JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 5, 308–316 (1992)

# QUANTITATIVE ASPECTS OF CHIRALITY. III. DESCRIPTION OF THE INFLUENCE OF THE STRUCTURE OF CHIRAL COMPOUNDS ON THEIR TWISTING POWER IN THE NEMATIC MESOPHASE BY MEANS OF THE DISSYMMETRY FUNCTION

L. A. KUTULYA
*Institute for Single Crystals, 60 Lenin Avenue, 310141 Kharkov, Ukraine*
V. E. KUZ'MIN* AND I.B. STEL'MAKH
*A. V. Bogatsky Physico-Chemical Institute of the Academy of Sciences of the Ukraine, 86 Chernomorskaya doroga, 270080 Odessa, Ukraine*
AND
T. V. HANDRIMAILOVA AND P. P. SHTIFANYUK
*Institute for Single Crystals, 60 Lenin Avenue, 310141 Kharkov, Ukraine*

**For a number of chiral α,β-unsaturated carbonyl compounds, cyclohexanone and cyclohexenone derivatives, existing essentially in the form of single molecular conformation, the correlation dependences were established between the values of the calculated dissymmetry functions (DF) with respect to atomic masses and atom refractions, and the induction effectiveness of helical ordering in the nematic mesophase (twisting power). Such correlative dependencies, as the examples show, allow one to predict safely enough the twisting power of new substances with the 'fixed' molecular conformation. Types of dissymmetry functions and kinds of correlative dependences, the most acceptable for these reasons, were revealed. Dissymmetry functions formed on the basis of atom refractions (polarizabilities) describe the influence of the molecular structures of chiral compounds on the twisting power with higher accuracy than those that characterize the dissymmetry of the atomic masses distribution, according to the important role of the dispersion forces in the formation of helical ordering in liquid crystalline systems. The components characterizing the distribution dissymmetry of atomic refractions and masses with respect to the long and two shorter axes as the peculiar characteristics of biaxiality of chiral molecules describe the influence of the molecular structure on the twisting power with the same accuracy as the general DF do. Thus influence of chiral dopant molecules on the interactions between molecules in the uniaxial mesophases is negligible within the limits of the DF method. Based on the calculations for model systems it is established that the presence of the non-linear cinnamoyl fragment has a decisive influence on the molecular dissymmetry of the chiral α,β-unsaturated ketones. The alkyl groups influence the molecular dissymmetry only slightly, but it is important that their presence ensures the stabilization of the chiral conformer with the defined helicity of the cinnamoyl fragment.**

## INTRODUCTION

Chiral organic compounds show the ability to induce helical supramolecular ordering in nematic and smectic mesophases.[1] Such effects are especially interesting in the case of nonmesogenic chiral dopants.[2,3] This phenomenon is quantitatively characterized by the twisting power value (β) of the chiral dopant in the given nematic phase, and also the sign of the induced helix, which are essentially dependent on the molecular structure of the components.[1,3] However, up to now the nature of such a dependence has been unclear and has usually been discussed in the literature on an empirical level.

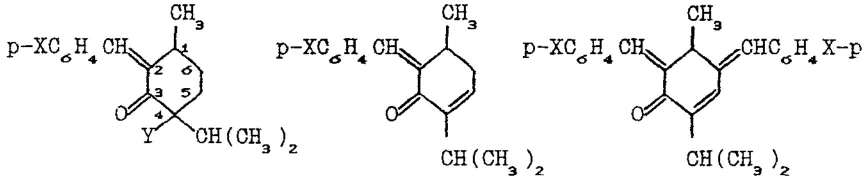
It is natural to assume that the most important characteristic of chiral compounds determining their twisting power is the 'chirality level' of the molecules because the achiral structures or racemates do not show the above-mentioned effects. It is also natural to consider that the higher the 'chirality level' of a dopant molecule, the stronger is its 'chiral' influence on the

---

*Author for correspondence.

0894–3230/92/060308–09$09.50

*Received 6 June 1991*
*Revised 7 January 1992*



**1**, Y=H; **2**, Y=Br **3** **4**

environment. In some cases, for a quantitative characteristic of the chirality of dopant molecules the Ugi–Ruch functions have been used.[4,5] Nevertheless, the possibilities of analysing changes in the twisting power on this basis are limited to series of structurally similar compounds the chirality of which is the result of various substitutions of the initial achiral molecular skeleton of a certain symmetry group. The Ugi–Ruch functions method cannot be applied either to compounds the chirality of which is determined by the simultaneous presence of several elements (central, axial, planar or helical chirality[6]) or to structures with a chiral skeleton.

In this work it seemed reasonable to apply the calculated dissymmetry functions (*DF*)[7] for a description of the influence of the structures of chiral compounds on their twisting power. Four series of chiral $\alpha,\beta$-unsaturated carbonyl compounds (**1**–**4**) and the structurally similar saturated ketone (–)-menthone [(–)-*trans*-2*S*,5*R*-2-isopropyl-5-methylcyclohexanone] were studied (see Table 1).

The twisting powers of these compounds were measured in two nematic solvents of the azomethine type, 4-methoxy- and 4-butyloxybenzylidene-4′-(*n*-butyl)aniline (**5** and **6**, respectively) (Table 1). Such a selection of nematic phases and chiral dopants is stipulated by the structural variations of compounds **1**–**4**, and also by the absence of specific interactions between the molecules in the named systems. The important thing is the existence of molecules of the selected chiral compounds chiefly in the form of single conformers, as will be shown below. This simplifies the solution of the problem of characterizing molecular dissymmetry within the limits of the method used because it does not require the statistical calculation of some co-existing conformers.

Apart from investigating the nature of the correlative $|\beta|$–*DF* dependence we also studied the influence of various structural fragments on the dissymmetry of molecules **1**–**4**, which should certainly be useful in 'designing' novel chiral compounds with the high twisting power.

