# CONFORMATIONAL ANALYSIS BY INFRARED LINEAR DICHROISM OF SOLUTES IN STRETCHED POLYETYLENE: THE TWIST ANGLE IN BIPHENYL AND 4,4'-DIBROMOBIPHENYL

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*Dedicated to Dr R. Zahradnik on the occasion of his 60th birthday.*

A method is proposed for using the IR linear dichroism of molecules embedded in stretched polyethylene and containing two weakly coupled symmetry-related subunits for the determination of the spatial relationship of the subunits. The procedure requires an IR LD measurement on the parent and on an isotopomer in which the equivalence of the subunits has been removed by isotopic substitution, without affecting the molecular shape or the orientation factors. The method has been tested on biphenyl, found to be planar, and 4,4'-dibromobiphenyl, found to be nearly orthogonally twisted in stretched polyethylene. Possible implications for the orientation mechanism are discussed briefly.

After a relatively slow start due primarily to experimental difficulties before the era of Fourier transform spectrometers, measurements of linear dichroism in the infrared spectra of solutes partially aligned in a stretched polymer (IR LD spectra) have become routine[1-3]. This very simple technique has been found useful for assigning the symmetries of vibrational states in symmetrical molecules[4-8] and for establishing the directions of vibrational transition moments in the molecular framework of low-symmetry species[8]. The latter contain information on the mutual coupling of local group vibrations. It has also found use for establishing the molecular orientation factors needed for the analysis of polarized UV-visible spectra of partially aligned low-symmetry molecules[9,10] and of those high-symmetry molecules whose spectra are complicated by the presence of severely overlapping bands[11].

IR LD measurements on several dozen organic molecules contained in stretched polyethylene[12] extended the empirical correlation between molecular shape and the magnitudes of the molecular orientation factors, $K_u = \langle \cos^2 u_Z \rangle$, where $u_Z$ is the angle between the $u$-th molecular axis and the stretching direction $Z$, and the pointed brackets indicate ensemble averaging. The existence of this correlation had been

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already well established from studies of UV-visible dichroism[13]. At least for aromatic molecules, for which most information is available, the absolute sense of the partial orientation induced by the stretched polyethylene environment, as given by the relative values of the three $K_u$ values, can be safely predicted from molecular shape. Moreover, fairly accurate a priori estimates of their numerical magnitudes are also possible by interpolation between the known values for molecules of related shape in the same polymer sample. The accuracy of these estimates is limited by the effects of factors other than molecular shape[1-3].

We now report an application of the stretched polymer IR LD technique to conformational analysis of solute molecules. The particular procedure used is generally applicable to high-symmetry molecules containing two substructures related by a symmetry element, whose vibrations can be uncoupled from each other when one substructure is isotopically substituted. The procedure provides information on the relative orientation of the two substructures, taking advantage of the fact that isotopic substitution has a very small effect on molecular alignment in stretched polyethylene[12] but can have a large effect on vibrational frequencies.

Since molecular conformation may in general depend on the nature of the environment, it is important to ask whether conformational information obtained in a stretched polymer is of relevance for more usual environments. We feel that it ought to be as relevant as information obtained in other special environments, such as single crystals. Frequently, the molecular conformation that really is of interest is that of a molecule placed in some biological receptor site of unknown structure. It is then useful to determine the conformation in a wide variety of environments in order to detect any persistent conformational preferences that the molecule might have, and a stretched polymer may as well be one of them.

Conversely, environmental sensitivity of molecular conformation may be useful as a probe of detailed structure of the polymer environment in the vicinity of a solute molecule. In a first application, we have therefore selected two related model molecules: Biphenyl, the sensitivity of whose conformation to the environment is legendary[14-18], and 4,4'-dibromophenyl, whose twisted conformation has not been known to be sensitive to the environment[19,20].

Previous use of stretched polymer linear dichroism in conformational studies on solutes utilized UV-visible linear dichroism[21-23], which offers its own set of advantages, but would not be useful for the present purpose. The chief virtues of working in the IR region are the far lower degree to which various transitions overlap, the larger number of transitions typically observable, the higher accuracy of the measurements, and often a higher degree of localization of transitions in the molecule.

