

Theoretical Calculation of the Optical Anisotropy of Substituted Cyclohexanes and Associated Bisphenyl Molecules Using Experimentally Derived Group Polarizabilities

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A general method for the formulation of polarizability tensor and computation of optical anisotropy of a series of substituted cyclohexanes and their bisphenyl fragments, which are model analogues of corresponding polymers is presented. The calculation makes use of the molecular geometry and conformations from force-field simulations and the anisotropic polarizability tensors of the constituent groups derived from experiments reported in the literature. Cyclohexanes with phenyl group substitution show higher anisotropy than those with methyl substituents. For the same substitution, a higher optical anisotropy is observed for equatorial orientation than axial. The optical anisotropy for the cyclohexanes is dependent on the orientation of the substituent group rather than on its position, whereas for the bisphenyl fragments the anisotropy is dependent on both these factors along with the conformation of the whole molecule. All the cyclohexyl substituted bisphenyl fragments show lower optical anisotropy than diphenylpropane, a model analogue of bisphenol A polycarbonate that is widely used in optical applications. The results presented here have implications and potential applications in the design of molecules as well as polymers for optical media.

1. Introduction

Optical properties of materials, especially polymers, are of importance in a variety of areas including information storage systems and media.^{1,2} Polymers are used as substrate material as well as memory layer in compact disks, among other peripheral purposes. For such applications, high birefringence and refractive index anisotropy renders the exact focus of the optical beam unsuitable for the purpose of reading and writing. Optical anisotropy of polymer chains is therefore of considerable fundamental and practical relevance in providing an understanding of material behavior and for the molecular design of materials with properties tailored toward specific applications. The chemical structure of the repeat unit and the conformations of the chain molecule, among other material processing factors, dictate their optical properties. An understanding of the effect of chemical structure of small molecular fragments (which can also form the repeating unit of a polymer chain), on their optical anisotropy, therefore becomes an important step toward providing qualitative as well as quantitative understanding of the property of the polymer at the macroscopic scale.

Some of the original work on bond polarizability ellipsoids via experiments, of various bonds in organic compounds, was pioneered by Le Fevre and co-workers, whose reports include studies on the polarizability of cyclohexane and organic molecules that are constituted in part by the cyclohexyl group.³ From the electric double refraction studies of cyclohexane in dilute solution, the longitudinal and the transverse bond polarizabilities of the C–C bond in cyclohexane have been derived.³ The work performed by Le Fevre and Le Fevre³ originated as an attempt to ascertain by experiment the polarizability components of the C–C bond in various organic compounds, as it was evident from prior work that these polarizabilities could not be reliably derived from measurements on simpler nonpolar paraffins. The valence optical scheme (VOS) combined with

accurate group polarizabilities has been fruitfully incorporated into a rotational isomeric state scheme for larger organic molecules, oligomers and polymer chains in the past, to calculate the mean-squared optical anisotropy, $\langle \gamma^2 \rangle$.⁴ The inputs to the calculation scheme based on the traditional bond polarizability approach are the bond polarizabilities constituting the specific organic molecule. The treatment according to VOS rests on the assumption that the polarizability tensor for the molecule may be formulated as the vectorial geometric sum of the contributions of individual bonds or of constitutive individual groups (fragments larger than individual bonds). Use of merely bond polarizability data does not provide the correct quantitative agreement with experimental data.

Statistical mechanical calculations of the optical anisotropy of oligomers of *n*-alkanes and poly(oxyethylene) were investigated by Patterson and Flory.⁵ Flory et al.⁶ have presented a study wherein the optical anisotropies of aliphatic esters (including cyclohexylidene based esters) were deduced from depolarized Rayleigh scattering (DRS) measurements in CCl₄ and compared to calculations based on polarizability tensors from electric birefringence measurements. The good agreement between calculated $\langle \gamma^2 \rangle$ and the experimental value validates the formulation of the anisotropy tensors for diesters as the sum of tensors for monoesters with appropriate contributions from the bonds of the cyclohexyl group. The successful utilization of the VOS–RIS approach is also exemplified by various reports on different organic molecules and polymer chains in the past.^{7–13} Of particular relevance to our present work, are the reports by Navard and Flory, which deal with alkylcyanobicyclohexyls and related compounds¹² and alkylcyanobiphenyls, alkoxyphenyls, and related compounds.¹³ These studies clearly showed the utility of the theoretical methodology based on tensorial addition of polarizability components taking into account environmental effects, to even cyclohexyl based organic compounds. Flory and Navard provided an extension of the methodology, used for molecules for which experimental data

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were available for validation, to new homologous molecules not included in the experiments.¹²

