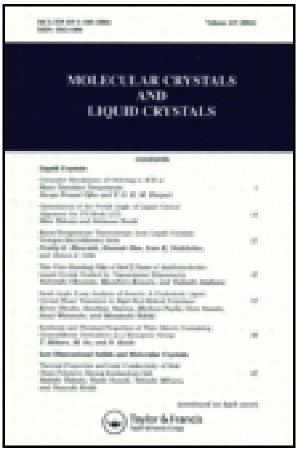

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Orientational Studies of Discotic Liquid Crystals using Fourier Transform Infrared Spectroscopy

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Version of record first published: 04 Oct 2006

To cite this article: Tania Perova, Antoni Kocot & Jagdish K. Vij (1997): Orientational Studies of Discotic Liquid Crystals using Fourier Transform Infrared Spectroscopy, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 301:1, 111-121

To link to this article: http://dx.doi.org/10.1080/10587259708041756

Mol. Cryst. Liq. Cryst., 1997, Vol. 301, pp. 111–121
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ORIENTATIONAL STUDIES OF DISCOTIC LIQUID CRYSTALS USING FOURIER TRANSFORM INFRARED SPECTROSCOPY

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Abstract From an analysis of the infrared dichroic ratio of several bands for triphenylene and truxene derivatives, a major influence of the substrate's structure on the bulk alignment of discotic liquid crystals has been found. Two different substrates: Si (amorphous) and ZnSe (polycrystalline) are used for these studies. The method of the sample being tilted out of the normal incident plane of IR beam has been used for investigating a 3-dimensional arrangement of the various segments of molecules in their discotic phases.

INTRODUCTION

The study of the organised supramolecular films is one of the most interesting topics of research in physical and chemical sciences. The study of supramolecular films is extremely interesting because it is scientifically intriguing as to how and why big molecules can form well organised structures in 3 dimensions. An understanding of the structure and dynamics is also important for understanding the mechanisms that cause phase transitions. The study is also of general interest for obtaining a better insight into the biological systems where similar organisations are known to exist. Discotic liquid crystals are known to form a special class of supramolecular films [1]. Columnar discotic phases are formed from molecules with a flat rigid core together with flexible aliphatic side chains [1]. The centres of the core form a rectangularly ordered (Dro)/disordered (Drd) or a hexagonal ordered (Dho)/disordered (Dhd) lattice in the plane normal to the column's axis [2]. Basically two alignments are possible: *side-on* (where the cores are parallel to the windows of the cell/substrate) and *edge-on* (where the cores are normal to the substrate). Many characteristic properties of devices based on discotic liquid crystals depend on the alignment of molecules in the discotic mesophases. The phenomena

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***author for correspondence**, Permanent addresses: [†]Vavilov State Optical Institute, St.Petersburg, 199034, Russia, ['] Institute of Physics, Silesian University, 40-007 Katowice, Poland concerning the nature of the surface and its interactions with the molecules of the nematic liquid crystals and their effects on the alignment of the liquid crystalline molecules is known for the last several decades [3], however no such influence of the surface on the alignment of discotic liquid crystalline molecules has so far been demonstrated. Vauchier et al [4] reported a planar orientation of molecules in the columnar discotic phase of some triphenylene derivatives using a perfect cleavage (001) surfaces of apophyllite (a lamellar tetragonal silicate) and a perfect cleavage of muscovite (a monoclinic mica). The problem of the dependence of the alignment on the type of substrate's structure has yet not been investigated in any greater detail. In this paper we describe the strong influence of the structure of the substrate, particularly of the polycrystalline structure of ZnSe, on the alignment of molecules in the columnar phase of discotic liquid crystals. The investigations are carried out using two different substrates, Si with amorphous structure and ZnSe with polycrystalline structure. Discotic liquid crystals used for these investigations are the two derivatives, of triphenylene (2,3,6,7,10,11-hexa-n-pentyloxytriphenylene, H5T) and truxene (2,3,7,8,12,13-hexa-n-decanoyloxytruxene, H10TX) [2].

