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CHIRALITY IN NONLINEAR OPTICS AND OPTICAL SWITCHING

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Abstract Chirality in molecular opto-electronics is limited so far to the use of optically active liquid crystals and a number of optical phenomena are related to the helical macroscopic structure obtained by using one enantiomer, only. In this paper, the use of chirality in nonlinear optics and optical switching is demonstrated. The additional options offered by the combination of circularly polarized light and chiral molecules gives rise to the observation of Second Harmonic Generation from centrosymmetric crystals of a racemic mixture. This phenomenon is due to the existence of optical activity in the hyperpolarizability. Chiroptical switching is observed in inherently dissymmetric molecules, that can undergo a photochemical isomerization of a strongly dextrorotatory isomer into a strongly laevorotatory isomer. Using circular dichroism the switching between these two pseudo-enantiomers can be monitored accurately.

INTRODUCTION

The interaction of light and matter is very prominent in the development of new electronic devices. The use of molecules into the field of opto-electronics is often referred to as the use of molecules that are optically active. However, the term optical activity of molecules is related to the interaction of light with *chiral* molecules¹. Lord Kelvin called any geometrical figure, or group of points chiral if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself². And from the day of recognition, stereochemistry has become one of the most important activities in chemistry³. Optical activity of molecules is well-known and its detection by polarimetry, circular dichroism, or optical rotatory dispersion is routinely performed. In sharp contrast with the prominent role of chirality in (bio)chemistry, optical activity of materials has

so far been considered of minor importance, although the area of liquid crystals is an exception⁴. By the combination of chiral molecules and opto-electronics, the circular polarization of light can be used as an additional interesting feature. Since opto-electronics is primarily performed with molecules in the solid state, chirality due to frozen-in chiral conformations (enanti conformers) can be used as well.

As stated above, the use of optically active materials is most pronounced in the area of liquid-crystals⁴. Cholesteric mesophases have been observed in the first liquid crystals and extremely high optical rotations and selective reflection of a narrow band of wavelengths are characteristic for these cholesteric mesophases⁵. Such properties are attributed to the macroscopic chiral helical structure of the cholesteric phase and not to the chirality of the individual molecules themselves. The light that is reflected has a wavelength that is proportional to the pitch of the helix. Moreover the reflection depends on the rotatory sense of the cholesteric phase. For example, lefthanded light can be transmitted while righthanded light is reflected. In contrast to normal reflections, no phase change and no inversion of the sense is observed⁶. A spontaneous macroscopic electric polarization is observed in a series of chiral smectic mesophases⁷. These molecules are studied in great detail with respect to the electro-optic effect in surface-stabilized ferroelectric liquid-crystal displays⁸. A very fast switching is observed and by now chirality has become arguably the most important and complex topic of research in liquid crystals today⁴.

Contrary to liquid crystals, the use of chirality and its peculiar effects on optics are rarely discussed in the area of nonlinear optics and optical switching. In this paper, we like to show the possible use of chirality and optical activity in these areas of opto-electronics.

CHIRALITY AND NONLINEAR OPTICS

In centrosymmetric structures the even order nonlinear susceptibilities ($\chi^{(2)}$, $\chi^{(4)}$, etc) are, in the electric dipole approximation, zero for symmetry reasons⁹. Recently, organics and polymers have been studied extensively in view of their potentially high nonlinear susceptibilities^{10,11}. In centrosymmetric crystals the centre of symmetry usually connects two identical molecules with each other. The second harmonic generation (SHG) with input field of frequency ω is governed by the molecular hyperpolarizability tensor $\beta_{ijk}(-2\omega, \omega, \omega)$. If a molecule is transformed by a centre of symmetry all μ 's change sign, resulting in a change of sign of $\beta(-2\omega, \omega, \omega)$. A pair of molecules related by a centre of symmetry, therefore, gives no contribution to the macroscopic susceptibility $\chi^{(2)}(-2\omega, \omega, \omega)$. Since for most of the organic molecules a two-level model accounts

already for most of the value of β_{ijk} , the hyperpolarizability is then given by ¹²:

$$\beta_{zzz}(-2\omega; \omega, \omega) = \frac{6}{\hbar^2} \frac{\mu_z^{on} \mu_z^{no} \Delta\mu_z (\omega_{on})^2}{((\omega_{on})^2 - 4\omega^2) ((\omega_{on})^2 - \omega^2)} \quad (1)$$

where $\Delta\mu_z$ is the difference between the dipole moment of the ground state and the excited state, $\mu_i^{on} = \langle 0 | \mu_i | n \rangle$, and ω_{on} the frequency of the optical transition.