### EXPERIMENTAL

The materials were commercial or available by standard procedures. Biphenyl-$d_5$ was prepared by the phenylation of benzene-$d_6$ with benzenediazonium fluoroborate and potassium acetate in the presence of 18-crown-6 (ref.[24]). Subsequent bromination with N-bromosuccinimide in propylene carbonate following the general procedure of ref.[25] yielded 4,4'-dibromobiphenyl-$d_4$. Biphenyl-$d_{10}$ was brominated under the same conditions to yield 4,4'-dibromobiphenyl-$d_8$. Before use, all materials were purified by gradient sublimation.

Linear low-density polyethylene pellets were obtained from Dow Chemical Company. The preparation of the sheets, their stretching to about 6 times the original length, and the incorporation of the solute from a chloroform solution, as well as the spectral measurements, have been described elsewhere[12]. The dichroic spectra were measured both at room temperature and at 20 K, using a closed-cycle cryostat (Air Products Co.). A single piece of stretched polyethylene was used for measurements on all isotopomers of a compound.

The orientation factors were obtained in the usual fashion[1-3] with an accuracy of $\pm 0.5\%$ from $K_u = d_u/(d_u + 2)$, where $d_u$ is the dichroic ratio, $d_u = E_{\parallel}/E_{\perp}$. The sum $K_x + K_y + K_z$ equaled $1 \pm 0.005$. For a highly accurate comparison of the orientation factors of several solutes, all were embedded and measured simultaneously in the same piece of stretched polyethylene. The actual numerical values obtained for the orientation factors varied slightly from polymer sheet to polymer sheet, without affecting the conclusions. The values shown in Table I were obtained in a single sheet for each compound and represent typical results averaged over several vibrations. Table II provides an illustration of the actual results for several vibrations measured on one sheet containing a mixture of solutes.

### RESULTS AND DISCUSSION

#### General

For the present purpose we need to consider the IR linear dichroism of a set of partially aligned molecules containing two weakly interacting subunits whose structures are identical, except possibly for isotopic substitution. Let us assume that the orientation factors of the molecule can be determined. This will be the case if the overall molecular symmetry is high, so that all transition moments have to be oriented

TABLE I

Orientation factors of biphenyl and 4,4'-dibromobiphenyl in stretched polyethylene at room temperature

| Compound | $K_x$ or $K_{x'}$ | $K_y$ or $K_{y'}$ | $K_z$ |
|---|---|---|---|
| Biphenyl-$d_0$ or -$d_5$ or -$d_{10}$ | 0·065 | 0·413 | 0·525 |
| 4,4'-Dibromobiphenyl-$d_0$ or -$d_{10}$ | 0·217 | 0·290 | 0·488 |
| 4,4'-Dibromobiphenyl-$d_4$ | 0·251 | 0·265 | 0·487 |

along one of the three molecular symmetry axes. However, we assume that three-fold or higher order symmetry axes are absent.

The subunits have characteristic IR frequencies, which depend on isotopic substitution, and are associated with local transition moments whose directions within the subunit are known. The subunits are mutually related in the molecular framework by one or more of the symmetry elements present. These symmetry elements are destroyed by isotopic substitution on only one of the subunits. When such substitution is performed on both subunits, symmetry is restored.

In the particular case of the biphenyls under investigation below, the subunits will be phenyl rings or substituted phenyl rings, the weak coupling will be provided by a single bond between them, and the symmetry elements are the two twofold rotation axes that pass through its mid-point (Fig. 1). The characteristic vibrations of the subunits are those of a singly or doubly substituted benzene, and their out-of-plane, short-axis in-plane, or long-axis in-plane polarization directions are known.

Each subunit contains $N$ atoms and is characterized by $3N - 6$ normal modes of vibration. At least some of them need to be well localized within the subunits and only weakly coupled to the rest of the molecule. In the parent molecule and in the symmetrical derivative that is isotopically substituted on both subunits, these $6N - 6$ vibrations can be approximated as the in-phase and out-of-phase combinations of the modes of the free subunits. If the symmetry element that interconverts the subunits