The optical anisotropies of model compound fragments constituting the polycarbonate of bisphenol A (model fragments of relevance to the present study here), have been calculated by Erman and co-workers through polarizability tensors formulated as sums of contributions from constituent groups.⁸ The compounds chosen for that study consists of dimethyl carbonate (DMC), methyl phenyl carbonate (MPC), diphenyl carbonate (DPC), and 2,2-diphenylpropane (DPP). DRS and electric birefringence were used to estimate the polarizability tensors of the constituent groups in these compounds. The effect of polarization of the phenyl ring by the O atom, to which it is connected, was correctly quantified in the group polarizability tensor. The optical anisotropy tensors calculated by a combination of the information on the structure, molecular group anisotropy, and force-field based conformations, agreed excellently with experimental data (for DPC calculated $\langle \gamma^2 \rangle = 77.2 \text{ \AA}^6$ as compared to experimental value of $72 \pm 4 \text{ \AA}^6$; for DPP calculated $\langle \gamma^2 \rangle = 43.62 \text{ \AA}^6$ as compared to experimental value of $40 \pm 2 \text{ \AA}^6$). This treatment was further extended to the optical anisotropy of the polycarbonate chain.⁹ A subsequent study by Floudas et al.¹⁰ showed that the optical anisotropy measured experimentally by DRS was in agreement with the result of Erman et al. and that $\langle \gamma^2 \rangle/x$ was 111.3 \AA^6 per repeat unit (obtained for a oligomer of $x = 5$), 117.3 \AA^6 for a repeat unit in a polycarbonate chain in solution, and 115 \AA^6 for a repeat unit of polycarbonate in the chain in the condensed bulk state. Therefore calculations of optical anisotropy in isolation (or with group polarizabilities derived from measurements in specific solvents) can be useful in extrapolating the property to even the condensed phase, which is the eventual long-term objective. DPP is of relevance to our present study as a benchmark molecule, because various bisphenyls studied here are structural variants due to modifications of the basic bisphenyl fragment, DPP, of a polycarbonate.

With the accurate data on the bond and group polarizability tensors available for the phenyl group as well as the cyclohexane group, one can suitably calculate the optical properties of such molecules of which these groups are the constituent fragments. This methodology obviates the need for time-consuming and detailed experiments when one is looking at such compounds for which calculations or experimental data are not yet available in the literature. The focus of the present paper is to derive the polarizability tensor and calculate the optical anisotropy of a series of substituted cyclohexanes and their associated bisphenyl moieties. The information derived on the optical properties of these monomer units will help to understand the structural and conformational features that control the optical anisotropy in such molecules and in their polymer chains.

2. Methodology

2.1. Polarizability Tensors and Optical Anisotropies of Substituted Cyclohexanes. The polarizability tensor for cyclohexane can be formulated from tensors, one for each C–C bond and the associated removal of two C–H bonds in forming the C–C bond (by adding up the polarizability tensors of the six C–C bonds, which in turn is obtained from Γ_{CC}).¹² The tensor for cyclohexane may also be equivalently formulated from the group contributions from two propane molecules.⁶ The approach given by Navard and Flory¹² is used here for the derivation of polarizability tensor and optical anisotropy of substituted cyclohexanes. The reference frame $X_0Y_0Z_0$, in which the polarizability tensor for cyclohexane is expressed, is given

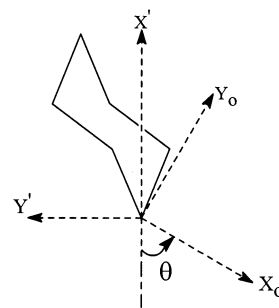


Figure 1. Coordinate reference frame of cyclohexane.

in Figure 1. For an equatorial bond (parallel to the X_0 axis),

$$\hat{\alpha}_e = \Gamma_{CC} \text{diag} \left[\frac{2}{3} \quad -\frac{1}{3} \quad -\frac{1}{3} \right]$$

where

$$\Gamma_{CC} = \Delta\alpha_{CC} - 2\Delta\alpha_{CH} \quad (1)$$

$\Delta\alpha_{CC}$ and $\Delta\alpha_{CH}$ are the group anisotropies of the C–C and C–H bonds respectively,⁵ and Γ_{CC} corresponds to the contribution to the polarizability due to the formation of a C–C bond and associated removal of two C–H bonds in the process. The tensor for the axial bond is obtained from that of the equatorial bond via the transformation

$$\begin{aligned} \hat{\alpha}_a &= R_Z(\tau)\hat{\alpha}_e R_Z^T(\tau) \\ &= \left(\frac{\Gamma_{CC}}{9} \right) \begin{bmatrix} -2 & -2\sqrt{2} & 0 \\ & 5 & 0 \\ & & -3 \end{bmatrix} \end{aligned} \quad (2)$$

where $\tau = \cos^{-1}(-1/3)$, is the tetrahedral bond angle.

The value of Γ_{CC} derived from DRS measurements on *n*-alkane homologues is 0.53 \AA^3 .⁵ Cyclohexane is considered to be made up of two equatorial, two gauche⁺ and two gauche⁻ bonds.¹² For cyclohexane, in which all the bond angles are tetrahedral, the polarizability tensor is derived as

$$\begin{aligned} (\hat{\alpha}_{CYX})_{X_0Y_0Z_0} &= 2(\hat{\alpha}_e + \hat{\alpha}_+ + \hat{\alpha}_-) \\ &= \left(\frac{\Gamma_{CC}}{9} \right) \begin{bmatrix} 4 & 4\sqrt{2} & 0 \\ & -10 & 0 \\ & & 6 \end{bmatrix} \end{aligned} \quad (3)$$


