## RESULTS AND DISCUSSION

Data on the conformations of the molecules of chiral compounds **1**–**4** and geometrical parameters of the molecules required for *DF* calculations were obtained from the results of experimental studies[8–10] and from theoretical conformational analyses by the force field method.[11,12] It was established that the molecules of compounds **1** and **2** have a chair-like conformation of the cyclohexanone fragment mostly with axial methyl and equatorial isopropyl groups[8,9] (form A) (Figure 1). The calculated conformational energy of such a *cis* structure of compound **1a** ($E^{A}_{conf.} = -7{\cdot}2$ kcal mol$^{-1}$) is considerably lower than that of any of the chair-like conformations with a *trans* orientation of alkyl groups ($E^{B,C}_{conf.} > 36$ kcal mol$^{-1}$) and any of twist forms (D) with *trans*-alkyl substituents (methyl is pseudo-axial, isopropyl is pseudo-equatorial) ($E^{D}_{conf.} = -4{\cdot}0$ kcal mol$^{-1}$). The *cis* structure (A) of compounds **1** is realized in spite of the fact that they are obtained from (–)-menthone, which has a *trans* configuration of 1,4-alkyl substitution.[13] This is favoured by the possibility of rapid epimerization of (–)-menthone into the corresponding *cis* isomer under the conditions of the synthesis of ketones **1** in a highly alkaline medium.[8,14]

From the conformational analysis and previous experimental data,[8,9] it follows that the structure of the enone grouping O=C—C=C in ketones **1** and **2** is essentially non-planar. In addition, the benzene ring in the structures of all ketones **1**–**4** is significantly rotated (by about 90°) with respect to the plane of the double bond. Therefore, the molecular chirality of the investigated ketones is determined not only by the existence of chiral centres but also by the non-planarity ('twisting') of the cinnamoyl $\pi$-electron system, determining its helical chirality.[6,8] The stereospecific nature of the non-planarity of the enone grouping seems to be the most important factor: the sign of the O=C—C=C torsion

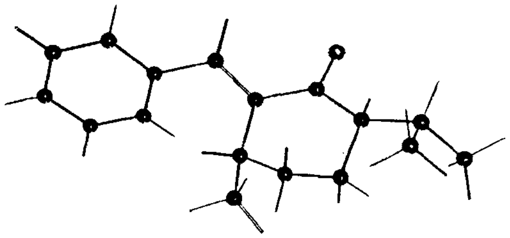


Figure 1. Conformation of compounds **1** and **2**

angle at the given configuration of chiral centres C-1 and C-4 is determined by the ring conformation and changes with its inversion. As the molecules of ketones **1** and **2** exist in the so-called 'fixed' conformation (A), they are characterized by a definite type of helical chirality. These peculiarities of the spatial structure of the molecules of the investigated chiral ketones are important for a correct analysis of the structure–twisting power relationship on the basis of the calculated dissymmetry functions.

For calculations of the *DF* of chiral compounds **1–4** the fundamental characteristic having the property of transferability, atomic mass (*M*), was primarily used as an atomic property. In addition, we used atomic refraction (*R*), the characteristic of atoms which, in general, unlike *M* does not fully meet the conditions of transferability.[15] The possibility of using *R* for the *DF* calculations in any specific case under consideration is determined by the non-planar structure of the $\pi$-electron system of compounds **1–4** and, as a result, by the absence of strong intrinsic molecular electronic interactions (optical intensity).

According to present-day theoretical concepts (see reviews[16,17]), the formation of ordering in liquid crystalline systems is defined by dispersion molecular interactions and also by steric repulsion, both having a stereospecific nature for chiral molecules. Therefore, the use of functions describing the dispersion force and steric force field dissymmetry for chiral molecules with regard to regularities of the variation of the twisting power seems to be theoretically valid.

For the dispersion forces, it is convenient to calculate the dissymmetry function on an atomic refraction basis; for the steric forces, an atomic mass basis will be the best. In general, these two types of forces can compete in controlling the resulting ordering for the systems under consideration. However, we suggest that, in very dilute solutions, these two force systems act in concert. Therefore, both calculation schemes for *DF* ($DF^M$ and $DF^R$) will describe nearly equivalently the ordering regularities in liquid crystalline systems.

The calculated $DF^M$ and $DF^R$ values for the studied chiral compounds are given in Table 1. Also presented are the *DF* values normalized[7] for the sum of masses

$$\left(DF_p^M = DF^M \Big/ \sum_{i=1}^{N} M_i\right)$$

Table 1. Experimental values of twisting power ($\beta$) and calculated dissymmetry functions of chiral compounds **1–4** and ( – )-menthone