In order to obtain a better understanding of the structure and the orientations of the discotic mesophases in 3 dimensions, a method of the sample being tilted out of the normal incident plane of the IR beam has been developed. This allows for investigations of the transition dipole moments of those segments of the molecules that lie along the normal to the windows of a LC cell. For normal incidence however, these moments coincide with the direction of the IR beam and hence do not absorb the beam. In this paper we report results for different IR bands in the discotic phase of H5T as a function of the angle between the normal to the windows of the cell and the direction of the IR beam.

EXPERIMENTAL

H5T was synthesised by Bengs et al [5] and H10TX was synthesised by Bock [6]. These discotic liquid crystalline samples in their isotropic phases were placed between two amorphous Si windows and between two polycrystalline ZnSe windows. The thickness of the measuring sample in the cell ranged from 5 to 8 μm. Windows were coated with a 0.2% solution of nylon 6/6 in methanol. The IR cell containing the sample sandwiched in between the windows was thermostated to within $\pm 0.1^0$ K using a programmable

For determining the value of the order parameter, Neff's method can be used (see [7] for details). The dichroic ratio R_i for an unpolarised beam is defined as follows:

$$R_i = \frac{I_D}{I_i} \qquad (1)$$

Here I_D is the integrated absorbance of the band in the discotic phase and I_i is the integrated absorbance in the isotropic phase. For isolated and well separated Lorentzian bands, the integrated intensities can be taken as their peak intensities. On adopting Neff's method of calculations for an unpolarised radiation, we find I_D as

$$I_D = \cos^2\alpha < \sin^2\theta > + \tfrac{1}{2}\sin^2\alpha < 1 + \cos^2\theta > \qquad (2)$$

As defined in [7], θ is the angle between the normal to the plane of aromatic core and the direction of the incident IR beam, α is the angle between the normal to the plane of the core and the direction of transition dipole moment vector p_i. The angle θ is different for different molecules and its average value determines the order parameter for the central parts of molecules. As shown in [7,8], we can find the order parameter S for $\alpha = 90^o$ or $\alpha = 0^o$. For vibrations with the transition dipole moment $\mathbf{p_i}$ lying in the plane normal to the direction of IR beam, we find

$$S = 2(R_i - 1) \qquad \text{(i.e. for } \alpha = 90^o\text{)} \qquad (3)$$

and for vibrations with p_i parallel to the direction of the incident IR beam

$$S = 1 - R_i \qquad \text{(i.e. for } \alpha = 0^o\text{)} \qquad (4)$$

A. The influence of the substrate's structure on the alignment of discotic liquid crystals. The IR spectra are found to be highly sensitive to the local structure and to the motions of the liquid crystalline molecules [7-9]. Our previous work has shown that aromatic vibrations in the wave number range 1500-1600 cm^{-1} as well as the C-H out-of-plane vibrations close to 800-850 cm^{-1} are the most sensitive indicators of ordering in discotic materials [7-8].

A relatively large value of the order parameter (ranging from 0.6 to 0.85) for the above mentioned bands has been found in our previous work [8] for H5T placed between two

Si windows. Based on the results for the intensity of the vibrations with transition dipole moments parallel to the core being higher in the discotic phase than in the isotropic phase and the inverse being true for vibrations with dipole moments perpendicular to the core, Kruk et al [7] deduced *side-on* type of alignment for the discotic phase of H5T. The results for H5T being placed between two ZnSe windows show that the alignment achieved is different to that obtained for the Si windows. Fig. 1 *a* shows that for Si windows, the intensity of the vibrations of the benzene ring is much lower in the discotic phase than in the isotropic phase. It follows from these results that the alignment achieved is either *edge-on* or approximately *edge-on*. Based on formula (3), we find that the order parameter (linearly related to the dichroic ratio) is only 0.4 for the C-H out-of-plane vibrations. At the same time, the order parameter for the benzene-O vibrations (1263 cm^{-1}) using equation (4) being a maximum is approximately 0.8. This is possibly due to the reason that C-H transition dipole moment is neither parallel nor perpendicular to the IR beam as was the case for a set of Si windows.