The polarizability tensor for methylcyclohexane (CYX-2) can be derived, by replacing a hydrogen atom from cyclohexane by a methyl group, in either the equatorial or axial position. This in effect is the formation of a C–C bond, with the contribution being Γ_{CC} . If the methyl group is oriented equatorially, then

$$\begin{aligned} (\hat{\alpha}_{CYX-2E})_{X_0Y_0Z_0} &= (\hat{\alpha}_{CYX})_{X_0Y_0Z_0} + \Gamma_{CC} \text{diag} \left[\frac{2}{3} \quad -\frac{1}{3} \quad -\frac{1}{3} \right] \\ &= \left(\frac{\Gamma_{CC}}{9} \right) \begin{bmatrix} 10 & 4\sqrt{2} & 0 \\ & -13 & 0 \\ & & 3 \end{bmatrix} \end{aligned} \quad (4)$$

and if the methyl group is in axial orientation, then

$$\begin{aligned} (\hat{\alpha}_{CYX-2A})_{X_0Y_0Z_0} &= (\hat{\alpha}_{CYX})_{X_0Y_0Z_0} + R_Z(\tau)\hat{\alpha}_e R_Z^T(\tau) \\ &= \left(\frac{\Gamma_{CC}}{9} \right) \begin{bmatrix} 2 & 2\sqrt{2} & 0 \\ & -5 & 0 \\ & & 3 \end{bmatrix} \end{aligned} \quad (5)$$

TABLE 1: Squared Optical Anisotropy of Substituted Cyclohexanes

structure	γ^2 (\AA^6)	structure	γ^2 (\AA^6)	structure	γ^2 (\AA^6)
	1.123		^a <i>E</i> 1.778 <i>A</i> 0.281		<i>EE</i> 2.996 <i>AE</i> 0.749 <i>AA</i> 0.000
	0.749		<i>E</i> 1.778 <i>A</i> 0.281		<i>E</i> 1.778 <i>A</i> 0.281
	<i>E</i> 1.778 <i>A</i> 0.281		1.123		1.123
	1.123		<i>EE</i> 3.370 <i>AE</i> 1.123		<i>E</i> 2.528 <i>A</i> 1.029
	2.247		2.247		<i>E</i> 13.030 <i>A</i> 11.533
	<i>E</i> 16.880 <i>A</i> 15.383		<i>E</i> 16.880 <i>A</i> 15.383		

^a Key: E, equatorial; A, axial; EE, equatorial, equatorial; EA, equatorial, axial; AA, axial, axial.

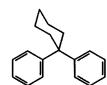
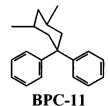
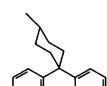
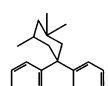
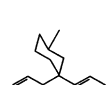

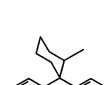
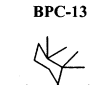

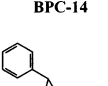
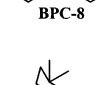
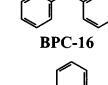
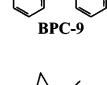
The optical anisotropy γ^2 , which is the quadratic tensor invariant, is obtained as

$$\gamma^2 = \frac{3}{2} \text{tr}(\hat{\alpha}\hat{\alpha}) \quad (6)$$

Following a similar procedure, the polarizability tensors for a variety of cycloaliphatic molecules can be derived by directional group additivity. The structures for which we present calculations of the polarizability tensors and optical anisotropy of a series of methyl- and phenyl-substituted cyclohexanes are provided in Table 1. For the phenyl-substituted cyclohexanes, it was observed from force-field minimizations (described in a later section), that the torsion about the Ph-cyclohexyl bond is zero. Hence, no additional transformation is required for group additivity, with the procedure being the same as that in the case of methyl groups, except that the polarizability tensor for the phenyl group⁷ (which is $\text{diag}[1.21 \ 1.21 \ -2.42]$) is made use of.

The substituted cyclohexanes studied in the present work are cyclohexane (CYX-1), methylcyclohexane (CYX-2), 1,4-dimethylcyclohexane (CYX-3), 1,1-dimethylcyclohexane (CYX-4), 1,1,4-trimethylcyclohexane (CYX-5), 1,1,3-trimethylcyclohexane (CYX-6), 1,1,2-trimethylcyclohexane (CYX-7), 1,1,4,4-tetramethylcyclohexane (CYX-8), 1,1,3,3-tetramethylcyclohexane (CYX-9), 1,1,2,2-tetramethylcyclohexane (CYX-10), 1,1,3,5-tetramethylcyclohexane (CYX-11), 1,1,3,3,5-pentamethylcyclohexane (CYX-12), 1,1,3,3,4,4-hexamethylcyclohexane (CYX-13), 1,1,2,2,3,3-hexamethylcyclohexane (CYX-14), 1-phenylcyclohexane (CYX-15), 1-phenyl-1,4-dimethylcyclohexane (CYX-

TABLE 2: Conformational Averaged Squared Optical Anisotropy of Cyclohexyl Substituted Bisphenyl Fragments

structure	$\langle \gamma^2 \rangle^a$ (\AA^6)	structure	$\langle \gamma^2 \rangle^a$ (\AA^6)
	14.733		<i>EE</i> 15.892 <i>AE</i> 12.950
	^b <i>E</i> 15.032 <i>A</i> 12.770		<i>E</i> 13.574 <i>A</i> 10.554
	<i>E</i> 15.032 <i>A</i> 12.873		11.464
	<i>E</i> 17.487 <i>A</i> 12.702		15.511
	13.052		<i>E</i> 21.448 <i>A</i> 21.865
	12.929		<i>E</i> 21.413 <i>A</i> 16.157
	19.362		

^a $\langle \gamma^2 \rangle$ obtained by averaging over the conformations. ^b Key: E, equatorial; A, axial; EE, equatorial, equatorial; EA, equatorial, axial; AA, axial, axial.

