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Optical Rotation of Achiral Pentaerythritol

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We report the optical rotatory power of pentaerythritol (PE, C(CH₂OH)₄), a carbon compound with tetrahedral coordination whose four hydroxymethylene groups are both chemically equivalent and related to one another by a symmetry operation of the second kind in the achiral point group *S*₄ ($\bar{4}$). While the optical rotation of an achiral molecule or ensemble of molecules may be counterintuitive to some,¹ it was predicted by Gibbs for the point groups *S*₄ and *D*_{2d} ($\bar{4}2m$),² and demonstrated by Hobden with crystalline AgGaS₂ and CdGa₂S₄.³

Symmetry arguments mandate that PE in the space group $\bar{I}4\bar{4}$ should be optically rotatory for some incident directions of linearly polarized light. This fact notwithstanding, the measurement of the optical rotatory power of a carbon compound with a tetrahedral atom having identical ligands is offered here, not only for its pedagogical value but also for the following reasons: (1) PE is the simplest organic crystal, with only three independent non-hydrogen atoms, for which the complete OR rotation tensor has been determined, and it is the only achiral molecular crystal so analyzed;⁵ (2) PE molecules have the full site symmetry of the crystallographic point group, and thus the crystal tensor may be analyzed as a simple sum of its molecular contributions; (3) The comparatively simple molecular and electronic structure of PE is amenable to the quantum mechanical analysis⁶ of its chiroptical properties.

It took 85 years between Gibbs's conjecture and Hobden's confirmation of the optical rotatory power of achiral crystals because of the difficulty in measuring OR in anisotropic media.⁷ As linear birefringence (LB) is often 10³ times larger than OR, great effort has been directed toward eliminating systematic errors in polarimetric experiments that obscure the minor chiroptical perturbations to the state of polarization. Hobden only succeeded by taking advantage of accidental equivalences of refractive indices at particular temperatures and wavelengths, rendering the crystal non-birefringent along low-symmetry directions.³ A general strategy for overcoming LB called HAUP (high-accuracy universal polarimetry) was first introduced by Kobayashi et al.⁸ and later refined by Kaminsky and Glazer.⁹ The latter's so-called "tilter" polarimeter that is utilized herein measures the intensity of light passing through a variable-angle linear polarizer and linear analyzer between which sits the sample that rotates on an axle *t* perpendicular to the wave vector of the light, *k*.

A tetragonal prism of PE measuring 2.9 × 2.4 × 0.4 cm³, was provided by S. Hausühl (Cologne). The crystal was sectioned into ~0.5-cm sided cubes with a wire saw wetted with water. Pieces from a {101} growth sector were cleaved parallel to (001) into 0.5–0.7 mm thick plates. The samples were mounted in the polarimeter on a calibrated, rotating wheel so that [001] was parallel with the rotation axis. Intensity measurements were made with 670

nm diode laser light in intervals of 5° as the sample was rotated by 360° about [001]. For each azimuthal angle *θ* the crystal was also tilted by ±30° in 0.5° intervals around *t* (inset Figure 1). At each of these positions, the angles of the polarizer and analyzer were varied by ±2°. ¹⁰

Linearly polarized light traversing a birefringent sample becomes elliptically polarized, with the semi-axes of the ellipse rotated from the azimuth by the angle *ρ*. This angle depends on the intrinsic OR of the sample *ρ*₀ by the proportionality constant (sin*δ*)/*δ*. Here, *δ*, the phase factor, is equal to 2π*LΔn*/λ, where *L* is the optical path length, λ is the wavelength, and Δ*n* is the LB. A tilt about *t* introduces an angle between *k* and the sample, leading to a characteristic modulation of the signal for progressive tilt angles (Figure 1). The interdependent quantities *ρ* and *δ* are found from a nonlinear least-squares fit of the intensity to the various contributing trigonometric terms.^{7–9} Fits of the data such as the representative set of tilts in Figure 1 give one of the points in the curve in Figure 2. The OR tensor is established from the ensemble.

For a crystal in the space group $\bar{I}4\bar{4}$, the only OR parameters are a magnitude and orientation in the *ab* plane (*ρ*₁₁ = −*ρ*₂₂ and *ρ*₁₂ = *ρ*₂₁); OR must be zero along [001]. The spatial variation of OR (deg/mm) was plotted in Figure 2:

$$\rho_{670\text{nm}}^{293\text{K}} = \begin{bmatrix} -5.9(0.2) & 2.6(0.2) \\ 2.6(0.2) & +5.9(0.2) \end{bmatrix}$$

The OR reached a maximum of −6°/mm when *θ* = 78° (Figure 2). However, until establishing the absolute direction in PE, *ρ*₁₁ and *ρ*₁₂ could just as well have been 5.9°/mm and −2.6°/mm, respectively.

The absolute directions of PE were established from the triplet phases using three-beam diffraction, a method that is independent of anomalous dispersion and well suited to organic compounds.^{11,12} Once a primary reflection *h*(150) was brought into its diffraction position, a secondary reflection *g*(114) was excited by a Ψ-scan about *h*, thereby causing interference between *h* and *g* manifest in reflections ±(*h* − *g*). The sign of the triplet phase Φ₃ = φ(*g*) + φ(*h* − *g*) − φ(*h*) is sensitive to the absolute structure.¹¹ In this way it was determined that [100], referred to the X-ray coordinates specified in the Supporting Information, is levorotatory. Thus, *ρ*₁₁ = −5.9°/mm and *ρ*₁₂ = 2.6°/mm.