In order to transform a molecule with high β values into a material without a centrosymmetric structure three main techniques of material engineering are available: crystal engineering, Langmuir-Blodgett thin film technology and the poling of dipoles in a polymer ¹¹. Optically active molecules are of special interest in crystal engineering since no centrosymmetry in crystals of these molecules is possible due to the absence of the mirror image in the crystal ^{10,13}. High $\chi^{(2)}$ values are reported for a series of these polar chiral crystals ¹⁴. Another interesting use of chirality to introduce macroscopic noncentrosymmetry is the spontaneous polarization of ferroelectric liquid crystals ¹⁵. The reported $\chi^{(2)}$ values are however low, primarily due to the fact that the polarity originates from a small dipole perpendicular to the molecular axis.

We introduced the use of chirality in nonlinear optics by studying SHG from centrosymmetric crystals of a racemic mixture ¹⁶. In these centrosymmetric crystals of racemic mixtures the centre of symmetry connects two different enantiomers of a chiral molecule ¹³. In eq (1) we have restricted the Hamiltonian describing the interaction between the field with the molecules to the electric dipole term. In fact this term is only the first in the multipole expansion ^{9,17}. In the Hamiltonian the two terms after the leading electric dipole term, viz, the magnetic dipole term and the electric quadrupole term, are generally considered as to be small and of the same order of magnitude. However, in many organic molecules a significant allowed magnetic dipole transition is present, while the quadrupole moment remains small ¹⁸. Using the magnetic dipole term, optical activity is explained. A significant theoretical contribution to the optical activity of higher terms is made by G. Wagnière ^{19,20}.

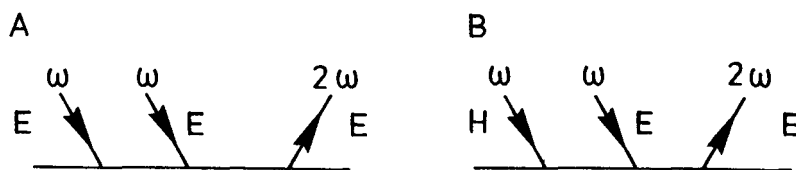


FIGURE 1 Generalized graphs for light-induced electric polarizations.

A schematic graph to present the light-induced electric polarizations is given in figure 1. The well-known presentation is A, using only electric dipole interactions for β , while B is the case where one electric dipole interaction is replaced by a magnetic dipole interaction.

Formally, the influence of the magnetic dipole moment can be incorporated into the electric dipole formalism by replacing^{18,21}:

$$\mu_j \rightarrow \mu_j \pm \frac{i}{c} m_j \quad (2)$$

where the \pm sign refers to the handedness of the incident beam and c is the velocity of light. For the enantiomers R and S the sign of m differs. The magnetic dipoles m are in first order responsible for the optical rotation and for the optical activity in the hyperpolarizability. The latter is simply illustrated by making the substitution of eq (2) in the expression (1) for the hyperpolarizability β_{zzz} . Use is made of the property that for real wave functions the transition moments μ and m are real and imaginary, respectively. The denominator of β_{zzz} then changes as follows,

$$\mu_i^{on} \mu_i^{no} \rightarrow (\mu_i^{on})^2 \pm 2 \frac{i}{c} \mu_i^{on} m_i^{on} + \frac{4i^2}{c^2} (m_i^{on})^2 \quad (3)$$

The eq's (1) and (3) result in a difference in magnitude of β_{zzz} for each enantiomer using left- or righthanded light. Hence, it is clear that for one enantiomer the β is increased upon irradiation with left circularly polarized light, while for the other enantiomer β decreases, or *vice versa*. This difference in β is referred to as the optical activity in the hyperpolarizability β ^{19,20}.