16), and 1-phenyl-3,3-dimethylcyclohexane (CYX-17). The computed optical anisotropies of these cyclohexanes are also provided in Table 1 along with the corresponding structures.

2.2. Polarizability Tensors and Optical Anisotropies of Cyclohexyl Substituted Bisphenyl Fragments. The approach described in the previous section for substituted cyclohexanes is now extended to deal with bisphenyls having cyclohexyl substituents at the C_α atom, which is the bridging atom connecting the two phenyl rings. In such cases, the polarizability tensor for the molecule and its optical anisotropy depend on the properties of the individual groups in the molecule and their relative geometric orientations dictated by the internal dihedral angles. The formulation of the polarizability tensors for these bisphenyl moieties (molecules) is presented here for the first time. The information on the polarizability tensors for cyclohexane and substituted cyclohexanes discussed earlier, together with the polarizabilities of the phenyl groups are made use of in the formulation of the polarizability tensor of the bisphenyl molecules. The structures of these molecules are provided in Table 2.

According to Erman et al.,⁸ DPP is considered to be formed from neopentane and two molecules of benzene according to

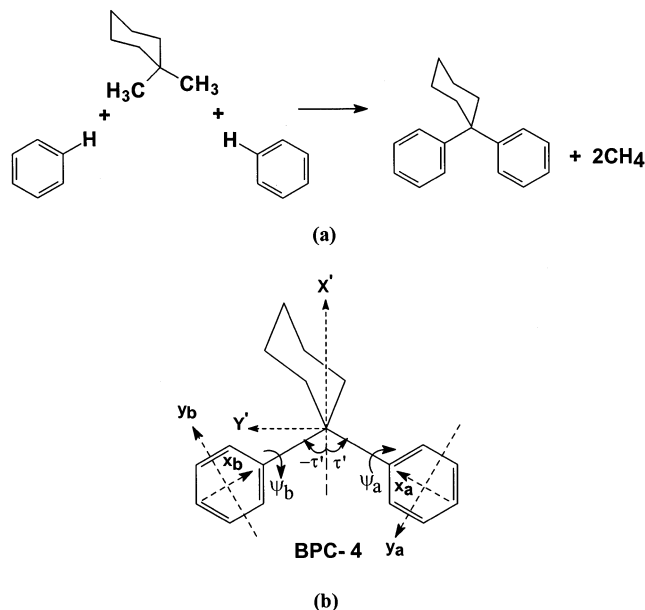
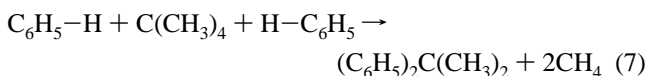


Figure 2. (a) Schematic of the formation of BPC-4 from CYX-4 and two phenyl groups. (b) Geometry of BPC-4 and coordinate reference frames of the phenyl and cyclohexyl groups.

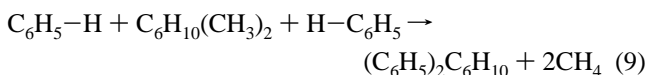
the hypothetical process



which involves no net change in the numbers of C–C and C–H bonds. With the neopentane molecule being symmetric, the polarizability tensor for the DPP molecule is formulated as

$$\hat{\alpha}_{\text{DPP}} = \hat{\alpha}_{\text{ph,a}} + \hat{\alpha}_{\text{ph,b}} \quad (8)$$

where the phenyl group tensors are both expressed in a common reference frame and are subjected to the effect of the isopropylidene group substitution at C_α. Following a similar procedure, the bisphenyl moiety (BPC-4) as shown in Figure 2, which now has a cyclohexyl group in its structure at the C_α atom, may be considered to be formed from 1,1-dimethylcyclohexane (CYX-4) and two molecules of benzene according to the hypothetical process (Figure 2),



Hence, the polarizability tensor for BPC-4 may be formulated from the sum of contributions from the two phenyl groups and CYX-4, with all tensors being expressed in a common reference frame X'Y'Z' (see Figure 2 for schematic), as

$$(\hat{\alpha}_{\text{BPC-4}})_{X'Y'Z'} = (\hat{\alpha}_{\text{ph,a}} + \hat{\alpha}_{\text{CYX-4}} + \hat{\alpha}_{\text{ph,b}})_{X'Y'Z'} \quad (10)$$

The polarizability tensor for CYX-4 may be derived from that of cyclohexane (CYX-1) by taking into account the replacement of two hydrogen atoms by two methyl groups, one axial and the other equatorial. Following the procedure described earlier on substituted cyclohexanes, the polarizability tensor for CYX-4 in the X₀Y₀Z₀ reference frame may be written as

$$(\hat{\alpha}_{\text{CYX-4}})_{X_0Y_0Z_0} = \left(\frac{\Gamma_{\text{CC}}}{9} \right) \begin{bmatrix} 8 & 2\sqrt{2} & 0 \\ & -8 & 0 \\ & & 0 \end{bmatrix} \quad (11)$$

