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Planar Hydrocarbons More Optically Active Than Their Isomeric Helicenes

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Supporting Information

ABSTRACT: Comparisons are made of the calculated optical rotation tensors of C_{2v}-symmetric, polyaromatic hydrocarbons and their [5]helicene, [6]helicene, and [7]helicene isomers. Seven ∩-shaped, planar compounds had, in each case, larger computed tensor elements than the chiral helicenes. Merely obviating the condition of solution averaging wholly changes expectations of the magnitudes and etiologies of optical activity. Symmetries of achiral compounds facilitate semiquantitative correlations between structure and optical rotation.

[*n*]Helicenes[1] are favorite compounds for students of optical activity: they look like they sound, are configurationally stable when $n \geq 6$, and have very large specific rotations.[2,3] They are the classic, so-called intrinsically dissymmetric chromophores. Their names reinforce the notion that screw-like geometries give rise to associated optical activities. This picture has become ingrained.[4] However, chirality is not required to produce the light-matter interactions that underlie optical activity.[5] Achiral molecules in isotropic solutions must be optically inactive, but molecules with symmetry D_{2d} or a nonenantiomorphous subgroup, S_4, C_{2v}, or C_s, achieve this by averaging equal and opposition rotations in symmetry related directions. The helix merely ensures that the *average* optical activity is not zero in solution. That is all. If measurements of the optical activity of oriented molecules were easy[6]—and we can expect that eventually they will be—helicenes would lose their pride of place, although not their overall chemical appeal.[7]

Computations of the optical rotation (OR) of oriented molecules are now easy thanks to the efforts of many during the past 15 years.[8] These advances permit us to predict, here, that the ORs of flat polycyclic aromatic hydrocarbons (PAHs), when oriented, exceed the most active directions of their isomeric helicenes.[9,10] In particular, we computed the long wavelength (633 nm) optical rotations of [5]helicene ($\mathbf{5_H}$), [6]helicene ($\mathbf{6_H}$), and [7]helicene ($\mathbf{7_H}$) as well as their respective ∩-shaped isomers with C_{2v} symmetry shown in Figure 1. $\mathbf{5_H}$ has two such constitutional isomers ($\mathbf{5_{A,B}}$), $\mathbf{6_H}$ has one ($\mathbf{6_A}$), and $\mathbf{7_H}$ has four ($\mathbf{7_{A,B,C,D}}$).[11] We made time-dependent density functional theory (TDDFT) calculations of nonresonant OR based on the linear response formalism[12] within Gaussian 09 (Revision B.01).[13] The B3LYP/6-311+G(d,p) and B3LYP/aug-cc-pVDZ levels of theory have been tested extensively for computations of this kind.[14] Gauge invariant atomic orbitals were used in order to obviate origin dependence. Structures were optimized with symmetry constraints using B3LYP/6-31G(d).

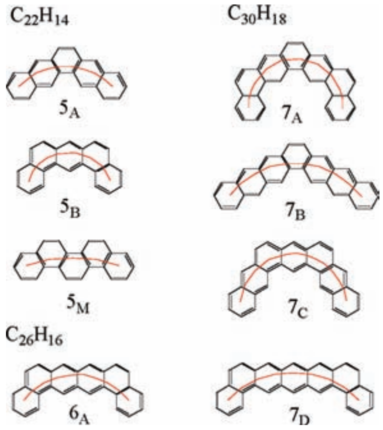

Figure 1. ∩-Shaped, C_{2v}, polycyclic aromatic hydrocarbon isomers of [5], [6], and [7]helicene ($\mathbf{5_H}$, $\mathbf{6_H}$, $\mathbf{7_H}$, not shown here). $\mathbf{5_A}$ - pentaphene; $\mathbf{5_B}$ - benzo[*m*]tetraphene; $\mathbf{5_M}$ - picene; $\mathbf{6_A}$ - dibenzo[*a,l*]tetracene; $\mathbf{7_A}$ - dibenzo[*a,o*]pentaphene; $\mathbf{7_B}$ - heptaphene; $\mathbf{7_C}$ - naphtha[2,3-*a*]pentaphene; $\mathbf{7_D}$ - dibenzo[*a,n*]pentacene. Arcs inscribed between terminal ring centroids. Arc angles: $\mathbf{5_A}$, 100°; $\mathbf{5_B}$, 150°; $\mathbf{5_M}$, 40°; $\mathbf{6_A}$, 100°; $\mathbf{7_A}$, 190°; $\mathbf{7_B}$, 100°; $\mathbf{7_C}$, 165°; $\mathbf{7_D}$, 90°. The coordinate system for the compounds defines *z* as the diad axis. *x* is perpendicular to the molecular plane.