| | | $-\beta(\mu m^{-1})$ | | Dissymmetry function | | | |
|---|---|---|---|---|---|---|---|
| Compound | X | Solvent **5** | Solvent **6** | $DF^M$ | $DF^R$ | $DF_p^M$ | $DF_p^R$ |
| **1a** | H | 19·9 | 16·6 | 3901 | 1313 | 16·12 | 17·56 |
| **1b** | F | 22·8 | 21·9 | 4828 | 1313 | 18·57 | 17·59 |
| **1c** | Cl | 29·6 | 26·5 | 5734 | 1584 | 20·74 | 19·89 |
| **1d** | Br | 32·8 | 26·5 | 7621 | 1750 | 23·74 | 21·21 |
| **1e** | $NO_2$ | 35·3 | 30·7 | 6301 | 1662 | 21·95 | 20·54 |
| **1f** | CN | 34·1 | 31·2 | 5457 | 1599 | 20·44 | 20·19 |
| **1g** | $OCH_3$ | 30·5 | 26·6 | 5593 | 1708 | 20·56 | 21·08 |
| **1h** | $OC_2H_5$ | 29·0 | 29·4 | 6409 | 1956 | 22·41 | 22·84 |
| **1i** | $C_6H_5$ | 41·9 | 37·4 | 8849 | 2895 | 27·83 | 28·70 |
| **2a** | H | 23·0 | 16·1 | 5985 | 1626 | 18·59 | 19·71 |
| **2b** | F | 27·6 | 22·4 | 7247 | 1626 | 21·31 | 19·73 |
| **2c** | Cl | 30·5 | 21·4 | 8531 | 1955 | 23·93 | 22·36 |
| **2d** | Br | 32·3 | 21·9 | 10380 | 2155 | 25·88 | 23·87 |
| **2e** | $NO_2$ | 36·6 | 31·0 | 9424 | 2061 | 25·68 | 23·23 |
| **2f** | $OCH_3$ | 32·8 | 24·3 | 8283 | 2066 | 23·53 | 23·27 |
| **2g** | $C_6H_5$ | 44·5 | 32·0 | 12860 | 3517 | 32·30 | 32·37 |
| **3a** | H | 16·7 | 12·8 | 3677 | 1169 | 15·32 | 16·11 |
| **3b** | F | 22·1 | 18·3 | 4606 | 1170 | 17·85 | 16·15 |
| **3c** | Cl | 23·5 | 22·8 | 5689 | 1494 | 20·72 | 19·29 |
| **3d** | Br | 24·4 | 22·6 | 7391 | 1677 | 23·17 | 20·88 |
| **3e** | $No_2$ | 26·7 | 28·5 | 6111 | 1584 | 21·44 | 20·11 |
| **3f** | $OCH^3$ | 28·0 | 25·8 | 5337 | 1537 | 19·77 | 19·51 |
| **3g** | $C_6H_5$ | 38·5 | 33·6 | 8612 | 2763 | 27·25 | 28·00 |
| **4a** | H | 11·4 | 6·2 | 5067 | 1646 | 15·35 | 15·94 |
| **4b** | Br | 28·6 | 17·9 | 10780 | 2341 | 22·08 | 19·70 |
| ( – )-Menthone | | 0·7 | — | 1114 | 315·8 | 7·33 | 7·18 |

and for the sum of atom refractions

$$\left(DF_p^R = DF^R \Big/ \sum_{i=1}^{N} R_i\right),$$

respectively, where $M$ is the atomic mass in atom units of the $i$th atom, $R$ is the atom refraction (cm$^3$) of the $i$th atom and $N$ is the number of atoms in the molecule. The application of these characteristics for a comparative analysis of molecular dissymmetry can be useful in the case of structures which differ considerably in the number of atoms.

A comparison of $DF_p^M$ and $DF_p^R$ values with the twisting power of ketones **1**–**4** (Table 1) shows that they change in a similar manner: they both increase with the introduction of bulky and extended substituents in the *para* position of the benzene ring. The substitution of a hydrogen atom in the C-4 chiral centre of compounds **1** for the larger volume and more easily polarizable bromine atom (ketones **2**) is accompanied by slight increases in $DF$ and $|\beta|$ values. The elimination of this chiral centre (ketones **3**) decreases the values of $DF_p^M$, $DF_p^R$ and $|\beta|$. The lowest values of the twisting power and $DF$ are obtained for (−)-menthone.

The regression analysis which was carried out (see Table 2) indicated a satisfactory correlative dependence between the experimental values $|\beta|$ and the calculated functions of dissymmetry described by equation (1) for the whole series of chiral dopants studied:

$$|\beta|^y = ax + b \tag{1}$$

where $y = 0{\cdot}5$–$1$, $x$ is the $DF$ used and $a$ and $b$ are parameters of the regression equation. Other possible regression equations (with values of $y > 1$ and also logarithmic, exponential, etc.) give a much poorer correlation between $|\beta|$ and $DF$ (calculated correlation coefficients $r \ll 0{\cdot}9$).

The analysis of the data in Table 2 shows first that the use of $DF^R$ values allows the twisting power–dissymmetry of chiral molecules relationship to be described with higher accuracy than $DF^M$ values (the

Table 2. Parameters of regression equations $|\beta|^y = ax + b$ for the whole series of chiral compounds **1**–**4** and (−)-menthone