The optical activity described above implies that if we irradiate a lattice of a centrosymmetric pair of enantiomers with a circularly polarized fundamental beam the R and S enantiomers will have different values of β and this difference will give rise to SHG. Prerequisite for a detectable SHG based on this mechanism is that the long-range order of each enantiomer is such that they are more or less in parallel. In other words, in these special cases of centrosymmetric crystals the electric dipole contributions vanish (figure 1 A), while the magnetic dipole or chiral contributions add up for both enantiomers (figure 1 B). Hence only magnetic dipole transitions contribute to a non-zero SHG.

For the verification of the hypothesis outlined above we studied centrosymmetric crystals of a racemic mixture. A single crystal of R,S-N-acetyl valine was grown from ethanol in the $P2_1/c$ space group. The structure of the two enantiomers, the unit cell packing and the crystal axes are given in figure 2.

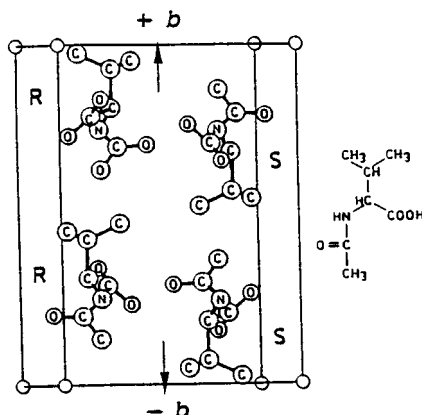


FIGURE 2 The unit cell of R,S-N-acetyl valine.

The unit cell consists of two R enantiomers and two S enantiomers. The array of R enantiomers with 2_1 symmetry yields a polar $+b$ axis, while the array of S enantiomers yields similarly a polar $-b$ axis^{13,22}.

The nonlinear optical measurements were performed using a Nd:YAG laser (2×10^8 W/cm², 30 ps) at 1064 nm. The ellipticity of the fundamental beam is generated by the birefringence of the crystal. SHG at 532 nm was detected through bandpass filters. The SH intensity was compared with that of a y-cut crystal quartz plate tuned to a Maker fringe maximum. Irradiation of the crystal with a plane wave directed perpendicularly to the b - c plane shows only minor SHG if the fundamental wave has its polarization parallel to the b or c plane. At intermediate values of Ψ , the angle between the crystal c axis and the direction of the polarization of the incoming wave, the fundamental beam becomes elliptically polarized by the birefringence of the crystal and the amount of SHG increases significantly, reaching a maximum at about $\Psi = \pi/4$ (Figure 3).

The observed intensity of the SHG is quadratic in the fundamental intensity and polarized parallel to the b axis. Furthermore, the observed dependence on the rotational angle ψ (see figure 4) agrees with the calculated function $\sin^2(2\psi)$, based on the quadratic dependence on $E(\omega) \cdot H(\omega)$. Similar results are obtained when the incoming wave is made circular polarized by a $1/4\lambda$ -plate.

Partial phase matching is obtained by rotating the crystal around its b axis. The maximum intensity of the SHG amounts to about 1% of that of the quartz plate and is at least six orders of magnitude larger than the SHG from centrosymmetric crystals of achiral molecules like 1,4-dichlorobenzene and hexamethylbenzene.

The data presented above are all in agreement with the proposed interaction term $^{eeh} \chi^{(2)}(-2\omega, \omega, \omega): E(2\omega) \cdot E(\omega) \cdot H(\omega)$. It is expected that this effect will be found in a number of other centrosymmetric crystals of racemic molecules, also.

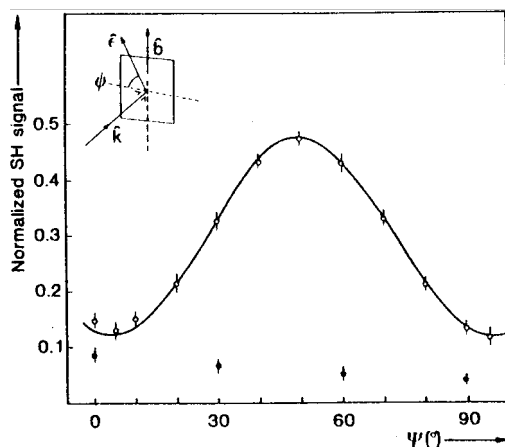


FIGURE 3 The intensity of SHG vs ψ , the angle between the crystal c axis and the linear polarization of the fundamental wave, incident perpendicularly to the b - c plane. The SHG measured with the analyzer parallel to the crystal b axis is given with the open symbols, while the closed symbols represent the SHG measurements with the analyzer parallel to the c axis. the solid line represents the calculated function of $\sin^2(2\psi)$, with a small offset in ψ that is within the experimental uncertainty.