The computational methodology needs to be chosen with care as TDDFT can underestimate the energies of the ^1L_a[15,16] excited states of linear acenes by failing to represent the ionic character of wave functions. Misjudged excitation energies affect the computed polarizabilities that enter the computation of OR.[17] Wong and Hsieh[18] offered a remedy through the use of range-separated functionals.[19] We repeated excitation energy calculations for $\mathbf{6_A}$ and $\mathbf{6_H}$ with range separated functionals CAM-B3LYP,[20−22] and LC-BLYP (Coulomb attenuating method and long-range correlated), as well as the CCSD[23] (coupled-cluster singles and doubles) method. Indeed, the first excitation energies increased for $\mathbf{6_A}$, and somewhat more for $\mathbf{6_H}$ (2717 and 3371 cm^{-1} respectively, using CAM-B3LYP, for example). The wavelengths in Tables 1 and 2 are systematically higher than the experimental values where available.[24] Correcting the energies of achiral $\mathbf{5_{A,B}}$, $\mathbf{6_A}$, and $\mathbf{7_{A,B,C,D}}$ would decrease the OR marginally relative to chiral $\mathbf{5_H}$, $\mathbf{6_H}$, and $\mathbf{7_H}$ but not enough to alter our conclusions of the relative magnitudes of the achiral and chiral PAH tensor elements in the discussion to follow. Moreover, any requisite

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Table 1. Computed Properties of Planar PAHs

PAH	first excited state (nm)	relative energies (kJ/mol)[a]	gyration tensor g_{xy}[b] (bohr^4/ molec.)		symmetric electric dipole−magnetic dipole polarizability G'_{xy} (bohr^4/ molec.)		reduced symmetric electric dipole−electric quadrupole polarizability A^{sym}_{xy} (bohr^4/ molec.·hartree)	
3	316	–	−27[c]	−28[d]	4.1[c]	4.1[d]	5.5[c]	4.6[d]
$\mathbf{5_A}$	401	−35.70	−154	−154	23	23	32	27
$\mathbf{5_B}$	368	−50.80	−145	−145	22	22	58	55
$\mathbf{5_M}$	351	−50.55	−54	−54	8.3	8.3	22	20
$\mathbf{6_A}$	457	−56.66	−239	−243	37	37	107	100
$\mathbf{7_A}$	402	−97.46	−370	−376	58	59	206	199
$\mathbf{7_B}$	501	−46.80	−512	−534	74	75	11	−6.4
$\mathbf{7_C}$	415	−81.50	−423	−431	66	67	219	211
$\mathbf{7_D}$	576	−60.41	−341	−346	54	55	217	211

[a] Relative to helicene isomers, $\mathbf{5_H}$, $\mathbf{6_H}$, $\mathbf{7_H}$. [b] *xy* plane perpendicular to diad. [c] B3LYP/6-311+G(d,p). [d] B3LYP/aug-cc-pVDZ.

corrections to the low lying energies would be obviated in the effective sum over excited states.

The average specific rotations calculated at 633 nm for the *M*-isomers of $\mathbf{5_H}$, $\mathbf{6_H}$, and $\mathbf{7_H}$ are −2336, −3839, and −5465 deg·cm^3/dm·g, respectively, using B3LYP/6-311+G(d,p) and −2378, −3859, and −5476 deg·cm^3/dm·g, respectively, using B3LYP/aug-cc-pVDZ.[25] These values are comparable to experimental values at 589 nm[2] and 633 nm[3] and closer to experiment than the values computed with functionals employed a decade ago.[26,27]

The expression for the gyration tensor is

$$g_{\alpha\beta} = \frac{1}{2\omega}\varepsilon_{\alpha\gamma\delta}\left[\frac{1}{3}\omega(A_{\gamma,\delta\beta} - A_{\delta,\gamma\beta}) + \varepsilon_{\lambda\beta\gamma}G'_{\delta\lambda} - \varepsilon_{\lambda\beta\delta}G'_{\gamma\lambda}\right] \tag{1}$$

where ε is the Levi−Cevita operator, G' is the electric dipole (μ)-magnetic dipole (m) polarizability and A is the electric dipole−electric quadrupole (Θ) polarizability, commonly defined elsewhere.[28] Here, we are using the sum over indices, the Einstein convention.

The components of the third rank $A_{\alpha,\beta\gamma}$, tensor can be reduced to a second rank tensor by $A_{\alpha\beta} = \varepsilon_{\gamma\delta\alpha}A_{\gamma\delta\beta}$.