| Solvent | $x$ | $y$ | $a$ | $S_a$[a] | $b$ | $S_b$[a] | $r$[a] |
|---|---|---|---|---|---|---|---|
| 5 | $DF^M$ | 1 | 0·0035 | 0·0003 | 3·5 | 2·2 | 0·899 |
| | $DF^R$ | 1 | 0·0142 | 0·0011 | 2·2 | 1·9 | 0·925 |
| | $DF_p^M$ | 1 | 1·44 | 0·08 | −2·4 | 1·6 | 0·961 |
| | $DF_p^R$ | 1 | 1·48 | 0·08 | −2·3 | 1·7 | 0·957 |
| | $DF^M$ | 0·5 | 0·00055 | 0·00005 | 1·23 | 0·38 | 0·879 |
| | $DF^R$ | 0·5 | 0·00221 | 0·00020 | 1·04 | 0·35 | 0·901 |
| | $DF_p^M$ | 0·5 | 0·234 | 0·010 | 0·14 | 0·20 | 0·976 |
| | $DF_p^R$ | 0·5 | 0·240 | 0·011 | 0·17 | 0·22 | 0·970 |
| | $DF(z)^M$ | 1 | 0·00155 | 0·00014 | 4·1 | 2·0 | 0·906 |
| | $DF(x,y)^M$ | 1 | 0·00523 | 0·00049 | 3·3 | 2·2 | 0·894 |
| | $DF(z)^R$ | 1 | 0·00604 | 0·0005 | 3·8 | 1·9 | 0·916 |
| | $DF(x,y)^R$ | 1 | 0·0214 | 0·0016 | 1·5 | 2·0 | 0·925 |
| | $DF(z)^M$ | 0·5 | 0·00024 | 0·00003 | 1·4 | 0·4 | 0·875 |
| | $DF(x,y)^M$ | 0·5 | 0·00082 | 0·00008 | 1·2 | 0·4 | 0·879 |
| | $DF(z)^R$ | 0·5 | 0·00092 | 0·00010 | 1·4 | 0·4 | 0·875 |
| | $DF(x,y)^R$ | 0·5 | 0·00338 | 0·0003 | 0·9 | 0·3 | 0·901 |
| 6 | $DF^M$ | 1 | 0·0025 | 0·0004 | 5·6 | 2·8 | 0·765 |
| | $DF^R$ | 1 | 0·0108 | 0·0014 | 3·7 | 2·5 | 0·828 |
| | $DF_p^M$ | 1 | 1·14 | 0·10 | −0·7 | 2·1 | 0·909 |
| | $DF_p^R$ | 1 | 1·18 | 0·10 | −0·6 | 2·2 | 0·907 |
| | $DF^M$ | 0·5 | 0·00046 | 0·00006 | 1·42 | 0·45 | 0·802 |
| | $DF^R$ | 0·5 | 0·00189 | 0·00023 | 1·17 | 0·41 | 0·843 |
| | $DF_p^M$ | 0·5 | 0·207 | 0·013 | 0·28 | 0·26 | 0·952 |
| | $DF_p^R$ | 0·5 | 0·212 | 0·014 | 0·31 | 0·28 | 0·947 |
| | $DF(z)^M$ | 1 | 0·00115 | 0·00017 | 5·5 | 2·6 | 0·789 |
| | $DF(x,y)^M$ | 1 | 0·00373 | 0·00062 | 5·6 | 2·8 | 0·755 |
| | $DF(z)^R$ | 1 | 0·00468 | 0·00059 | 4·6 | 2·3 | 0·837 |
| | $DF(x,y)^R$ | 1 | 0·0161 | 0·0022 | 3·4 | 2·6 | 0·821 |
| | $DF(z)^M$ | 0·5 | 0·00020 | 0·00003 | 1·5 | 0·4 | 0·807 |
| | $DF(x,y)^M$ | 0·5 | 0·00068 | 0·00010 | 1·4 | 0·5 | 0·799 |
| | $DF(z)^R$ | 0·5 | 0·00080 | 0·00010 | 1·4 | 0·4 | 0·826 |
| | $DF(x,y)^R$ | 0·5 | 0·00288 | 0·00034 | 1·1 | 0·4 | 0·849 |

[a] $S_a$ and $S_b$ are the mean square deviations of parameters $a$ and $b$, respectively; $r$ is the correlation coefficient.

correlation coefficients obtained are noticeably higher in the former case). This agrees with existing ideas[18] on the role that dispersion interactions play in forming the ordering in liquid crystalline systems. The changes in the dissymmetry of the dispersion force field caused by the molecular polarizability of chiral dopants exert a decisive influence on the changes in twisting power among other analysed structures. However, the differences stated virtually disappear when using the corresponding normalized *DF* ($DF_p^M$ and $DF_p^R$).

Attention is also drawn to the fact that the $|\beta|$–*DF* correlation dependences in nematic solvent **6**, irrespective of the type of *DF* used are characterized by lower correlation coefficients than for corresponding dependences in nematic solvent **5**. This peculiarity and also the lower twisting power of chiral dopants in medium **6** in comparison with medium **5** and the tendency for levelling of its differences are, in the end, controlled by the more elastic properties of smectogenic nematic solvent **6** compared with **5**.[19]

According to the data for the nematic solvent **5**, a more accurate description of the correlation between $|\beta|$ and $DF^R(DF^M)$ is given by linear correlation dependence (1) with $y = 1$, whereas using the normalized $DF_p^M$ and $DF_p^R$ values higher correlation coefficients were obtained with $y = 0{\cdot}5$. The same situation is valid for $|\beta|$–$DF_p^M$ ($DF_p^R$) dependences in nematic solvent **6**. As regards the higher correlation coefficients obtained when using the normalized $DF_p^M$ and $DF_p^R$ values compared with the correlative dependence $|\beta|$–$DF^M$ ($DF^R$), it is possible that an important role is played by the fact that with such normalization of *DF* the differences in molecular dissymmetry disappear and the range of relative changes in *DF* decreases, leading to the apparent rise in the accuracy of the correlation.

Apparently, the ranges of $|\beta|$ and *DF* values for the chiral compounds investigated here is not large enough to show a convincing preference for any specific type of *DF* ($DF^M$ or $DF_p^M$, $DF^R$ or $DF_p^R$) or for a particular regression equation (1) with $y = 0{\cdot}5$–$1$ for a description of the twisting power–molecular dissymmetry relationship at this stage of the investigation. Subsequent broader investigations of chiral compounds especially with smaller and higher *DF* values than for **1–4** will allow the form of the correlative $|\beta|$–*DF* to be specified. The establishment of the correlative dependence between these values is more important as this dependence is determined for the whole range of chiral dopants differing both in the structures of the chiral cyclohexanone or cyclohexenone molecular fragments and in the character of the $\pi$-electron system. This opens up the possibility of non-experimental screening of chiral components of induced cholesteric systems proceeding from the calculated *DF* values and theoretical conformational analysis. Thus an increase in the number of benzene rings in structures **1** may be useful because $DF^R = 5643$, $DF_p^R = 44{\cdot}05$, $DF^M = 17\,160$ and $DF_p^M = 43{\cdot}56$ are calculated for derivative **1** with $X = 4'\text{-}C_6H_5C_6H_4$, which are higher than the corresponding values obtained for the investigated compounds **1–4**.