We now propose that a related phenomenon due to another interaction term ${}^{hee}\chi^{(2)}(-2\omega, \omega, \omega):H(2\omega).E(\omega).E(\omega)$, will be present in a large number of organic crystals of racemic mixtures, as well ²³. In figure 4 the corresponding graph is presented. To the best of our knowledge this interaction term has not been considered before. If this interaction term is active, SHG from a centrosymmetric crystal of a racemic mixture results from a non-vanishing *radiating* magnetic dipole transition.

In order to find experimental evidence for this new interaction term, we studied a number of racemates. Non-zero SHG from a single crystal of R,S-serine is observed. In contrast to the R,S-*N*-acetyl valine case, the maximum SHG in R,S-serine is observed when the fundamental beam is parallel to the pseudopolar b axis of the crystal and, hence, not circularly polarized.

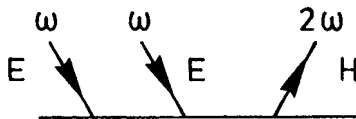


FIGURE 4 Schematic graph for a radiating magnetic dipole transition.

A change in the angle between the polarization of the fundamental beam and the b axis of the crystal results in a decrease in SHG, with a minimum for the fundamental beam parallel to the c axis. The observed SHG in R,S-serine is mainly polarized parallel along the b axis. These data are all in agreement with SHG due to the interaction term ${}^{hee}\chi^{(2)}(-2\omega, \omega, \omega):H(2\omega).E(\omega).E(\omega)$.

Although the phenomenon of optical activity in the hyperpolarizability is explained by using chiral molecules and racemates, it is worthwhile mentioning that in crystals of non-chiral molecules a conformational frozen-in chirality (enantiocoformism) is observed in many cases. A first example of SHG from a centrosymmetric crystal of such enantiocoformers is found in cinnamic amid. X-ray analysis shows that a helical twist is present in the molecule²⁴. A significant SHG of the type ${}^{hee}\chi^{(2)}(-2\omega, \omega, \omega):H(-2\omega);E(\omega).E(\omega)$ is observed for a single crystal of cinnamic amid.

With the experimental evidence presented above, the existence of optical activity in the hyperpolarizability is demonstrated in an indirect way. In the centrosymmetric crystal the electric dipole contributions cancel, while the magnetic dipole or chiral contributions remain. Since organic molecules can possess significant magnetic dipole transitions, upto 20% of the electric dipole transition, it should be possible to detect this phenomenon directly, similarly to that for α using Optical Rotatory Dispersion. Since the SH intensity is quadratic in the $\chi^{(2)}$ and hence in β , the anisotropy in SHG, being $\Delta SH/SH$ will be related to the ratio $(m_z^{on})^2/(\mu_z^{on})^2$. In other words, in order to measure this ΔSH accurately a sensitive experimental set-up has to be combined with molecules that possess a reasonable β and a significant optical activity. Inherently dissymmetric molecules are the molecules of choice. A research programme to synthesize these kind of molecules and to build such a special SHG apparatus is in progress²⁵.

CHIRALITY AND OPTICAL SWITCHING

The general theme of optical switching can be investigated using a number of different concepts, to wit nonlinear optical effects, liquid crystalline effects, thermotropic effects, etc. Photochemical switchable bistable molecules have recently attracted much attention due to possible applications in reversible optical data storage²⁶. So far investigations on bistable switchable molecules have been focussed on the cis-trans isomerizations of (aza-)stilbenes²⁷ and reversible photocyclization reactions²⁸, whereas detection of both bistable states has mainly be limited to differences in UV/VIS spectra. A limited number of reports are presented, in which a photochemical transformation of an achiral molecule gives rise to a change in conformation of a chiral polymer^{29,30}. This change in conformation is accompanied by a change in optical rotation or circular dichroism

spectrum. Both pendant photochromic (aza-)stilbene groups at chiral polymers and dissolved spiropyrans in cholesteric liquid crystalline poly(L-glutamates) are investigated. In all cases reported so far the thermal back reaction at room temperature or the photoinstability of the photochromic molecule prohibited a pure photoreversible scheme. Furthermore, Green et al. have studied in great detail the optical rotation of helical polyisocyanates and its dependence on temperature³¹.