The symmetrized components of $A_{\alpha\beta}$ correspond to the total $A_{\alpha,\beta\gamma}$ contribution to the corresponding $g_{\alpha\beta}$. For the ∩-shaped PAHs, the only nonzero gyration tensor element is g_{xy}.[29] This can be found using

$$g_{xy} = \frac{1}{2\omega}\left(G'_{xy} + G'_{yx} - \frac{1}{6}\omega A^{sym}_{xy}\right) \tag{2}$$

where

$$A^{sym}_{xy} = \frac{1}{2}(A_{z,xx} + A_{y,zy} - A_{x,zx} - A_{z,yy}) \tag{3}$$

In Table 1, we report the unique gyration tensor element, g_{xy}, for the C_{2v} compounds. Gyration can be related to OR in a given direction by taking the magnitude of the tensor in the direction of light propagation (OR $\approx -\boldsymbol{n}^{\mathrm{T}}\cdot\boldsymbol{g}\cdot\boldsymbol{n}$). The |OR| of the ∩-shaped PAHs, $\mathbf{5_{A,B}}$, $\mathbf{6_A}$, and $\mathbf{7_{A,B,C,D}}$ along the directions ±*xy* (Table 1) exceed those for the most active direction of their helicene isomer in each comparison (Table 2). Representations of the OR anisotropy of $\mathbf{6_A}$ and $\mathbf{6_H}$ are compared in Figure 2. The ORs of the members of this series vary as $\mathbf{7_B} > \mathbf{7_C} > \mathbf{7_A} > \mathbf{7_D} > \mathbf{6_A} > \mathbf{5_A} > \mathbf{5_B}$. Larger molecules are more responsive. G' follows the same trend. The A terms, scaled as they are by $\omega/3$, typically contribute only a few percent of g for this class of molecule.

The overall OR trend among the set of seven compounds can be reckoned by treating the conjugated hydrocarbons as wire arcs inscribed between the terminal ring centroids (Figure 1).[30] If we imagine that electromagnetic radiation drives one electron from one terminus to the other, the associated transition magnetic dipole moments are then proportional to the sectors of a unit circle[31] defined by the arcs, and the associated transition electric dipole moments are proportional to the distance between the terminal rings. To a good approximation, these quantities can be reckoned with a straightedge, compass, and protractor. Crudely speaking, the product of this distance and area should be proportional to OR. In this way, the predicted OR trend would be $\mathbf{7_C} > \mathbf{7_B} > \mathbf{7_A} > \mathbf{7_D} > \mathbf{6_A} > \mathbf{5_B} > \mathbf{5_A}$, approximately the rank based on electronic structure calculations above, albeit evaluated by simple geometry with the disregard of wave functions. Computations of optical rotation using sums over excited state wave functions have been difficult to interpret.[32]

If an electron travels from left to right in the compounds in Figure 1, then the electric dipole moment points to the left and the magnetic dipole moment points out of the page. This means that if the wave vector is traveling along *xy*, the moments make antiparallel projections on the wave vector. This corresponds to a positive OR at long wavelength. It is important in drawing these judgments to be clear about sign conventions. The physicist's electric dipole, used here, points by convention to the positive charge. And, gyration is not synonymous with OR, as they are opposite in sign by convention. The computed signs are also in accord with what we would predict from a variety of other classical considerations. For $\mathbf{5_H}$, $\mathbf{6_H}$, and $\mathbf{7_H}$, left-handed helices are levorotatory on average, with the sign dominated by the component normal to the helix axis. This agrees with Tinoco's observations for oriented copper helices[33] as well as the free electron model.[34] This is also the expectation on the basis of classical electronic polarizability theory[35] applied to helices by Glazer and Stadnicka.[36] The latter authors showed that light propagating along a left-handed helix will experience a levorotation if the tangential polarizabilties are dominant, the scenario expected for aromatic compounds. The ∩-shaped compounds are also left-hand screws when viewed obliquely from the *xy* direction referred to Figure 2. They will have the sign of the response in *xy* as a three-dimensional object along the helix axis.

Table 2. Computed Diagonalized Tensors for *M*-Helicenes[a]

		diagonal gyration tensor (bohr^4/molecule)					
		B3LYP/6-311+G(d,p)			B3LYP/aug-cc-pVDZ		
[*n*]-helicene	first excited state (nm)	g_{xx}	g_{yy}	g_{zz}	g_{xx}	g_{yy}	g_{zz}
$\mathbf{5}_{\mathbf{H}}$	372	−121[a]	75	104	−123	77	105
$\mathbf{6}_{\mathbf{H}}$	388	−155	133	136	−157	133	137
$\mathbf{7}_{\mathbf{H}}$	408	−172	165	192	−175	167	193

[a] *z* is parallel to the diad axis. *x* is the helix axis.