We were also able to compare the twisting powers calculated using dissymmetry functions of various types and obtained correlative dependences (1) ($|\beta|^{\text{calc.}}$) and experimental values ($|\beta|^{\text{exper.}}$) for two compounds of series **4** obtained recently[10] (**4c**, $X = OCH_3$, and **4d**, $X = C_6H_5$) (see Table 3). A satisfactory correspondence between $|\beta|^{\text{calc.}}$ and $|\beta|^{\text{exper.}}$ should be obtained. It is remarkable that such a correspondence can be observed for the data in nematic solvent **6** also where the correlation coefficients for equation (1) with $y = 1$ are considerably lower than those for the corresponding data in nematic solvent **5**. The best agreement between $|\beta|^{\text{calc.}}$ and $|\beta|^{\text{exper.}}$ values for both compounds in nematic solvent **5** is obtained when the molecular dissymmetry $DF^R$ and the correlative equation (1) with $y = 1$ are used.

It is interesting that $|\beta|^{\text{calc.}}$ values obtained when using the normalized values $DF_p^M$ and $DF_p^R$ in nematic solvent **5** are considerably underestimated in comparison with the experimental values (two times less for compound **4c**). This agrees with the above-stated ideas concerning these *DF* peculiarities. On the other hand, the high $|\beta|^{\text{exper.}}$ value for compound **4c** in nematic solvent **5** (considerably higher than in medium **6** or for compound **4b** with much higher *DF* values) possibly reflects the effect of some structural similarity of molecules of nematic solvent **5** and chiral dopant **4c** (the existence of similar *p*-methoxybenzylidene fragments), the importance of which was stated by others.[20–22] The influence of this additional specific factor is not, of course, taken into account in the *DF* values.

While analysing the structure–twisting power relationship, it should be taken into account that the influence of foreign particles on the properties of liquid crystalline system can be considered not only within the limits of the general properties of the dissymmetry of chiral molecules but also with regard to their biaxiality. The problems of the influence of the biaxiality of mesogenic molecules and foreign particles on the thermodynamic properties of mesophases within the limits of the traditional physical views have been considered by several groups.[18,23–27] The results of these investigations are ambiguous and do not allow this problem to be solved even at the level of the construction of a correlative dependence.

In connection with this, it seems to be appropriate to make an attempt to consider the influence of the biaxiality of the chiral dopant molecules on their effectiveness in inducing helical ordering in the mesophase (the twisting power) within the limits of the *DF* method, since it allows one, as shown above, to describe the influence of molecular structure on $\beta$ safely enough at

Table 3. $|\beta|^{\text{calc.}}$ values for compounds **4c** ($X = OCH_3$) and **4d** ($X = C_6H_5$) calculated using correlative dependences (1) and (2)

| Compound | Type of *DF* used | Correlation equation | *y* Values in correlation equation (1) | $|\beta|^{\text{calc.}}$ in nematic solvents ($\mu m^{-1}$) | |
|---|---|---|---|---|---|
| | | | | **5** | **6** |
| **4c** ($X = OCH_3$)[a] | $DF^M$ | (1) | 1 | 29·3 | 24·0 |
| | $DF^R$ | (1) | 1 | 32·5 | 26·8 |
| | $DF_p^M$ | (1) | 0·5 | 20·9 | 17·6 |
| | $DF_p^R$ | (1) | 0·5 | 21·1 | 17·8 |
| | $DF(z)^M$ | (1) | 1 | 29·0 | 24·0 |
| | $DF(x, y)^M$ | (1) | 1 | 29·5 | 24·2 |
| | $DF(z)^R$ | (1) | 1 | 31·4 | 26·0 |
| | $DF(x, y)^R$ | (1) | 1 | 32·8 | 26·9 |
| | $DF(z)^M$, $DF(x, y)^M$ | (2) | — | 29·0 | 23·1 |
| | $DF(z)^R$, $DF(x, y)^R$ | (2) | — | 33·1 | 26·1 |
| **4d** ($X = C_6H_5$)[b] | $DF^M$ | (1) | 1 | 50·4 | 39·1 |
| | $DF^R$ | (1) | 1 | 60·8 | 48·3 |
| | $DF_p^M$ | (1) | 0·5 | 44·1 | 36·4 |
| | $DF_p^R$ | (1) | 0·5 | 42·7 | 35·2 |
| | $DF(z)^M$ | (1) | 1 | 50·8 | 40·2 |
| | $DF(x, y)^M$ | (1) | 1 | 50·0 | 38·9 |
| | $DF(z)^R$ | (1) | 1 | 61·8 | 49·6 |
| | $DF(x, y)^R$ | (1) | 1 | 59·4 | 46·9 |
| | $DF(z)^M$, $DF(x, y)^M$ | (2) | — | 50·6 | 39·0 |
| | $DF(z)^R$, $DF(x, y)^R$ | (2) | — | 61·6 | 49·2 |

[a] *DF* values calculated for compound **4c**: $DF^M = 7378$, $DF^R = 2137$, $DF_p^M = 18{\cdot}92$, $DF_p^R = 18{\cdot}45$, $DF(z)^M = 16\,060$, $DF(x, y)^M = 5001$, $DF(z)^R = 4574$ and $DF(x, y)^R = 1461$. Experimental values of $|\beta|$ are $40{\cdot}4 \pm 1{\cdot}7\ \mu m^{-1}$ in nematic solvent **5** and $20{\cdot}1 \pm 3{\cdot}5\ \mu m^{-1}$ in nematic solvent **6**.