The transformation of the CYX-4 polarizability tensor from X₀Y₀Z₀ to X'Y'Z' (Figure 1) can be effected by the following relation, where θ is one-half of the tetrahedral bond angle (54.75°).

$$(\hat{\alpha}_{\text{CYX-4}})_{X'Y'Z'} = R_Z(\Theta)(\hat{\alpha}_{\text{CYX-4}})_{X_0Y_0Z_0}R_Z^{-1}(\Theta) \quad (12)$$

The individual original reference frames in which the phenyl and the cyclohexylidene groups are expressed in the bisphenyl fragment are shown in Figure 2. The polarizability tensor for BPC-4 in the frame X'Y'Z' may thus be formulated by transforming the phenyl groups “a” and “b” from the x_ay_az_a and x_by_bz_b reference frames, respectively, to X'Y'Z' and then adding these on to the contributions from CYX-4 in the X'Y'Z' frame. The transformations of the phenyl groups a and b are given by⁸

$$(\hat{\alpha}_{\text{ph,b}})_{X'Y'Z'} = R_Z(-\tau')R_x(\psi_b)(\hat{\alpha}_{\text{ph,b}})_{xyz}R_x^{-1}(\psi_b)R_Z^{-1}(-\tau')$$

$$(\hat{\alpha}_{\text{ph,a}})_{X'Y'Z'} = R_Z(\tau')R_x(\psi_a)(\hat{\alpha}_{\text{ph,a}})_{xyz}R_x^{-1}(\psi_a)R_Z^{-1}(\tau') \quad (13)$$

wherein the phenyl group polarizability tensor in the xyz frame is diag[1.21 1.21 -2.42]. The torsions (ψ_b, ψ_a) and the bond angle (2τ) needed for the calculation are schematically shown in Figure 2. Performing the transformations for CYX-4 and phenyl groups a and b and adding, gives the polarizability tensor for BPC-4 in the X'Y'Z' frame. A similar procedure is adopted for the calculation of the polarizability tensors and optical anisotropies of all the other bisphenyl moieties in our investigation here, using the tensors of their corresponding cyclohexanes and the bond angles and torsions. A sample calculation for the bisphenyl fragment, BPC-5 formed from CYX-5 is provided in the Supporting Information section.

For all molecules the bond angles and torsions were determined from conformational energy calculations of the bisphenyl fragments using the InsightII software package.¹⁴ The PCFF force-field was used for the conformational analysis and calculations.¹⁵ Bisphenyl molecules were minimized until the potential energy gradient was less than 10⁻³ kcal/(mol Å). We performed conformational analysis and derived the energy maps of a few bisphenyl molecules by varying ψ_b and ψ_a simultaneously. The minimum energy torsions corresponding to each bond were found to be the same when doing a systematic conformational search about each of the two bonds separately. Hence further calculations were done by systematic variation of a single torsion (such as either ψ_b or ψ_a) from -180° to +180° in 5° increments by constraining the torsion at a specific value accompanied by simultaneous relaxation of other degrees of freedom in the system at every specific torsion of the bond. A force constant of 1000 kcal/mol rad² was applied for constraining the torsion. The relaxation was performed using a combination of steepest descent and conjugate gradient methods till the energy gradient was less than 10⁻³ kcal/(mol Å) for each specific conformer. From the conformational energy maps, the lower energy torsional values were identified. From the energies of the optimized structures (cases where both equatorial and axial substitutions were possible), the statistical weights according to Boltzmann distribution at 300 K were calculated. Energy optimization was also done for different substituted cyclohexanes to compute the relative population of the various conformers at 300 K. These population weights were in turn used for estimating the energy-weighted averaged optical anisotropy wherever applicable.

The various bisphenyl fragments studied in the present work are 1,1-diphenylcyclohexane (BPC-4), 4-methyl-1,1-diphenylcyclohexane (BPC-5), 3-methyl-1,1-diphenylcyclohexane (BPC-6), 2-methyl-1,1-diphenylcyclohexane (BPC-7), 4,4-dimethyl-

1,1-diphenylcyclohexane (BPC-8), 3,3-dimethyl-1,1-diphenylcyclohexane (BPC-9), 2,2-dimethyl-1,1-diphenylcyclohexane (BPC-10), 3,5-dimethyl-1,1-diphenylcyclohexane (BPC-11), 3,3,5-trimethyl-1,1-diphenylcyclohexane (BPC-12), 3,3,4,4-tetramethyl-1,1-diphenylcyclohexane (BPC-13), 2,2,3,3-tetramethyl-1,1-diphenylcyclohexane (BPC-14), 4-phenyl-1,1-diphenylcyclohexane (BPC-16), and 3-phenyl-1,1-diphenylcyclohexane (BPC-17). The structures of these compounds are given in Table 3.