TABLE II

An example of experimental results: orientation factors $K$ of vibrations in 4,4′-dibromobiphenyl-$d_0$ and -$d_4$ in stretched polyethylene

| Compound | Polarization | $\tilde{\nu}$ cm$^{-1}$ | $K$ | | |
|---|---|---|---|---|---|
| | | | $1^a$ | $2^a$ | $3^a$ |
| $d_4$ | $y'$ | 515 | 0·2652 | 0·2661 | 0·2647 |
| $d_4$ | $z$ | 660 | 0·4884 | 0·4841 | 0·4847 |
| $d_0$ | $z$ | 673 | 0·4863 | 0·4847 | 0·4901 |
| $d_4$ | $x'$ | 798 | 0·2505 | 0·2489 | 0·2506 |
| $d_0$ | $x$ | 808 | 0·2173 | 0·2185 | 0·2162 |
| $d_4$ | $x'$ | 824 | 0·2510 | 0·2514 | 0·2519 |
| $d_0$ | $y$ | 845 | 0·2909 | 0·2897 | 0·2903 |
| $d_4$ | $z$ | 993 | 0·5081 | 0·5108 | 0·5029 |
| $d_0$ | $z$ | 1 073 | 0·4916 | 0·4884 | 0·4861 |
| $d_0$ | $z$ | 1 080 | 0·5141 | 0·5099 | 0·5182 |

[a] Results of three independent room-temperature spectral measurements on the same doped polymer sheet containing both isotopomers.

is a twofold rotation axis, which we shall label $x$, the $3N - 6$ in-phase combinations will be polarized along $x$, and the $3N - 6$ out-of-phase combinations will be polarized along directions in the $yz$ plane. If the symmetry element that relates the subunits is a mirror plane, which we shall label $yz$, the in-phase vibrations will be polarized along directions in the $yz$ plane and the out-of-phase ones along $x$. Since we are assuming a high total symmetry, in either case the $yz$-polarized vibrations can actually only be polarized along $y$ or along $z$. A measurement of the dichroic ratios of a few $x$, $y$, and $z$ polarized vibrations will establish the orientation factors $K_x$, $K_y$, and $K_z$ of the principal axes of the orientation tensor.

In the case of the biphenyls discussed below, $N = 11$, $3N - 6 = 27$, and $6N - 12 = 54$. The remaining six vibrational modes describe the relative motion of the two subunits: a stretch of the bond that joins them, and a torsion and four bending motions about this bond. In a twisted biphenyl $(D_2$ symmetry), we choose as the symmetry axis $x$ that relates the two subunits the one that is closer to the out-of-plane directions $(x'$ and $x'')$ of the two rings, $y$ will be the other axis that interconverts the rings and is closer to their in-plane axes $(y'$ and $y'')$, and $z$ will be the long axis of the molecule (Fig. 1).

Isotopic substitution has only a minute effect on the orientation factors of molecules in stretched polyethylene as long as it does not change the molecular shape, which is the primary factor controlling molecular orientation. Only in very small molecules, such as chloroform, has the effect of deuteration on the orientation factors been detected[12]. Thus, for the large molecules of interest here, a sizeable difference between the $K_u$ values measured on the parent molecule and on the symmetrical iso-
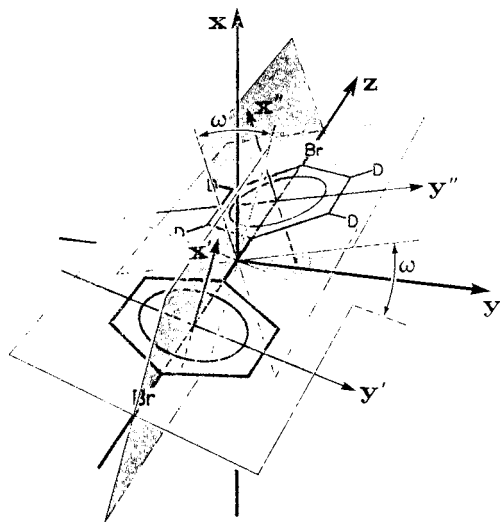


FIG. 1

The geometry of a twisted biphenyl derivative

topically substituted derivatives in which the two subunits are still equivalent will be a sure indication that the isotopic substitution causes a change in the molecular shape. Although this would be very interesting, it will be rare and in the following we consider the case in which the orientation factors remain unchanged upon symmetrical isotopic substitution which preserves the equivalence of the two subunits. When isotopic substitution in both subunits does not change molecular shape enough to affect the orientation measurably, it is reasonable to assume that such substitution in only one of the subunits does not do so either.

The shape of a molecule in which the isotopic substitution has been performed on one side only will thus still have the same twofold symmetry, so that the molecule will still have the same known orientation factors $K_u$ and the same directions for its principal orientation axes. However, when it comes to nuclear masses, the molecule lacks the symmetry element that interconverts the subunits, and therefore may well have quite different moment directions for its vibrational transitions than its truly symmetrical isotopomers. These transition moment directions thus need not lie in the $x$, $y$, or $z$ axes. They will be the only unknowns in the evaluation of stretched sheet IR LD measurements on the unsymmetrical isotopomer.