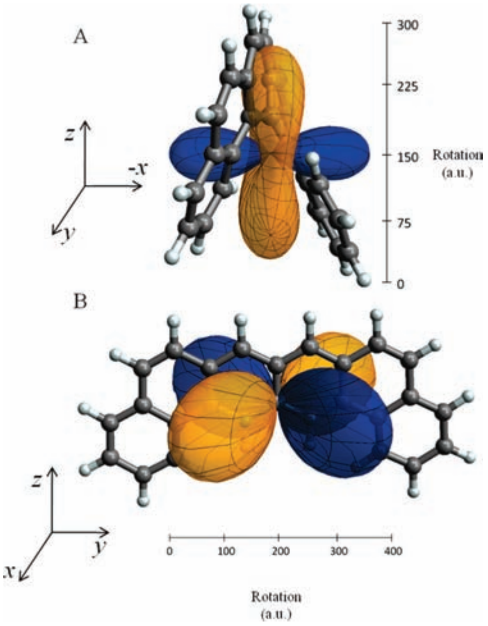

Figure 2. Comparison of representation surfaces of OR tensors for (A) $\mathbf{6}_{\mathbf{H}}$ and (B) $\mathbf{6}_{\mathbf{A}}$ in au (bohr^4/molecule). Blue (yellow) = dextrorotation (levorotation).

The results of this study, summarized in Table 1, confirm along with quantum chemistry what has been established already for metamaterials and interpreted wholly within the realm of classical mechanics. Arrays of C_{2v} shaped split-ring resonators rotate linearly polarized microwaves with dextrorotation or levorotation, depending on the direction in which the array is tilted from normal incidence.[37] The hydrocarbons here are behaving analogously—not exactly like simple wires, but nearly so.

As a control, we also computed the OR of C_{2v} picene named $\mathbf{5}_{\mathbf{M}}$ because it is M-shaped not ∩-shaped. The significantly smaller arc angle in $\mathbf{5}_{\mathbf{M}}$ limits the circulation of charge. As expected, its maximum |OR| is smaller than in any principal direction of its helicene isomer, $\mathbf{5}_{\mathbf{H}}$. Naturally, in the limit of an infinite number of rings in the zigzag phene series of which phenanthrene (**3**) and $\mathbf{5}_{\mathbf{M}}$ are the first two members with C_{2v} symmetry,[38] the OR must approach zero.

The road to experimental confirmation of the predictions herein is hard. There are no crystal structures of any of the compounds in the **5**, **6**, and **7** series. Moreover, they would have to crystallize in a space group with an optically active point group whether enantiomorphous or nonenantiomorphous in order to extract any information about OR. **3** is the smallest member of the series of C_{2v} ∩-shaped PAHs. Not surprisingly, because it is comparatively diminutive, its OR is modest (Table 1). However, it is cheap and crystallizes in the optically active space group $P2_1$.[39] As such, its OR in principle can be measured and the results compared with computation. Unfortunately, the linear birefringence of **3** is enormous (0.372 at 546 nm)[40] and likely to overwhelm the OR. Also, the arrangement of the molecules in the crystal necessitates considerable averaging of OR in the unit cell as the screw axis exchanges dextrorotatory and levorotatory directions of molecules. Strikes aside, we have nevertheless engaged these measurements via Mueller matrix polarimetry.[41]

During the past several years we have aspired to reframe sophomore chiroptical pedagogy. Toward this end, we measured the OR of achiral crystals composed of a simple tetrahedral carbon compound (pentaerythritol, $C(CH_2OH)_4$) with four identical, astereogenic substituents.[42] We also computed the OR of one oriented H_2O molecule whose intuitive electronic structure facilitates interpretation.[43] The symmetries of achiral molecules simplify the semiquantitative analysis of optical activity and assist the realization of the centuries-old ambition of judging optical activity from molecular geometry alone.[44] Here, we showed that planar hydrocarbons are fitting subjects for chiroptical analyses. The only requirement for the study of the OR of optically active, achiral molecules is that they cannot be randomly oriented.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Complete ref 13, Cartesian coordinates for all structures, and chiroptical output including optical rotation, electric dipole−magnetic dipole, and electric dipole−electric quadrupole polarizabilities. This material is available free of charge via the Internet at http://pubs.acs.org.

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