We have studied the use of chirality in a reversible photochemical reaction aiming at monitoring the two bistable states of a molecule with circular dichroism³². In order to use optical activity for this kind of studies, two important requirements have to be fulfilled. At first, molecules with extremely large optical rotations should be used. This can be obtained by using inherently dissymmetric molecules, in which the electric and magnetic dipole transition moments are more or less parallel oriented and both allowed^{18,21}. Secondly, the photochemical reaction should transform a dextrorotatory molecule into a levorotatory molecule. Two possible schemes for chiroptical molecular switches are considered. The first switch envisaged, is the result of a photochemical interconversion of two enantiomers, P and M of (helical) inherent dissymmetric alkenes such as phenanthrene-1,2,3,4-tetrahydro-4-(9-fluorenylidene) using left- or right circularly polarized light. Since complete transformation of one enantiomer into the other is impossible a non 1:1 ratio (depending upon the g-value) in the photostationary state (i.e. deracemization) might be achieved using CPL. Work in this area is in progress³³.

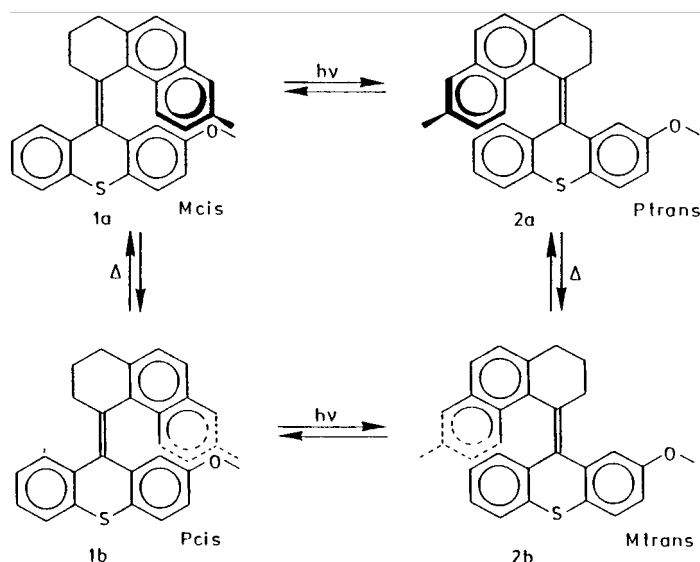


FIGURE 5 The four isomers of the chiroptical switch and the possible (photo- and thermal induced) interconversions.

Recently Schuster and Zhang investigated this concept in the liquid crystalline phases of 4-cyano-4'-n-pentylbiphenyl by a triplet isomerization of a 1,1'-binaphthyl derivative³⁴. Although photoracemization by linear polarized light of 5% dissolved optically pure 1,1'-binaphthyl compound caused the transition from the cholesteric to the nematic phase, the reverse process leading to enantiomeric enrichment and hence the formation of a cholesteric phase out of the nematic phase failed so far.

In an alternative approach we studied the photoisomerization of two pseudo-enantiomeric forms of a chiral compound using non-polarized light, demonstrating the feasibility of a chiroptical molecular switch. The bistable molecules are enantiomers of cis- and trans-4-[9'-(2'-methoxy)thioxanthylidene]-7-methyl-1,2,3,4-tetrahydrophenanthrene (Figure 5, 1 and 2). Both compounds are sterically overcrowded chiral olefins, that can be resolved in thermally stable enantiomers 1a and 1b or 2a and 2b, respectively. The synthesis of 1 and 2 is described elsewhere³⁵. The circular dichroism spectra of 1a and 2a, being different molecules, are roughly mirror images of each other which is in accordance with the P and M helicity of these inherent dissymmetric structures (Figure 6). Unlike other overcrowded ethylenes the enantiomers of 1 and 2 are stable at room temperature. The thermal racemization of M-cis (1a) into P-cis (1b) in p-xylene shows first order kinetics with a racemization barrier of 111 kJ/mol. Furthermore, no thermal cis-trans isomerization (1a \rightleftharpoons 2a) is observed under ambient conditions as determined by ¹H NMR and HPLC analyses.