On the assumption that the intensity of the beam for the bands through the sample in the isotropic phase is the same for both sets of windows (a plausible assumption once the spectra of windows is subtracted), we can roughly estimate the average angle with which the cores are oriented with respect to the plane of the windows by comparing dichroic ratios of the two samples placed in-between the different windows. The angle ϕ with which the cores are inclined to the windows can be related to the dichroic ratio of in-plane vibrations for the two sets of windows by the following equation

$$\cos\phi = \frac{R_{ZnSe}}{R_{Si}} \qquad (5)$$

where R_{Si} and R_{ZnSe} are the dichroic ratios for Si and ZnSe windows for a particular vibration lying in the plane of the core. Based on these results, the angle with which the cores are tilted with respect to the plane of ZnSe windows is found to be 57^0 compared to the orientations of the cores relative to the Si windows. The dichroic ratio on which the order parameter is dependent is governed not only by the ordering of the molecules but also by the orientation of the cores relative to the plane of the windows of the cell. The dichroic ratio will be a maximum or a minimum value depending on whether the transition dipole moment is parallel or perpendicular to the windows of the cell for the case when the IR beam (unpolarised) is incident normal to it. The transition dipole moments parallel to the windows will absorb the maximum intensity, whereas those transition dipole moments inclined to the windows will exhibit a dichroic ratio less than the maximum (for details see [8]). We therefore analyse the dichroic ratio of the various absorption bands. We find that the dichroic ratio for the C-C in plane vibrations of the benzene ring is the highest for the case of the Si substrate, whereas for the case of the

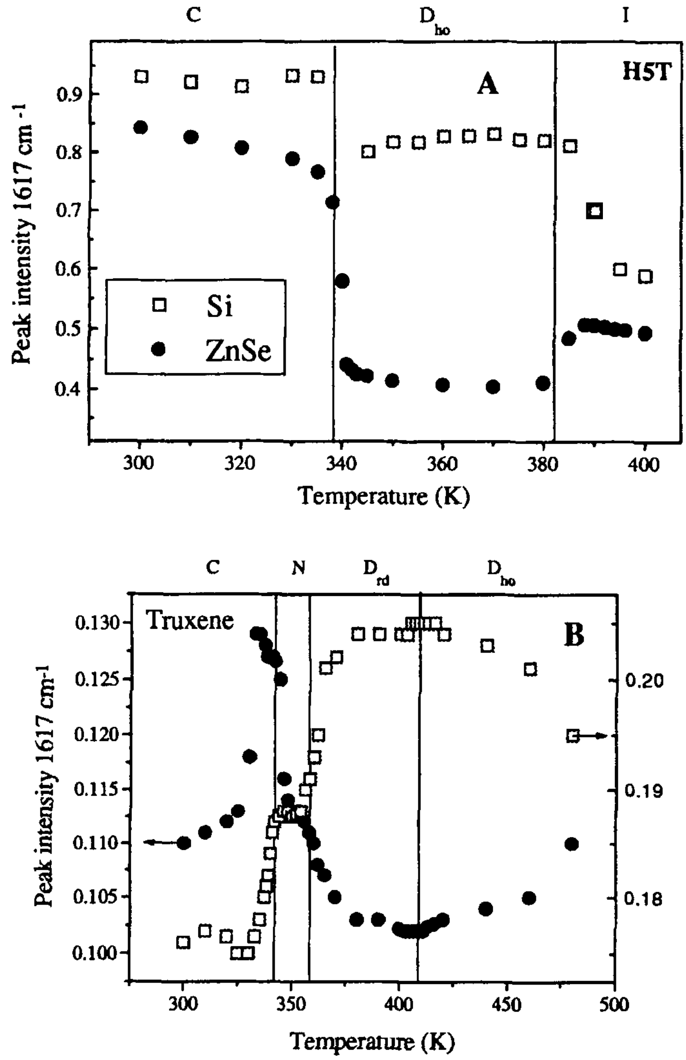


FIGURE 1. Dependence of peak intensity on temperature for (A) tryphenylene and (B) truxene.

ZnSe substrate the dichroic ratio of the benzene-O band is the maximum. For determining the ordering of discotic liquid crystals using infrared dichroic measurements, a number of vibration bands need to be analysed. The maximum value of the order parameter obtained by equations (3) or (4) indicates whether the transition dipole moments are parallel (or perpendicular) to the substrate's surface.