In particular, the frequencies of at least some if not all of the $3N - 6$ internal vibrations of the isotopically substituted free subunit will now be different from those of the intact free subunit. If the isotopic perturbation is large and the coupling between the subunits weak, the coupling of the previously degenerate internal modes of the two subunits in the molecule under investigation can be neglected altogether. We shall assume that this neglect is justified for at least a few of the vibrational transitions. As a result, the moment directions of these transitions will be given by those in the isolated subunits.

Assuming the IR transition moment directions within the free subunits to be known, and assuming that they are affected only negligibly by interactions between the two now inequivalent subunits , a stretched polymer IR LD measurement on the unsymmetrical isotopomer will therefore yield information on the mutual orientation of the two subunits in the molecule and thus on molecular conformation.

It is worth noting that in the limit of extremely weak coupling between the subunits the degeneracy between the local modes of the subunits may not be lifted at all in the parent molecule and its symmetrical isotopomer within the accuracy defined by the linewidths. Then, any linear combination of the two local modes represents an acceptable stationary wavefunction, and the localized representation may be the most natural. Actually, since we are dealing with molecules in solution, in which the environment never has the high symmetry of the molecule, the localized description will represent the correct stationary wavefunctions as soon as the coupling between the subunits becomes weaker than the symmetry-lowering part of the interaction with the solvent. However, this does not affect our results, since in a uniaxial sample, the observable dichroic ratio for an overlapping pair of absorption lines due to

a degenerate transition will be the same whether the two components of the transition are localized on separate but symmetry-related subunits or delocalized over the whole molecule. In the former case, the polarized intensities originate from two transition moments of equal length and of equal orientation relative to the symmetry axis, one on each subunit; in the latter case, from two mutually perpendicular transition moments of generally unequal length, directed along two molecular symmetry axes.

There are two particularly favorable cases in which the knowledge of the three $K_u$ values for the principal orientation axes and of the orientation factor $K_f$ of the $f$-th transition provide specific solutions for the direction of the $f$-th transition moment $\mathbf{M}_f$ in the $xyz$ frame[1]. The orientation factor $K_f$ of a transition is defined in a fashion similar to the orientation factor $K_u$ of an axis:

$$K_f = d_f/(d_f + 2),\qquad (1)$$

where $d_f$ is the dichroic ratio of the $f$-th transition.

If two of the $K_u's$ are equal, $K_y = K_z$, or if $\mathbf{M}_f$ is known to lie in the $xy$ plane, the angle $\phi_f^x$ between $\mathbf{M}_f$ and the $x$ axis is given by

$$\tan^2 \phi_f^x = (K_f - K_x)/(K_y - K_f).\qquad (2)$$

Similar relations hold when $x$, $y$, and $z$ are permuted. Since we have assumed all along that the molecule under investigation is of high symmetry, it is likely that one or the other of the above conditions is satisfied so that a very specific conclusion about the conformation of the molecule can be drawn. This will be the case for our examples, biphenyl and 4,4'-dibromobiphenyl.

*Biphenyls*

Partially twisted conformations of biphenyl and its symmetrically substituted derivatives are of $D_2$ symmetry, planar ones are of $D_{2h}$ symmetry, and orthogonally twisted ones are of $D_{2d}$ symmetry. These molecules satisfy the requirements of the above section and belong to a large class of molecules in which the two subunits are planar, connected by a single bond, and each posseses an additional plane of symmetry passing through the connecting bond. Fig. 1 shows that the two symmetry planes of a subunit $(x'z,\ y'z$ and $x''z,\ y''z)$ are not symmetry elements of the whole molecule, except in the $D_{2h}$ and $D_{2d}$ limits. The twist angle will be labeled $\omega$ and is equal to zero for planar biphenyls and to 90° for fully twisted biphenyls.

The assignment of vibrations in the IR spectrum of biphenyl[14] and 4,4'-dibromobiphenyl[20] is well established and the analysis of the dichroic spectra of biphenyl, biphenyl-$d_5$, biphenyl-$d_{10}$, 4,4'-dibromobiphenyl, 4,4'-dibromobiphenyl-$d_4$, and

4,4'-dibromobiphenyl-$d_8$ was straightforward, yielding the $K_u$ values listed in Table I. The measurements at 20 K and at room temperature led to qualitatively identical conclusions.