3. Results and Discussion

3.1. Optical Anisotropy of Substituted Cyclohexanes.

Structures of substituted cyclohexanes and calculated optical anisotropies are provided in Table 1. Cyclohexane (CYX-1) in its chair conformation exhibits a small anisotropy of 1.123 \AA^6 and is in agreement with the experimental value.¹² Methyl substitutions on the cyclohexane ring lead to a variety of different results for its optical anisotropy. The presence of a methyl group substituent at the apex carbon of the chair conformation (CYX-2) could result in either an increase or a decrease in the optical anisotropy depending on the orientation of the bond connecting the methyl group to the cyclohexyl ring. The axial orientation results in a substantial lowering of the anisotropy. Two methyl groups, one at each of the apex carbon atoms, again gives a similar result compared to a single methyl group, in that the optical anisotropy could be higher than that of unsubstituted cyclohexane or lower depending on the methyl group orientations. When both methyls are oriented axially, the molecule is optically isotropic; that is the optical anisotropy is zero. On the basis of averaging using Boltzmann energy weights for the three orientational configurations, the energy-weighted averaged optical anisotropy of CYX-3 is 2.782 \AA^6 , which is higher than the value for unsubstituted cyclohexane as well as single methyl-substituted cyclohexane.

In a situation where two methyl groups are attached to the same carbon atom (CYX-4), the anisotropy is lower than for cyclohexane, which exemplifies the effect of the relative positioning of multiple methyl substituents on the cyclohexyl ring, in terms of the optical anisotropy relative to that for cyclohexane. When two methyl groups are present on cyclohexane, only their relative orientations with respect to the ring dictate the optical anisotropy but not the carbon position at which they are substituting. This is also substantiated by our calculations on molecules where the methyls are not specifically located at the apex carbon atom of the cyclohexyl chair conformation, which are not presented here. It is interesting to note that molecule CYX-5, where there are three methyl groups, has the same optical anisotropy as CYX-2, which has only one methyl group, indicating that the additional set of paired methyl groups in CYX-5 does not in effect contribute to the optical anisotropy.

In case of set-III molecules (CYX-8–11), which have four methyl substituents on the ring, the *optical anisotropy is exactly the same as that for cyclohexane*, irrespective of the relative disposition of the pairs, which again is an interesting result. This is also found to be true when the methyls do not occur as pairs. The dependency of optical anisotropy on the relative orientations of single substituent methyl groups with respect to the cyclohexane ring is again brought out in the form of an enhancement of anisotropy for EE orientations compared to AE orientations, whereas AA orientation is energetically very prohibitive (as in CYX-11). In the next set of molecules, CYX-12, CYX-13, and CYX-14, where there are greater numbers of methyl substituents, either 5 or 6, the optical anisotropy is always

higher than that for unsubstituted cyclohexane. The optical anisotropy, however, does not just increase with the number of methyl substituents. As seen before, an axial methyl group orientation, as in the case of CYX-12, reduces the optical anisotropy in comparison with unsubstituted cyclohexane.

The final set of molecules contains a phenyl group substituent on the cyclohexyl ring (CYX-15, CYX-16, and CYX-17). The anisotropy of the cyclohexane substituted with a phenyl group is substantially higher than when a methyl group is the substituent. The anisotropy is critically dependent on the relative orientation of the bond connecting the phenyl group to the cyclohexyl ring, with the axial orientation giving a lower anisotropy in comparison to the equatorial orientation. This effect is reduced when methyl groups substitute on the cyclohexyl ring in addition to the phenyl group. Similar to the behavior observed in the case of methyl-substituted cyclohexanes, even in the case of phenyl-substituted cyclohexanes, the orientation of the bond connecting the phenyl group to the cyclohexane matters, whereas the relative positioning of the phenyl ring does not affect the optical anisotropy value. A significant increase in the anisotropy is seen when one compares cyclohexane (CYX-5) with substituted cyclohexane having a phenyl ring (CYX-16). This increase is higher than the optical anisotropy of benzene, which is 13.17 \AA^6 . The difference therefore can be attributed to the polarizability contribution from the C–C bond connecting the phenyl ring to the cyclohexane ring.

In this series of substituted cyclohexanes, the optical anisotropy is always higher for the equatorial than for the axial orientation, which is in accordance with the experimental findings reported for cyclohexyl halides.³ When the substituent is equatorial, the polarization of the electron cloud of this bond is in the same plane as the equatorial plane of cyclohexane (along which the polarizability is maximum) and enhances the polarizability and optical anisotropy of the whole molecule. On the contrary when the substituent is axially oriented, the polarization of the electrons of this bond is at an angle of 109.5° to the equatorial plane. This can be considered as being almost perpendicular to the equatorial plane and hence results in a lower anisotropy of the molecule.

3.2. Conformational Effects in Bisphenyls. Conformational energy calculations were performed using the PCFF force-field¹⁵ through Discover available in InsightII,¹⁴ for bisphenyl fragments BPC-4 to BPC-16 (results shown in Table 2). These calculations provide the various minimum energy torsions. These results are used to rationalize the optical anisotropy properties of bisphenyls where conformational effects in addition to intrinsic polarizabilities of various fragments can affect the overall optical anisotropy. The bond angle $2\tau'$ was obtained from the global minima of each of these molecules. The minimum energy torsional states and the bond angles for the fragments are listed in Table 1S provided as Supporting Information with this paper. These fragments can be categorized into two sets: one set in which the rotational freedom about the (ψ_a, ψ_b) torsion is unhindered and have eight minimum energy conformations (BPC-4, BPC-5, BPC-6 (E), BPC-7 (E), BPC-8, BPC-11 (EE), BPC-16 (E) and BPC-17 (E)) and the other set in which the minima is reduced to four due to unfavorable steric interactions from an axially oriented methyl group (BPC-6 (A), BPC-7 (A), BPC-9, BPC-10, BPC-11 (EA), BPC-12 (E), BPC-13 and BPC-14). The exclusion of the remaining four symmetric conformers, which were otherwise of lower energy in the first set, is due to unfavorable steric interactions between the methyl hydrogens and those on the phenyl rings, because of the axial orientation

of the methyl groups. For bisphenyls BPC-16 and 17 with the phenyl groups equatorially oriented in the para and meta positions, respectively, the freedom of rotation is unaffected by the phenyl substituents and the conformational analysis leads to eight symmetric lower energy conformers. The bond angle $2\tau'$ decreases only slightly as the steric strain in the bisphenyl fragment increases.