The analysis of the infrared data of truxene H10TX also shows a strong influence of the substrate's structure on the alignment (see Fig. 1 B). As seen from Fig. 1 B, the dependence of the peak intensity of C-C aromatic stretching vibration, for the discotic phase, on temperature for H10TX in ZnSe windows is exactly opposite to that for the Si windows. However the frequency of the band maximum shows similar temperature dependencies for both sets of windows (see Fig. 2).

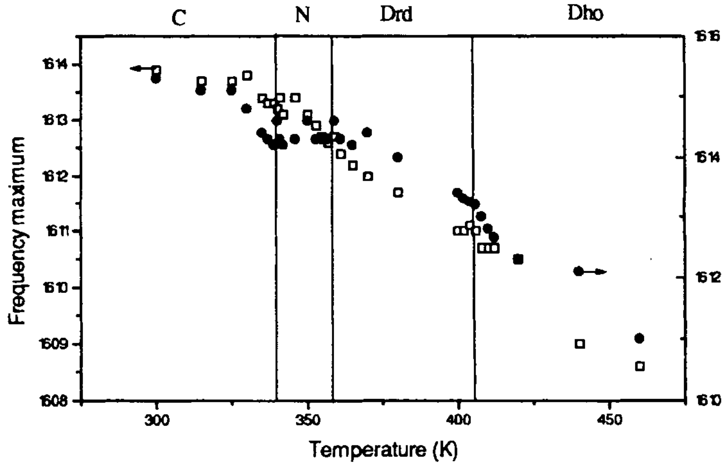
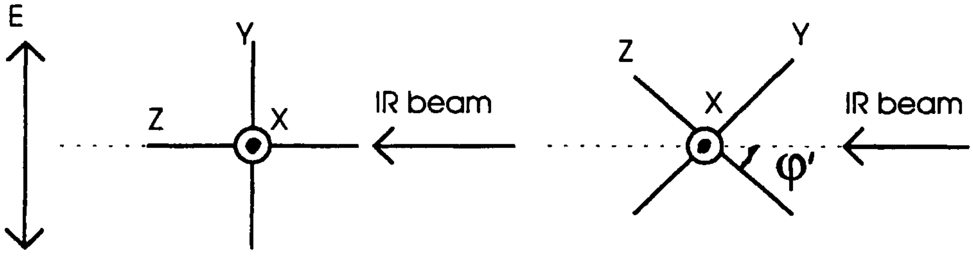


Fig. 2. The dependence of the frequency maximum of the aromatic stretching vibration (1617 cm^{-1}) on temperature for H10TX contained in ZnSe (•) and Si (□) cells.

B. Method of the sample tilt for study of orientations in discotic mesophase

Figs. 3 *a* and *b* show schematic of the sample in its tilted geometry. X-Y-Z are the sample axes. The direction of IR beam and of the polarised electric vector of the light (E) are shown in these figures. In these figures, X axis is perpendicular to the plane of the paper along which the sample is rotated. The window plane is the X-Y plane whereas normal to the windows is the Z axis. In Fig. 3 a, the direction of IR beam is coincident with the Z axis, whereas in Fig. 3 b it makes an angle φ'. IR measurements for H5T discotic liquid crystal placed between two Si windows are carried out as a function of sample tilt angles up to 50°.

We have selected this arrangement because *side-on* type of alignment for this material was established from our previous work. It means that the transition dipole moments for some vibrations (in particular for the C-C aromatic core stretching vibrations) lye in the plane of the windows. However for some other vibrations such as the C-H out of plane vibrations, the transition dipole moments are directed normal to the plane of windows.



(a) ***(b)***

FIGURE 3. Schematic of the sample in its tilted geometry

Hence the intensity of these two absorption bands will change with the sample tilt. In order to compare the intensity of bands from different tilt angles, we must consider that
i) the actual optical path length does vary with the angle of the sample tilt;
ii) the orientation of transition dipole moments changes with respect to the electric vector of the IR beam.