Both for biphenyl and for its dibromo derivative, the orientation factors are equal for the parent and the perdeuterated compound, in which the two phenyl rings are equivalent. We conclude that deuteration does not change the shape of the molecule and that the above outlined method is applicable.

The differences in the orientation factors of the parent and of the dibromo derivatives are interesting. Based on its increased molecular length, one might have expected a larger $K_z$ value for the latter. It is actually somewhat smaller, and this suggests a decreased degree of planarity in the dibromo derivative. This is supported more unequivocally by a consideration of the values of $K_x$ and $K_y$. These differ considerably in biphenyl itself, suggesting a large difference in the $x$ and $y$ dimensions of the molecule, which in this polymer certainly does not orient like a rod. On the other hand, in 4,4'-dibromobiphenyl the values are much closer to each other, compatible with a larger twist angle. At 90° twist, the two values would have to be equal by symmetry.

While arguments of this kind may provide qualitative guidance concerning the differences in molecular shape, it is only a consideration of the $K_u$ values of the unsymmetrical half-deuterated derivatives, biphenyl-$d_5$ and 4,4'-dibromobiphenyl-$d_4$, that provides quantitative information using Eq. (2).

In both cases, only three distinct $K$ values are observed among all of the vibrations recorded. We note first that for both unsymmetrical compounds, the value of $K_z$ is the same as in the respective symmetrical compounds. This comes as no surprise since the $z$ axis remains as a symmetry axis regardless of which of the three degrees of deuteration we employ, so that $z$-polarized transitions must remain $z$-polarized even in the half-deuterated species. This observation merely provides additional reassurance that deuteration indeed does not affect measurably the nature of the molecular alignment and the orientation factors.

In Table I, $K_{x'}$ is the $K$ value observed for "out-of-plane" polarized transitions of the two half-deuterated biphenyls and $K_{y'}$ is the one observed for "in-plane" polarized transitions. From these values and the orientation factors $K_x$ and $K_y$, the angles $\phi_f^x$ and $\phi_{f'}^y$ between the vibrational transition moments and the $x$ and $y$ axes can now be evaluated using Eq. (2).

If the coupling of the vibrations of the deuterated and the undeuterated phenyl ring is sufficiently weak that their transition moments are those expected for the isolated rings and thus are either polarized along the central bond directions $z$, or perpendicular to one or the other ring, the angles $\phi_f^x$ and $\phi_{f'}^y$ are simply related to the twist angle $\omega$ (Fig. 1). The transition moments will be directed along $x'$ or $x''$ in the case of "out-of-plane" vibrations, and thus will be perpendicular to $z$ and at an angle $\phi_f^x = \omega/2$ to the $x$ axis. They will be directed along $y'$ and $y''$ in the case of "in-plane" vibrations, and thus again perpendicular to $z$ but now at an angle

$\phi_{f'}^y = \omega/2$ to the $y$ axis. To the extent that vibrational coupling between the two rings is not negligible, the observed angles $\phi_f^x$ and $\phi_{f'}^y$ will differ from $\omega/2$. For the two kinds of vibration, it is possible to cast Eq. (2) into forms which are particularly easy to visualize in a geometrical representation (cf. Fig. 1):

$$K_{x'} = K_x \cos^2{(\omega/2)} + K_y \sin^2{(\omega/2)} \tag{3}$$

$$K_{y'} = K_x \sin^2{(\omega/2)} + K_y \cos^2{(\omega/2)} \,. \tag{4}$$

For biphenyl-d$_5$, $K_{x'} = K_x$ and $K_{y'} = K_y$, and we conclude that the twist angle $\omega$ is zero within an experimental uncertainty of about $10°$, deduced from a consideration of the uncertainties of the measured $K$ values.

Biphenyl has been reported to have a twist angle of $45°$ in the gas phase[14], $0°$ in a crystal above 40 K and $10°$ below 40 K, and about $20-30°$ in solution and in a melt (for brief reviews see refs[14,16]). In cyclohexane[17] and rare gas[18] matrices the molecule is planar. Now we can add stretched polyethylene to the list of environments which induce planarity.