3.3. Optical Anisotropy of Bisphenyl Fragments. For each bisphenyl in the series studied here, the conformations as described by the torsions are symmetric with respect to the plane formed by the $C_{Ph}-C_{\alpha}-C_{Ph}$ bond angle (Table 1S in Supporting Information) and this molecular symmetry leads to the same optical anisotropy for the various conformers. The structures and the optical anisotropies are listed in Table 2. The polarizability tensors and optical anisotropies were calculated for both the E and A conformers (wherever applicable). Conformational energy calculations show that for BPC-11–17, the axial conformers are energetically highly unfavorable and hence these were not used in the calculation of weighted averaged anisotropy. The conformation as shown for BPC-4 (the bisphenyl from CYX-4) in Figure 2 corresponds to equatorial phenyl ring “a” and axial phenyl ring “b”, for which all calculations were performed (the other orientation of CYX ring only makes the phenyl rings different but the optical anisotropy is the same as in the first orientation).

We first consider unsubstituted cyclohexylidenebisphenyl and the single methyl-substituted cyclohexylidenebisphenyl set of molecules (BPC-4, BPC-5, BPC-6, and BPC-7). The optical anisotropy of BPC-4 is significantly lower than the experimentally derived optical anisotropy of DPP (value of $40 \pm 2 \text{ \AA}^6$ taken from ref 8), which is the bisphenyl analogue of bisphenol A polycarbonate. We formulated the polarizability tensor for DPP from the group polarizabilities of phenylene groups (including the effects of isopropylidene group substitution) and the torsions ψ_b and ψ_a (50° , 50°) and bond angle $2\tau'$ (110.7°). The torsions and the bond angles in this calculation were obtained from PCFF-based conformational energy calculations of DPP. The calculated optical anisotropy obtained for DPP is 39 \AA^6 , which shows that the torsions and the bond angles from the PCFF-based calculations are able to reproduce the experimental optical anisotropy for DPP very well. We expect the same to be applicable for all cyclohexyl-substituted bisphenyls in this study. The cyclohexyl group makes the bisphenyl fragment more isotropic; i.e., it tends to increase the polarizability in the three mutually perpendicular directions and reduces the relative polarizability differences, which in turn results in lower anisotropy.

Similar to the result seen earlier for substituted cyclohexanes, even in the case of cyclohexylidenebisphenyls, in comparison to unsubstituted cyclohexylidenebisphenyls, when a methyl group is substituted at the para position of the cyclohexyl ring (the apex carbon atom), the anisotropy is higher for the equatorial conformer (15.03 \AA^6) but lower for the axial conformer (12.77 \AA^6). The minimum energy torsions and the bond angles in BPC-5 are comparable to those of BPC-4, which means the conformation of the bisphenyl fragment is not altered by the methyl group at the para position of the cyclohexyl ring, and therefore the optical anisotropy differences arise solely due to the polarizability differences. The two isomers BPC-5 and BPC-6 give similar optical anisotropies and the position of the methyl substituent does not matter. However, conformationally, the axial orientation of the methyl group is preferred in the case of the ortho-substituted methyl bisphenyl, contrary to the meta- and para-substituted isomers where equatorial substitution is

favorable. The axially oriented methyl group conformers of all these compounds have almost similar optical anisotropies. The energy-weighted average anisotropy of ortho-substituted BPC-7 is 13.562 \AA^6 , which is lower than that for the other two isomers (14.947 \AA^6 and 15.01 \AA^6 , respectively for BPC-5 and -6), but this compound will have a high level of nonbond interatomic repulsion.

Isomers of doubly substituted pair of methyls on the bisphenyls (BPC-8–10) give lower conformationally (equatorial and axial) averaged optical anisotropy compared to singly substituted methyl bisphenyls. When the methyl groups are in meta,meta' positions (BPC-11), there can be three distinct conformers with respect to their orientation viz., EE, AE (EA), and AA. The probability that the two methyl groups will be in AA orientation is small at 300 K (the AA conformer energy is 9 kcal/mol higher than that of EE conformer), and hence the calculation was not done for this conformer. In this case also the EE conformer with both methyls in the equatorial orientation has higher anisotropy than that of the AE conformer. It should be noted that anisotropy of BPC-9 (with a pair of methyl group at the meta position, one axial and the other equatorial) is almost the same as the AE conformer of BPC-11 (12.93 and 12.95 \AA^6 , respectively); however other physical properties of these structurally different molecules could be quite different. Both these bisphenyls exhibit conformations with similar energies as well. The conformationally energy weighted average anisotropy of 15.831 \AA^6 for BPC-11 is, however, higher than that of all the other methyl-substituted bisphenyls in the list of compounds studied here. This effect is due to the presence of two separately substituting methyl groups each in their equatorial orientations, which is an effect seen earlier in the case of substituted cyclohexanes as well.