Because light is refracted in going through media of different refractive indices, the angle φ the electric vector makes with the Y axis in the film is related to the angle [9,10] of the sample tilt, φ', through Snell's law

$$n_1 \sin\varphi' = n_{2z} \sin\varphi'' = n_{3z} \sin\varphi \qquad (6)$$

where n_1 is the refractive index of the first medium, n_{2z} is the refractive index of the second medium, φ'' is the angle of refraction, n_{3z} is the refractive index of the third medium and φ is the angle of refraction in this medium. If we regard the first medium as the air, second medium as the cell window and the third medium as the liquid crystalline layer itself, we can ignore the second medium for analysis of the results, such that

$$n_1 \sin\varphi' = n_{3z} \sin\varphi \,. \qquad (7)$$

The true absorbance A_t of the film is related to the measured absorbance, A_m, by the following expression

$$A_t = A_m \cos\varphi \,, \qquad (8)$$

φ can be found from (7) if n_{3z} and φ' are known. φ' is read out from the scale connected to the cell holder and n_{3z} is estimated in the first instance from the refractive index of the sample in the isotropic phase.

Figs. 4 a and 4 b show results of the tilted cell for the various bands in the discotic phase of H5T. A dramatic change in the 832 cm^{-1} band compared to the 816 cm^{-1} band is seen. It means that for the C-H out of plane vibrations (832 cm^{-1}), the preferable orientation is in the plane normal to the plane of the windows. However the intensity of 816 cm^{-1} remains constant (a small increase for higher angles is due to imperfect correction for the thickness). Hence a dramatic increase in the intensity of 832 cm^{-1} band with sample tilt provides an evidence that this band is directed normal to the core. The corrected peak intensity as a function of the tilt angle for these bands is shown in Figs. 5 and 6. Interestingly the two bands: 868 and 893 cm^{-1} shown in Fig. 5 exhibit opposite dependencies on tilt angle. While the intensity of the band 868 cm^{-1} increased with increasing tilt angle, that of the band 893 cm^{-1} is decreased. Usually low-frequency vibrational bands in the region 800-900 cm^{-1} are assigned to the C-H aromatic out of plane deformations. However for the bands in the region 870-900 cm^{-1} these could alternatively be assigned to the C-C alkyl stretching vibrations [11]. From these investigations, we make a precise assignment of the 893 cm^{-1} band to be the C-C in-plane alkyl stretching vibration, since its intensity exhibits opposite dependence on the tilt angle to that of the perpendicular bands at 868 cm^{-1} (C-H out-of-plane deformation).

The dependence of the C-C aromatic stretching vibration (1617 cm^{-1}) is shown in Fig. 6. This band while oriented parallel to the plane of the windows, has shown a dramatic decrease in its intensity on going to the isotropic phase. These results and those from IR dichroisms give us a precise information about the alignment and the orientations of the