For 4,4'-dibromobiphenyl, $K_{x'}$ and $K_{y'}$ are different from $K_x$ and $K_y$, respectively, and this molecule clearly has a non-zero twist angle. Since $K_{x'} \neq K_{y'}$, the twist angle is less than $90°$, but since the two values are quite close, it cannot be much less than $90°$. Its magnitude can be obtained from the measurement on the three vibrations of 4,4'-dibromobiphenyl-d$_4$ whose dichroism we were able to measure particularly accurately (Table II). Two of these are "out-of-plane" polarized, at 798 and 824 cm$^{-1}$, and yield $K_{x'} = 0.2507 \pm 0.001$, one is "in-plane" polarized, at 515 cm$^{-1}$, and yields $K_{y'} = 0.2653 \pm 0.001$. Substituting the value of $K_{x'}$ into Eq. (3), we obtain a twist angle of $85 \pm 2°$. Using $K_{y'}$ and Eq. (4), we obtain a twist angle of $60.5 \pm 2°$.

The discrepancy between the two results is most likely due to the existence of weak vibrational coupling between the two phenyl rings, which distorts the transition moments from directions exactly perpendicular to $(x', x'')$ or exactly parallel to $(y', y'')$ the aromatic rings ($\phi_f^x$ and/or $\phi_{f'}^y$ deviate from $\omega/2$). Since the two "out-of-plane" vibrations at 798 and 824 cm$^{-1}$ have exactly the same dichroism, and since they involve primarily hydrogen motion, less likely to couple across the central bond, we tend to take the value $85°$ as more closely representative of the molecular geometry. Thus, the conclusion is that in stretched polyethylene 4,4'-dibromobiphenyl is highly twisted. The twist angle is of the order of $60-85°$, with the higher values more probable.

It is likely that the discrepancy between the transition moment directions $\phi_f^x$ and $\phi_{f'}^y$ derived from the dichroism of different vibrations can be turned from a nuisance to an asset in that it can be used to study the finer details of vibrational force fields. We plan to address this subject in the future.

Our result for the twist angle of 4,4'-dibromobiphenyl in stretched polyethylene can be compared with the values 38° and 42° obtained for two inequivalent molecules in the unit cell of a single crystal by X-ray analysis[19]. The conformation of this biphenyl derivative thus is twisted in stretched polyethylene as it is in the crystal[19] and in solution and melt[20], and the actual value of the twist angle has now been shown to be sensitive to the environment.

It is curious that the dibromo substitution has such a large effect. The $\pi$ bond order cannot be affected much, and the shape of the sigma framework in the critical region of the inter-ring bond is affected very little: The length of this bond is 1·496 Å* in biphenyl[26] and 1·496 and 1·453 Å in the two crystallographically inequivalent but nearly equally twisted molecules of the dibromo compound[19]; the C2C1C6 angle is 117·9° in biphenyl and 119·2° and 120·6° in the two inequivalent molecules of the dibromo derivative; the average C1C2 distance is 1·397 Å in biphenyl and 1·378 and 1·392 Å in the inequivalent molecules of the derivative.

The torsional potential apparently is so very flat that the resulting minor differences in the inter-ring distances between the *ortho* hydrogens are sufficient to shift the position of the minimum along the torsion coordinate substantially. It is then reasonable that environmental effects could have a large influence on the twist angle of the 4,4'-dibromo derivative and not only biphenyl itself.

Our result, planar biphenyl in stretched polyethylene, suggests that the environment of aromatic solute molecules in this medium is organized and stiff rather like that in a crystal or a polycrystalline domain and not disorganized and malleable like that in a liquid solutions. Stretched polyethylene contains microcrystalline and amorphous domains. It is highly improbable that solute molecules could penetrate into the interior of the crystallites but it is also improbable that the interior of the amorphous phase looks very regular and crystal-like, offering sites that force the guest biphenyl molecules into planarity. A way out of the dilemma is to accept the proposal that aromatics accumulate in the interface between the crystallites and the amorphous regions, originally proposed on the basis of quite different evidence[27] and since supported by other results[28]. This arrangement can be viewed as adsorption − possibly epitaxial adsorption[28] − of the aromatics on the specific surfaces of the microcrystals, and is also compatible with the observation of a very narrow orientational distribution of pyrene and 2-fluoropyrene based on fluorescence polarization measurements[29]. It is difficult to draw conclusions on this subject from the results we have obtained for 4,4'-dibromobiphenyl, since its equilibrium twist angle in additional media, such as fluid solutions, is not known.

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*    1 Å = 10$^{-10}$ m.

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