[b] *DF* values calculated for compound **4d**: $DF^M = 13\,390$, $DF^R = 4127$, $DF_p^M = 27{\cdot}78$, $DF_p^R = 26{\cdot}53$, $DF(z)^M = 30\,150$, $DF(x, y)^M = 8922$, $DF(z)^R = 9610$ and $DF(x, y)^R = 2704$. Experimental values of $|\beta|$ are $63{\cdot}9 \pm 1{\cdot}5\ \mu m^{-1}$ in nematic solvent **5** and $37{\cdot}5 \pm 3{\cdot}0\ \mu m^{-1}$ in nematic solvent **6**.

the level of correlative dependences. Proceeding in such a way, parallel to the general dissymmetry functions $DF^M$ and $DF^R$ for the studied chiral compounds, we calculated their components $DF(z)^M$, $DF(x, y)^M$, $DF(z)^R$ and $DF(x, y)^R$ characterizing the molecular dissymmetry with respect to molecular long ($z$) and short ($x, y$) axes respectively. Every function $DF(z)$, $DF(x)$ and $DF(y)$ was calculated, according to Ref. 7, as the geometrical mean level of dissymmetry ($LD^{S_i}$) with respect to all specific ways of carrying out the operation of symmetry $S_i$ for a molecule in the given system of coordinates, e.g.

$$DF(Z) = \sqrt[4]{LD^{S_1^z} LD^{S_2^z} LD^{S_4^z} LD^{S_6^z}}$$

The functions $DF(x, y)$ were correspondingly calculated as the geometrical mean of functions $DF(x)$ and $DF(y)$ with respect to two much shorter molecular axes. $DF(z)$ and $DF(x, y)$ values within the limits of the *DF* method are a peculiar characteristic of the biaxiality of chiral molecules.

The calculated $DF(z)$ and the $DF(x, y)$ values are given in Table 4. Their comparison with the set of $DF^M$ and $DF^R$ values for the same compounds **1–4** (Table 1) shows complete similarity of the changes in $DF^{M(R)}$ values and their components $DF(z)^{M(R)}$ and $DF(x, y)^{M(R)}$. It can be noted that the relative change in $DF(z)^{M(R)}$ values in the series of compounds **1–4** is slightly larger than that in $DF(x, y)^{M(R)}$ values [the ratio of $DF(z)^{M(R)}$ values for compounds **4d** and **3a** is 3·9–4·1; the corresponding ratio of $DF(x, y)^{M(R)}$ values is 3·3–3·4; see Tables 3 and 4].

To clarify the relationship between the twisting power $|\beta|$ of the biaxial chiral molecules and the components of their dissymmetry $DF(z)$ and $DF(x, y)$, it seems to be simplest and valid enough to use the following linear two-parameter correlative dependences:

$$|\beta| = aDF(z)^{M(R)} + bDF(x, y)^{M(R)} + c \qquad (2)$$

For comparison, the single-parameter correlative dependences $|\beta|$–$DF(z)$ and $|\beta|$–$DF(x, y)$ are also considered. The results of the regression analysis carried out (Tables 2 and 5) show that the twisting power of compounds **1–4** correlates with the components of molecular dissymmetry $DF(z)$ and $DF(x, y)$ with virtually the same accuracy as when using the general characteristics of dissymmetry $DF^M$ and $DF^R$.

Table 4. Calculated components of dissymmetry functions with respect to long [$DF(z)$] and short [$DF(x, y)$] molecular axes for chiral compounds **1**–**4** and ( – )-menthone

| Compound | X | Component of dissymmetry functions | | | |
|---|---|---|---|---|---|
| | | $DF(z)^M$ | $DF(x, y)^M$ | $DF(z)^R$ | $DF(x, y)^R$ |
| **1a** | H | 8129 | 2702 | 2771 | 904 |
| **1b** | F | 10692 | 3244 | 2770 | 904 |
| **1c** | Cl | 13290 | 3767 | 3531 | 1061 |
| **1d** | Br | 18998 | 4826 | 4012 | 1156 |
| **1e** | $NO_2$ | 14894 | 4098 | 3737 | 1164 |
| **1f** | CN | 12460 | 3611 | 3570 | 1070 |
| **1g** | $OCH_3$ | 12801 | 3697 | 3839 | 1189 |
| **1h** | $OC_2H_5$ | 14903 | 4203 | 4540 | 1284 |
| **1i** | $C_6H_5$ | 21952 | 5619 | 7241 | 1831 |
| **2a** | H | 10785 | 4458 | 3114 | 1175 |
| **2b** | F | 13998 | 5214 | 3113 | 1175 |
| **2c** | Cl | 17281 | 5994 | 3947 | 1376 |
| **2d** | Br | 24228 | 6792 | 4391 | 1497 |
| **2e** | $NO_2$ | 19325 | 6581 | 4172 | 1449 |
| **2f** | $OCH_3$ | 16566 | 5858 | 4261 | 1438 |
| **2g** | $C_6H_5$ | 28094 | 8698 | 8020 | 2329 |
| **3a** | H | 7390 | 2594 | 2448 | 808 |
| **3b** | F | 9830 | 3153 | 2448 | 809 |
| **3c** | Cl | 12354 | 3860 | 3154 | 1028 |
| **3d** | Br | 17768 | 4766 | 3596 | 1145 |
| **3e** | $NO_2$ | 13859 | 4058 | 3347 | 1090 |
| **3f** | $OCH_3$ | 11885 | 3576 | 3459 | 1025 |
| **3g** | $C_6H_5$ | 20672 | 5559 | 6638 | 1782 |
| **4a** | H | 10238 | 3565 | 3370 | 1150 |
| **4b** | Br | 24755 | 7110 | 5087 | 1588 |
| ( – )-Menthone | | 1644 | 917 | 517 | 247 |

Table 5. Parameters of regression equations $|\beta| = aDF(z)^{M(R)} + bDF(x, y)^{M(R)} + c$ for the whole range of chiral compounds **1**–**4** and ( – )-menthone