The A conformer of BPC-12 exhibits the lowest optical anisotropy in this series of bisphenyls studied but is highly unfavorable, its energy being 6 kcal/mol above the equatorial conformer. Hence the optical anisotropy for BPC-12 can be equated to that of its equatorial conformer. Compared to BPC-9, the greater anisotropy for BPC-12 arises from the equatorial methyl substitution at the alternate meta position. The interesting result for BPC-12 having multiple methyl substituents is its lower optical anisotropy compared with the unsubstituted cyclohexylidenebisphenyl BPC-4. The $\langle \gamma^2 \rangle$ for BPC-13 corresponds to the lowest value of conformationally and orientationally averaged optical anisotropy in the entire set of bisphenyls we have studied.

Bisphenyls with an additional phenyl group at the para or meta position of the cyclohexyl ring show the maximum anisotropy among the compounds studied here, similar to the earlier observations made in the case of substituted cyclohexane compounds. This is due to the fact that the phenyl groups are more polarizable than the methyl groups and hence show higher optical anisotropy. On the basis of the calculations, the equatorial conformers are found energetically more favorable and the distribution of the axial conformers at 300 K was found to be insignificant (0.07 and 0.14% for BPC-16 and 17, respectively). The equatorial conformers in both meta and para substitution have similar anisotropies, which falls in line with the results on the respective cyclohexanes (CYX-16 and 17). But the axial conformers show different anisotropies for their corresponding bisphenyl fragments, which is attributed to the differences in the conformational behavior of the two bisphenyls. In all molecules the E and EE conformers invariably showed greater anisotropy than A, AE, and AA conformers. Consider BPC-8–10 where the methyl groups are in the para, meta, and ortho

positions, respectively. The optical anisotropy of the bisphenyl moiety does not arbitrarily increase with the number of methyl groups on the cyclohexyl ring but is determined by the position and the orientation of the methyl groups, as seen from the results for BPC-8–10, 13, and 14.

Conformational effects are very important in understanding the results on the molecules studied here. The reduction in the optical anisotropy observed in BPC-4 when compared to DPP can be ascribed to the difference in the geometry and conformation of the bisphenyl fragment due to the presence of cyclohexyl group at the C_α atom. With the phenyl rings being inequivalent in cyclohexyl-substituted bisphenyls, the torsional conformation of the axial and equatorial phenyl rings are 70° and 55° , respectively, in contrast to 50° conformation of either phenyl ring in DPP. In the former case, the axial ring due to unfavorable 1,3-diaxial interactions adopts an orientation that is nearly perpendicular, leading to a lowering of the anisotropy of the bisphenyl fragment. The conformations of other cyclohexyl-substituted bisphenyl fragments are similar to that of BPC-4 (other than exclusion of a few minima in some cases) except for BPC-10 and 14. Due to the ortho methyl groups in BPC-10 and 14, the conformations of the bisphenyls are (50° , 45°) and (60° , 50°), respectively, for the (ψ_b , ψ_a) torsions and are more or less similar to that in DPP. As expected these compounds have higher anisotropies than their meta- and para-substituted counterparts whose conformations are similar to BPC-4.

4. Conclusions

Optical anisotropies of a series of substituted cyclohexanes and their corresponding bisphenyl molecules are derived in this work, via tensorial summation of experimentally derived optical polarizabilities of constitutive groups such as cyclohexane group, C–C bond, and phenyl group. The torsions and the bond angles of the bisphenyl fragments associated with these substituted cyclohexyl fragments were derived from force-field based conformational energy calculations. The optical anisotropies of substituted cyclohexanes and bisphenyl moieties are reported here for the first time. The trend observed for the lower optical anisotropy of axial substitutions when compared to equatorial agrees well with experimental reports on cyclohexyl halides in the literature. The highest optical anisotropy was observed for the phenyl-substituted cyclohexanes, both for substituted cyclohexanes as well as substituted cyclohexylidene bisphenyls. In the series of methyl-substituted cyclohexanes, the molecule where the unpaired methyl groups were both equatorially oriented showed the maximum anisotropy. The optical anisotropy of the substituted cyclohexanes depends on the orientation and not on the position of the substituents, but in bisphenyl moieties it is dependent on the conformation of the whole fragment along with the position and orientation of the substituents. All bisphenyl molecules investigated here show lower anisotropy than DPP, which is the model analogue of the polycarbonate of bisphenol A. With the fundamentally attractive

set of insights provided by the present study on the molecular structure–optical property behavior of small but complicated fragments, along with the specific additional information that would still be required on the overall conformational behavior of polymer chains, one would be able to structurally construct particular chain molecules with desired optical properties. The results provided in this study indicate that these molecules can be considered as potential monomers for synthesis of polymers, which will have lower single chain anisotropy and eventually lower intrinsic birefringence. It is expected that the calculations done on the monomer fragments may be used as a promising tool for designing new monomers for polymer synthesis for optical applications.

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Supporting Information Available: A table of geometrical parameters of bisphenyl fragments and an appendix describing the formulation of the polarizability tensor and optical anisotropy for BPC-5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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