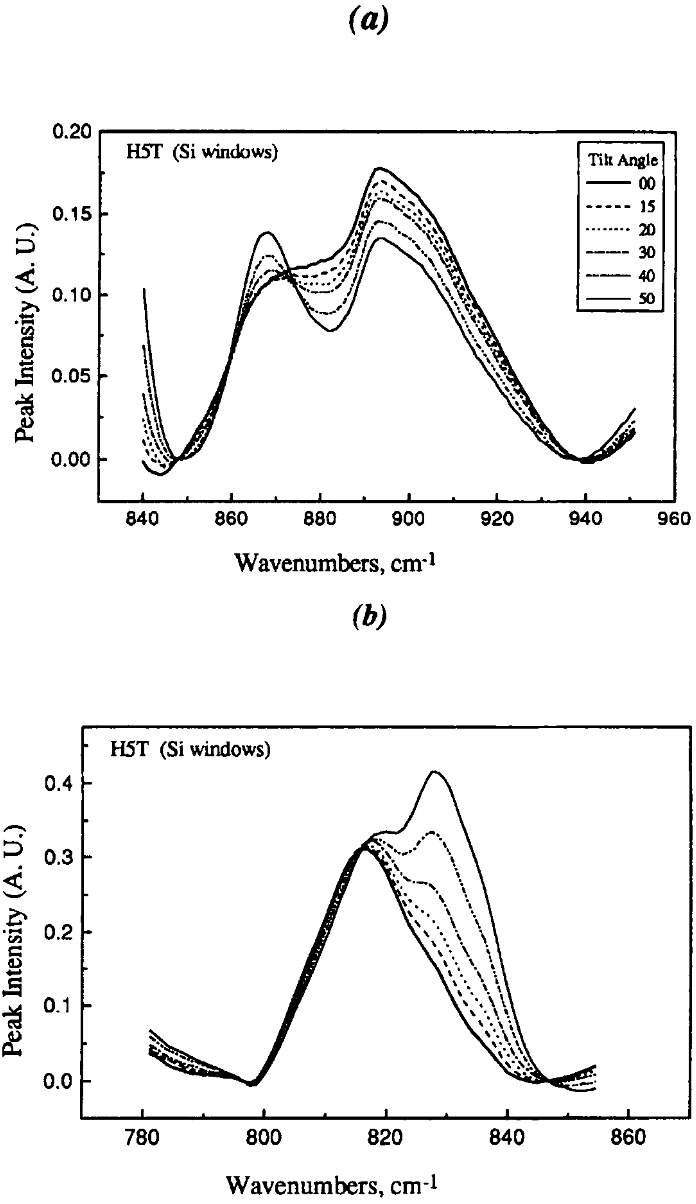


FIGURE 4. Infrared spectra of triphenylene (in Si windows) at different sample tilt angles.

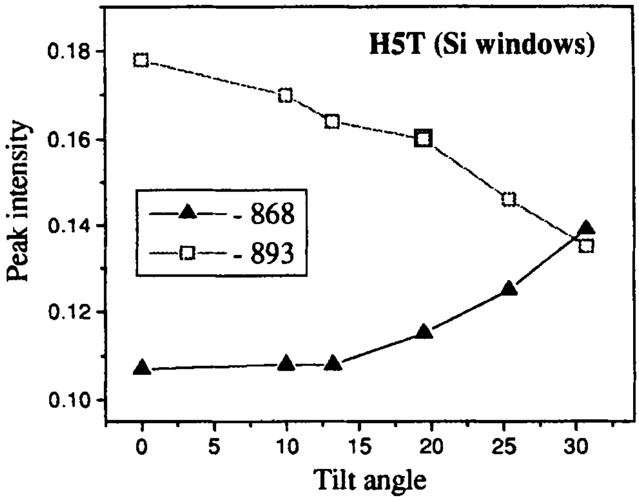


Figure 5. Peak intensity of vibrational bands (868 and 893 cm^{-1}) vs. corrected tilt angle.

various segments of molecules in the discotic phase. The results for 1617 and 832 cm^{-1} bands provide an evidence for *the side-on* type of alignment of H5T molecules in the discotic phase when sandwiched between the Si windows.

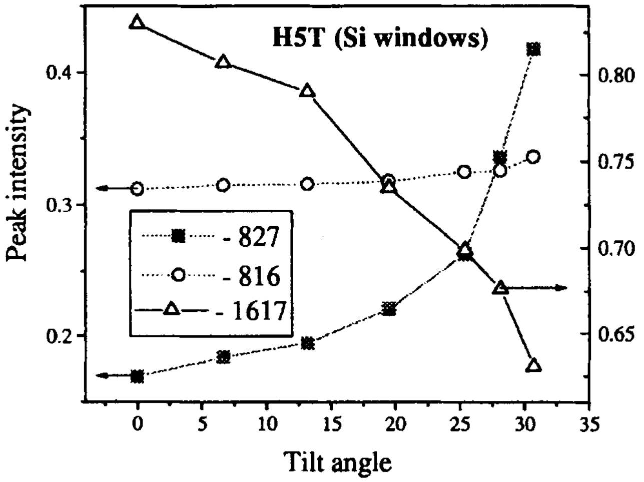


FIGURE 6. Dependence of the peak intensity on the corrected tilt angle.

CONCLUSIONS

The results confirm that the cores of triphenylene and truxene show *side-on* alignment on the Si substrate, whereas on ZnSe substrate the cores are *tilted* at an angle of 57° to the surface. These results therefore show that the structure of the substrate whether amorphous (Si) or polycrystalline (ZnSe) plays an important role in determining the type of alignment achieved for discotics. The method of rotating the sample along an axis at right angles to the IR beam is found to be extremely useful for studying the orientations of disk like molecules in discotic liquid crystals.

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