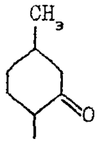
| Solvent | $DF$ used | $a$ | $S_a$[a] | $b$ | $S_b$[a] | $c$ | $S_c$[a] | $r$[a] |
|---|---|---|---|---|---|---|---|---|
| **5** | $DF(z)^M$, $DF(x, y)^M$ | 0·00137 | 0·00059 | 0·00061 | 0·002 | 3·9 | 2·2 | 0·899 |
| | $DF(z)^R$, $DF(x, y)^R$ | 0·0017 | 0·0022 | 0·016 | 0·008 | 2·0 | 2·1 | 0·921 |
| **6** | $DF(z)^M$, $DF(x, y)^M$ | 0·0016 | 0·0007 | – 0·0017 | 0·0024 | 5·9 | 2·7 | 0·778 |
| | $DF(z)^R$, $DF(x, y)^R$ | 0·0040 | 0·0028 | 0·0022 | 0·0097 | 4·4 | 2·6 | 0·823 |

[a] $S_a$, $S_b$ and $S_c$ are mean square deviations of parameters $a$, $b$ and $c$, respectively; $r$ is the correlation coefficient.

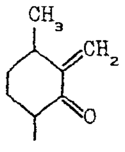
This agrees with the model Van der Meer,[18] according to which the calculation of molecular biaxiality gives only a non-essential contribution to the energy of the interaction between molecules of helically ordered systems. It seems to be that in uniaxial liquid crystalline media (nematic solvents **5** and **6** used here are related to such media) the influence of the biaxiality of the molecules of chiral dopants is revealed only locally and does not affect the overall order parameters.[18]

The use of functions $DF(z)^{M(R)}$ and $DF(x, y)^{M(R)}$ and the general characteristics of dissymmetry $DF^{M(R)}$ allows one to predict satisfactorily the $|\beta|$ values of new chiral compounds on the basis of correlative dependences of types (1) and (2) (Table 3).

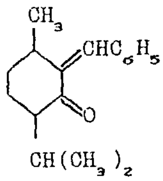
To determine possible ways for a directed search for effective chiral dopants similar to the studied ketones **1**, it is expedient to follow the changes in $DF^R$ and $DF_p^R$ values with consecutive structural changes in molecules **7**–**14**.



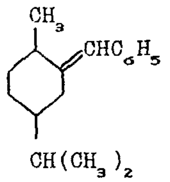
**7**, $DF^R = 356$, $DF_p^R = 8 \cdot 1$



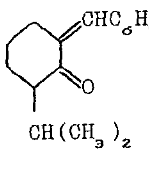
**8**, $DF^R = 573$, $DF_p^R = 10 \cdot 4$



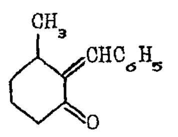
**9**, $DF^R = 1335$, $DF_p^R = 17{\cdot}9$



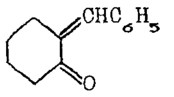
**10**, $DF^R = 1321$, $DF_p^R = 18{\cdot}2$



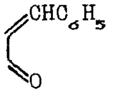
**11**, $DF^R = 1159$, $DF_p^R = 16{\cdot}8$



**12**, $DF^R = 1257$, $DF_p^R = 18{\cdot}6$



**13**, $DF^R = 1082$, $DF_p^R = 17{\cdot}5$



**14**, $DF^R = 234$, $DF_p^R = 6{\cdot}2$

When calculating the *DF* values of the molecules their geometry was naturally considered to be similar to those in structures **1**. It is evident that the introduction of a 2-methylene group into the molecule of (+)-isomenthone (**7**; giving **8**) affects the $DF^R$ and $DF_p^R$ values comparatively weakly. However, the subsequent introduction of a phenyl group with the formation of structure (**1**, X = H) (**9**) sharply increases (almost doubles) $DF_p^R$. Close values of $DF^R$ and $DF_p^R$ are also obtained for the 2-benzylidene derivative of *p*-menthane (**10**). It is characteristic that the values of $DF^R$ and particularly of $DF_p^R$ vary slightly on passing to structures **11**–**13**, differing from **9** by the absence of one or both alky substituents.

Overall it is obvious that in the case of ketone **13** the dissymmetry of the molecule is controlled only by the non-planarity of the cinnamoyl fragment. However, the model non-planar cinnamoyl system **14** is characterized by a relatively low dissymmetry, that is, the incorporation of this group in a six-membered ring is an important factor. Hence the investigation indicates that fixing the position of the cinnamoyl group in a non-planar *s-cis*-conformation due to the chiral six-membered ring is one of the ways to obtain chiral structures with both high dissymmetry and high twisting power. The character of alkyl substitution in the ring is important only in connection with the necessity for stabilization of one conformer with a certain helicity of the cinnamoyl system. The number of chiral centres in the ring is not of much importance. The introduction of extended *para* substituents in the benzene ring, as follows from Table 1, is also a reason for some increase in molecular dissymmetry.

Hence we conclude that there are certain possibilities of using the calculated *DF* values to describe the influence of the molecular structure of chiral compounds on one of their important properties stipulated by the molecular chirality, viz. the effectiveness of the induction of helical ordering in the nematic mesophase.

## EXPERIMENTAL

The measurements of the sign and absolute values of the twisting power of chiral compounds was described previously.[28] Conformational energies of the structures under investigation were calculated according to the force field method[12] with Scott–Scheraga parameters.[29] The calculations of *DF* values were carried out as described in Part I.[7] The values of the atom refractions according to Eisenlohr–Vogel[30] were used.

## CONCLUSION

For many chiral carbonyl compounds, cyclohexanone and cyclohexenone derivatives, existing almost entirely in the form of one molecular conformation, the correlative dependences between the values of the calculated dissymmetry functions with respect to atomic masses and atom refractions and the induction effectiveness of helical ordering in the nematic mesophase (twisting power) have been established. The important aspect is that such correlative dependences are observed for groups of compounds that differ in the structures of both the chiral cyclic skeleton and the exocyclic $\pi$-electronic substituent, allowing one to predict with acceptable accuracy the twisting power of new substances with a 'fixed' molecular conformation.

