4.41 (s, 2 H); 3.83 (s, 3 H); 3.33 (s, 3 H); 2.77 (dd, 1 H, *J* = 15.9, 6.3 Hz); 2.30 (d, 2 H, *J* = 7.5 Hz); 2.13 (m, 1 H, *J* = 15.9 Hz); 1.99 (s, 3 H); 1.9—1.5 (m, 8 H); 1.30 (m, 2 H); 1.06 (m, 2 H); 1.03 (s, 3 H); 0.88 (s, 3 H). MS, *m/z* (I_{rel} (%)): 492 $[M]^+$ (18), 433 (12), 432 (40), 400 (17), 229 (13), 228 (13), 227 (11), 214 (19), 213 (100), 211 (32), 209 (14), 199 (11), 197 (13), 191 (10), 190 (62), 189 (11), 187 (12), 186 (16), 175 (14), 173 (21), 171 (13), 165 (18), 161 (21), 160 (25), 159 (45), 157 (16), 145 (18), 143 (13), 135 (30), 131 (13), 129 (16), 128 (13), 115 (12), 105 (19), 91 (20), 81 (19).

3-β-Acetoxy-16*E*-(2,3,4-trimethoxybenzylidene)androst-5-en-17-one (2d). The yield was 70%, m.p. 186—188 °C (from

MeOH). Found (%): C, 73.28; H, 7.82. $C_{31}H_{40}O_6$. Calculated (%): C, 73.20; H, 7.93. IR (KBr), ν/cm^{-1}: 1728, 1712 (C=O); 1628 (C=C). ^{1}H NMR ($CDCl_3$, 200 MHz), δ: 7.72 (br.s, 1 H, $=CH_\beta$); 7.26 (d, 1 H, J = 8.5 Hz); 6.71 (d, 1 H, J = 8.5 Hz); 5.41 (dd, 1 H, C(6)H, J = 4.2, 2.1 Hz); 4.60 (m, 1 H, C(3)H); 3.90 (s, 3 H); 3.89 (s, 3 H); 3.87 (s, 3 H); 2.78 (dd, 1 H, J = 15.8, 5.6 Hz); 2.39 (td, 1 H, J = 14.0, 2.6 Hz); 2.37—2.12 (m, 3 H); 2.03 (s, 3 H); 1.94—1.52 (m, 9 H); 1.46—1.29 (m, 2 H); 1.22—1.04 (m, 2 H); 1.07 (s, 3 H); 0.97 (m, 3 H). MS, m/z (I_{rel} (%)): 508 $[M]^+$ (10), 478 (37), 477 (100), 418 (16), 417 (52), 191 (47), 181 (25), 105 (10).

3-β-Acetoxy-16*E*-(4-difluoromethoxy-3-methoxybenzylidene)-androst-5-en-17-one (2e). The yield was 74%, m.p. 129—131 °C (from MeOH). Found (%): C, 70.21; H, 7.23. $C_{30}H_{36}F_2O_5$. Calculated (%): C, 70.02; H, 7.05. IR (KBr), ν/cm^{-1}: 1777, 1711 (C=O); 1628 (C=C). ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 7.38 (br.s, 1 H, $=CH_\beta$); 7.20 (d, 1 H, J = 8.5 Hz); 7.14 (d, 1 H, J = 8.5 Hz); 7.10 (br.s, 1 H); 6.59 (t, 1 H, J = 74.8 Hz); 5.42 (dd, 1 H, C(6)H, J = 4.2, 2.1 Hz); 4.61 (m, 1 H, C(3)H); 3.91 (s, 6 H); 2.87 (dd, 1 H, J = 15.9, 5.7 Hz); 2.43 (td, 1 H, J = 14.0, 2.6 Hz); 2.39—2.29 (m, 2 H); 2.18 (dm, 1 H, J = 16.9 Hz); 2.04 (s, 3 H); 1.99 (dm, 1 H, J = 12.5 Hz); 1.91—1.53 (m, 8 H); 1.45—1.34 (m, 2 H); 1.20—1.06 (m, 2 H); 1.09 (s, 3 H); 0.98 (m, 3 H). MS, m/z (I_{rel} (%)): 515 $[M]^+$ (4), 455 (32), 454 (100), 214 (16), 213 (85), 212 (81), 187 (18), 145 (12), 107 (11), 105 (27), 91 (24), 81 (17).

Simulation of possible conformers of the studied structures and the full optimization of their geometric parameters were performed by the AM1 method accomplished in the MOPAC 6.0 program package. The starting structures for the optimization were obtained using the program of model construction in HyperChem 5.

Determination of the sign of the helical twisting power of the CAd under study was carried out as described earlier.[33] The absolute values of the helical twisting power β induced by CAd in the nematic solvent 5CB was determined using the ratio[33]

$$\beta = (P_{T_{red}} \cdot C \cdot r)^{-1}, \quad (1)$$

where P is the pitch of the induced helix at the reduced temperature (T_{red}), C is the CAd concentration expressed in mole fractions, r is the enantiomeric purity of the additive, which is equal to 1 for the most part of natural products obtained by modification; $T_{red} = 0.98 \cdot T_i$ (T_i is the isotropic transition temperature).

Selective light reflection spectra of the LC composites in the nematics E63 and LC-1289 were recorded on a Perkin—Elmer Lambda 35 UV/VIS spectrometer. The planar-oriented LC samples with a layer thickness of 10 μm were used. The helical pitch (P) in the N*-systems was determined by the formula

$$P = \lambda_{max}/n,$$

where n is the average refractive index of LC: n = 1.586 (see Ref. 42) and 1.5 for E63 and LC-1289, respectively.

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