We calculated the OR tensor elements of a PE molecule with the X-ray geometry using the linear response method¹³ as embodied in the Dalton molecular electronic structure program.¹⁴ Dalton computes both the electric dipole–magnetic dipole contribution to the rotatory strength as well as the electric dipole–electric quadrupole contribution, which is nonzero for oriented molecules.^{15,16} The expression of the symmetric OR tensor for oriented molecules was derived by Buckingham and Dunn,¹⁷

$$\mathcal{G}_{\alpha\beta} = \frac{1}{2}i \left[G'_{\alpha\beta} + G'_{\beta\alpha} + \frac{1}{3}\omega(\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta} + \epsilon_{\beta\gamma\delta}A_{\gamma\delta\alpha}) \right]$$

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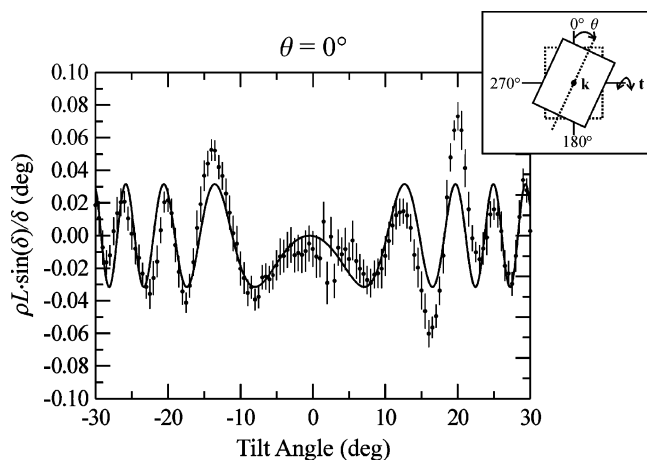


Figure 1. Fit to an OR measurement at 670 nm. ρ is the optical rotation in degrees, L is the sample thickness, and δ is the phase factor ($\delta = 2\pi L\Delta n/\lambda$, where Δn is the birefringence and λ is the wavelength). (Inset) Measurement geometry: θ is the sample rotation angle, k is the wave vector, and t is the tilt axis.

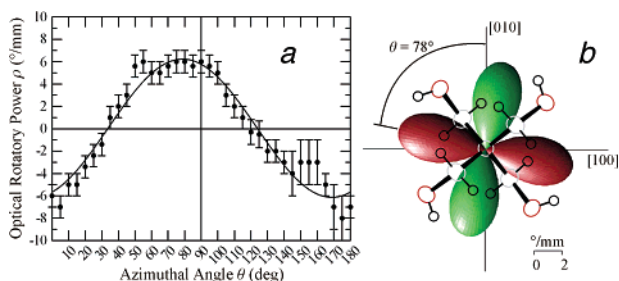


Figure 2. (a) OR (deg/mm) in the ab plane plotted as a function of the azimuthal rotation θ of a PE (001) plate about the wave vector k . Off-axis values obtained by tilting the crystal. (b) Representation surface of OR tensor. Green is dextrorotatory, red, levorotatory.

where G' is the electric dipole–magnetic dipole polarizability, the trace of which contributes to OR in isotropic systems, ω is the light frequency, ϵ is the Levi–Civita operator, and A is the electric dipole–electric quadrupole polarizability, which averages to zero for isotropic media. OR for an oriented system is the sum of the electric dipole–magnetic dipole and the electric dipole–electric quadrupole coupling terms of all excited states of appropriate symmetry with the ground-state wave function. This sum over all states can now be avoided with linear response theory.¹³

We obtained $\rho_{11} = -\rho_{22} = -38^\circ/\text{mm}$ and $\rho_{12} = \rho_{21} = +9^\circ/\text{mm}$ corresponding to a maximum of $-39^\circ/\text{mm}$ at 83° counterclockwise from [010] in the crystallographic basis.¹⁸ Although the quantum tensor (computed at 670 nm) is closely aligned with the measured tensor, it differs in magnitude by a factor of 6.5. Here, the difference between the gas-phase model and crystalline state measurement becomes apparent.¹⁹

If we conceive of the PE molecule in the direction of the maximum absolute values of ρ shown in Figure 3 as two pairs of homochiral helical wires of closely bonded atoms, indicated by the red and green arrows, sharing the central carbon, we would expect the signs of OR both measured and calculated. This interpretation is a gross oversimplification of a sum of contributions from many electronic transitions but nevertheless may prove to be instructive in guiding a qualitative understanding of the orientational dependence of OR that is rooted in quantitative measurements and computations.

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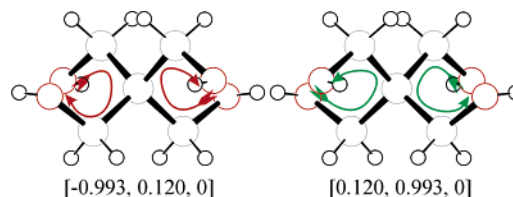


Figure 3. View of PE along most rotatory directions indicated by vectors in brackets. Improper four-fold axis is vertical. Oxygen atoms are red. Left view is levorotatory. Right view is dextrorotatory.

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Supporting Information Available: Coordinates to which the absolute directions in PE are referred, Dalton output for calculated tensor, and three-beam diffraction data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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$$\varphi = A \frac{\delta}{\pi^2 - \delta^2} \sin^2 \left(\frac{\delta - \pi}{2} \right)$$
 where A is a constant amplitude. A signal of this form was first observed in 1996 by W.K. in KH_2PO_4 for samples cut perpendicular to the optic axis. The signal followed the expected tensorial behavior, was independent of light intensity, was dependent on the quality of the surfaces, and is likely related to differential circular reflection. It is the subject of further investigation.
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