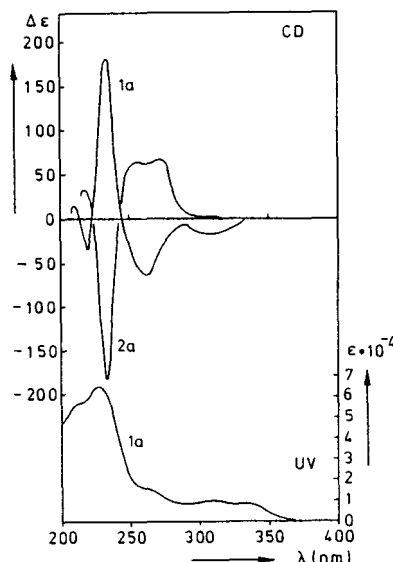


FIGURE 6 The circular dichroism spectra of 1a and 2a and the UV spectrum of 1a as measured in n-hexane ($1.8 \cdot 10^{-5}$ mol/l).

However, upon irradiation with light of 300 or 250 nm, cis-trans isomerization occurs. Irradiation of M-cis at 300 nm selectively yields an M-cis/P-trans mixture of 64/35 ratio, whereas no P-cis and M-trans are formed. Irradiation at 250 nm gives a photostationary state containing a ratio M-cis/P-trans of 68/32. The difference in photostationary state has been monitored by circular dichroism (Figure 7). A modulated signal is obtained upon an alternating irradiation of the mixture with light of 250 and 300 nm, respectively. The cycle between the photostationary states could be repeated for more than 10 times without notable racemization or degradation.

These experiments show that photoisomerization between pseudo-enantiomeric helical systems can be used as a key principle in molecular switching devices. Synthesis of polymer-pendant chiral olefines and switching in the amorphous as well as in the liquid crystalline phase are under investigation³³.

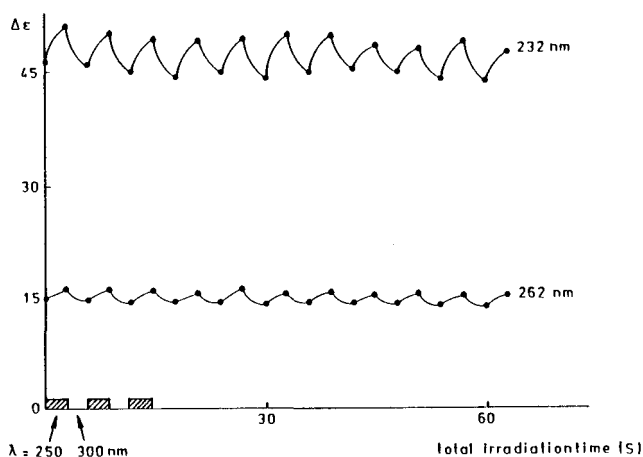


FIGURE 7 The modulation in circular dichroism as detected by 232 and 262 nm of the mixture P-cis/M-trans in n-hexane/isopropanol 9:1 upon irradiation with alternating light of 250 and 300 nm respectively. The switching time is 3 seconds.

CONCLUSIONS AND PROSPECTS

In this paper the unique features of chirality in opto-electronics are addressed. It is shown that chirality is not only of utmost importance in liquid crystals, but gives new possibilities in other areas of molecular devices as well. It is demonstrated that optical activity in the second order susceptibility is present, giving rise to SHG in centrosymmetric crystals of racemic mixtures of enantiomers or enanti conformers. The high rotational strength of inherently dissymmetric twisted olefines is used in the demonstration of a chiroptical molecular

switch. Hereby a leavorotatory helical molecule is transformed into a dextrorotatory helical molecules. The modulation in circular dichroism monitors the photoisomerization.

Since optical properties in opto-electronics are the key functions to play with, it is expected that chirality and the circular polarization of light will become increasingly important. Not only to obtain a new effect, but also as a probe to study 3-dimensional conformations of molecules at hand. For example, it is assumed that the π -conjugation in polymers like polythiophenes and its dependence on conformation can be studied in detail by using optical active derivatives. Furthermore it is foreseen that the role of enantioconformers will become more prominent in the near future.

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