Types of dissymmetry functions and of correlative dependences that are most acceptable for this purpose were established. Dissymmetry functions formed on the basis of atom refractions (polarizabilities) describe the influence of the molecular structure of chiral compounds on the twisting power with higher accuracy than those which characterize the dissymmetry of the atomic mass distribution, according to the important role of the dispersion forces in the formation of helical ordering in liquid crystalline systems.

The components characterizing the distribution dissymmetry of atomic refractions and masses with respect to the long and the two shorter axes as peculiar characteristics of the biaxiality of chiral molecules describe the influence of the molecular structure on the twisting power with the same accuracy as do the general *DF* values. Hence, within the limits of the *DF* method, it was confirmed that the biaxiality of a dopant molecule does not have a significant effect in uniaxial mesophases.

Based on the calculations for model systems, it was established that the existence of the non-planar cinnamoyl fragment has a decisive influence on the molecular dissymmetry of chiral $\alpha,\beta$-unsaturated cyclohexanone and cyclohexenone derivatives. Alkyl groups influence the molecular dissymmetry only slightly, but it is important that their existence ensures the stabilization of a single chiral conformer with the defined helicity of the cinnamoyl fragment.

## REFERENCES

1. G. S. Chilaya, *Rev. Phys. Appl.* **16**, 193–208 (1981).
2. A. D. Buckingham, G. P. Ceasar and M. B. Dunn, *Chem. Phys. Lett.* **3**, 540–541 (1969).
3. G. Gottarelli and G. P. Spada, *Mol. Cryst. Liq. Cryst.* **123**, 377–388 (1985).
4. W. J. Richter and E. H. Korte, *Ber. Bunsenges. Phys. Chem.* **82**, 812–814 (1978).
5. E. H. Korte, P. Chingduang and W. J. Richter, *Ber. Bunsenges. Phys. Chem.* **84**, 45–50 (1980).
6. M. Nogradi, *Stereokhimiya. Osnovnye kontzeptzii i prilozheniya* (in Russian), pp. 45, 63. Mir, Moscow (1984).
7. V. E. Kuz'min, I. B. Stel'makh, M. B. Bekker and D. V. Pozigun, *J. Phys. Org. Chem.* (POC 352).
8. L. A. Kutulya, N. S. Pivnenko, I. B. Nemchyonok, T. V. Handrimailova, G. P. Semenkova, V. I. Biba and V. G. Tishchenko, *Zh. Obshch. Khim.* **57**, 397–415 (1987).
9. L. A. Kutulya, T. V. Handrimailova, V. I. Biba, N. S. Pivnenko and V. P. Gavrilenko, *Zh. Obshch. Khim.* **58**, 1793–1804 (1988).
10. L. A. Kutulya, N. S. Pivnenko, T. V. Handrimailova, V. I. Biba, S. S. Oleinik, G. P. Semenkova and L. I. Protsenko, *Zh. Obshch. Khim.* **59**, 191–204 (1989).
11. U. Burkert and N. L. Allinger, *Molecular Mechanics* ACS, Washington (1982).
12. L. A. Kutulya, V. E. Kuz'min, I. B. Stel'makh, I. B. Nemchyonok and T. V. Handrimailova, *Zh. Obshch. Khim.* **60**, 737–749 (1990).
13. C. Djerassi, *Optical Rotatory Dispersion. Applications to Organic Chemistry* McGraw Hill, NY (1960).
14. N. A. Bergman, *Acta Chem. Scand., Ser. A* **33**, 577–582 (1979).
15. A. N. Vereshchagin, *Polarizueniost molecul* (in Russian). Nauka, Moscow (1980).
16. G. S. Chilaya and L. M. Lisetski, *Usp. Fiz. Nauk.* **134**, 279–304 (1981).
17. M. Cotter, *Mol. Cryst. Liq. Cryst.* **97**, 29–47 (1983).
18. B. W. Van der Meer, Thesis, Groningen (1979).
19. A. V. Tolmachev, Yu. A. Grinchenko and V. G. Tishchenko, *Kristallografiya* **33**, 786–787 (1988).
20. J. M. Ruxer and G. Solladié, *Mol. Cryst. Liq. Cryst. (Lett.)* **41**, 109–114 (1978).
21. G. Gottarelli, P. Mariani, G. P. Spada, E. Samori and A. Forni, *Tetrahedron* **39**, 1337–1344 (1983).
22. G. Gottarelli, M. Hibert, B. Samori, G. Solladié, G. P. Spada and R. Zimmerman, *J. Am. Chem. Soc.* **105**, 7318–7321 (1983).
23. H. Schroder, *Liquid Crystals of One- and Two-Dimensional Order*, pp. 196–204. Garmisch-Partenkirchen (1980).
24. R. M. Hornreich and S. Shtrikman, *Phys. Rev. A* **29**, 3444–3446 (1984).
25. Y. R. Lin-Liu and M. A. Lee, *Phys. Rev. A* **28**, 2580–2583 (1983).
26. A. N. Zakhlevnykh and M. I. Shliomis, *Zh. Eksp. Teor. Fiz.* **86**, 1309–1319 (1984).
27. B. W. Van der Meer and G. Vertogen, *Phys. Lett. A* **71**, 486 (1979).
28. I. B. Nemchyonok, A. V. Tolmachev, L. A. Kutulya and V. G. Tishchenko, *Zh. Fiz. Khim.* **60**, 635–639 (1986).
29. R. A. Scott and H. A. Scheraga, *J. Chem. Phys.* **42**, 2209–2215 (1965).
30. K. P. Mishchenko and A. A. Ravdel (Eds), *Kratkij spravochnik physico-khimicheskih velichin* (in Russian), p. 117. Khimiya, Moscow, Leningrad (1965).