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Achiral Chiroptics

Optical Rotation of Achiral Compounds

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circular dichroism · crystallography ·
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Oriented achiral molecules and crystals with D_{2d} symmetry or one of its non-enantiomorphous subgroups, S_4, C_{2v}, or C_s, can rotate the plane of transmitted polarized light incident in a general direction. This well-established fact of crystal optics is contrary to the teaching of optical activity to students of organic chemistry. This Minireview gives an overview of the measurement and calculation of the chiroptical properties of some achiral compounds and crystals. Methane derivatives with four identical ligands related by reflection symmetry are quintessential optically inactive compounds according to the logic of van’t Hoff. Analysis of the optical activity of simple achiral compounds such as H_2O and NH_3 provides general aspects of chiroptics that are not readily broached when considering chiral compounds exclusively. We show here, through the use of group theoretical arguments, the transformation properties of tensors, and diagrams, why some achiral, acentric compounds are optically active while others are not.

1. Introduction

Most chemists receive their first lesson on optical rotation (OR) in organic chemistry courses at university. We learn in such settings that the observation of OR is a test for the chirality of molecules in isotropic liquid phases. A corollary of this lesson, sometimes stated explicitly, is that enantiomorphism is a necessary condition for OR. The organic chemistry textbook that one of the authors (B.K.) used as a student states that “the same non-superimposability of mirror images that gives rise to enantiomerism also is responsible for optical activity.”[1] Unfortunately, the link between optical activity and enantiomorphism is not only introduced early and reinforced relentlessly in a chemist’s education, it is wrong. [2]

It is well-known to some that oriented systems belonging to some non-enantiomorphous point groups will indeed be optically active for some directions of incident light, but this fact, albeit qualified, has failed to make substantive inroads in the science of molecular chirality, despite the articulate lessons of Barron,[3] O’Loane,[4] and Hansen,[5] among others.[6,7]

Here, we give an overview of the natural chiroptical properties of achiral crystals revealed by polarimetry, and of achiral molecules predicted by computation. By including achiral molecules and crystals, we broaden the number and kinds of systems in which we can study the vexing phenomenon of OR. Particularly instructive are the structure–chiroptics relationships of simple achiral compounds.

The prejudicial link between optical activity and enantiomorphism is inherited from Pasteur, who recognized that only chiral compounds are optically active in solution. Sohncke mistakenly extended this association between optical activity and enantiomorphism to crystals.[8] Optical rotation of non-enantiomorphous crystals with the point groups D_{2d} ($\bar{4}2m$) and S_4 ($\bar{4}$) was first predicted by Gibbs.[9] He imagined a crystal composed of helices and recognized that “… if the axes of the right-handed molecules are parallel to the axis of X, and those of the left-handed molecules to the axis of Y, their effects would counterbalance one another when the wave-normal is parallel to the axis of Z. But when the … beam of linearly polarized light … is parallel to the axis of X, the left-handed molecules would produce a left-handed (negative) rotation of the plane of polarization, the right-handed molecules having no effect; and when the wave-normal is parallel to the axis of Y, the reverse would be the case.” In other words, incident light may encounter enantiomorphous paths with opposite activity along different directions within the same material. Achiral molecules and crystals can have

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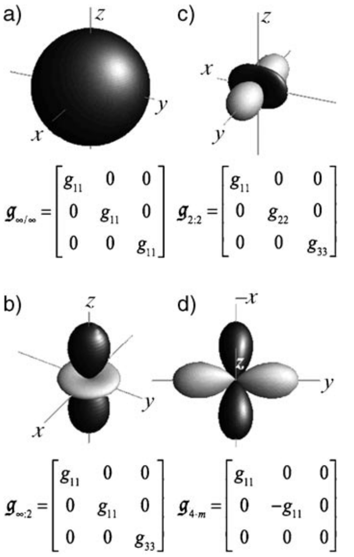
chiral directions in precisely the same way that apolar molecules and crystals can have polar directions.[10] Nevertheless, distinguished scientists such as van't Hoff[11] and Lowry[12] both state that neither optically rotatory molecules nor crystals can be mirror-symmetric.

Pockels showed, by applying the symmetry operations for C_{2v} ($mm2$) and C_s (m) as the transformation matrices in the definition of a second rank axial tensor (see appendix), that these cyclic point groups join D_{2d} ($\bar{4}2m$) and S_4 ($\bar{4}$) among those that are optically active.[13] Thus, among the acentric, non-enantiomorphous point groups, D_{2d} ($\bar{4}2m$) and its achiral subgroups are compatible with optical activity.[14]

The most general condition[15] for OR is therefore not enantiomorphism, but non-centrosymmetry. However, although necessary, non-centrosymmetry is not a sufficient condition. The groups T_d ($\bar{4}3m$), C_{3h} ($\bar{6}m$), and D_{3h} ($\bar{6}m2$), for example, are acentric but optically inactive. Likewise, the polar, achiral groups C_{nv} where $n > 2$ are inactive.[16]



$$\boldsymbol{g}_{\infty/\infty} = \begin{bmatrix} g_{11} & 0 & 0 \\ 0 & g_{11} & 0 \\ 0 & 0 & g_{11} \end{bmatrix} \quad \boldsymbol{g}_{2:2} = \begin{bmatrix} g_{11} & 0 & 0 \\ 0 & g_{22} & 0 \\ 0 & 0 & g_{33} \end{bmatrix}$$

$$\boldsymbol{g}_{\infty:2} = \begin{bmatrix} g_{11} & 0 & 0 \\ 0 & g_{11} & 0 \\ 0 & 0 & g_{33} \end{bmatrix} \quad \boldsymbol{g}_{4\cdot m} = \begin{bmatrix} g_{11} & 0 & 0 \\ 0 & -g_{11} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Figure 1. Representation surfaces of four canonical optical rotation tensors. d) Rotatory response of the non-enantiomorphous, optically active crystals. Light and dark surfaces indicate opposing signs of the effect.

2. Optical Rotation Tensors

Optical rotation (also circular dichroism) is described by a second rank, axial tensor (***g***) embodied in one of four canonical forms illustrated in Figure 1. These tensors correspond to the symmetry groups K, D_∞, D_2, and D_{2d} in the Shoenflies notation, which is adhered to from hereon for convenience (The corresponding symbols in the international notation are ∞/∞, ∞:2, 2:2, and $\bar{4}m$, Figure 1);[17,18] ***g*** relates the rotational strength to the coordinate axes of the molecule or crystal and to the direction of light propagation with respect to that coordinate system. The first three tensors (Figure 1 a–c) describe the OR of the pure rotational groups without mirror symmetry: polyhedral point groups (I, O, and T), dihedral and cyclic point groups with rotation axes greater than two ($D_{n>2}$ and $C_{n>2}$, where n is an integer), and those with twofold axes (D_2, C_2) or no symmetry elements (C_1). The representation surfaces indicate the strength of OR as a function of direction.

The optically rotatory non-enantiomorphous groups are associated with the fourth canonical tensor (Figure 1 d) that has two axes with equal and opposite rotations. The trace of this last tensor disappears, which is consistent with the observation that the orientationally averaged optical activity

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for a collection of molecules described by this tensor will be zero. As chiroptical measurements are made almost exclusively on orientationally averaged systems,[19] the activity of achiral compounds or crystals is very rarely manifest.[20] Consequently, an infelicitous linkage has grown between the science of molecular chirality and measurement of chiroptic properties. The latter term gives evidence that this false association has invaded language, thereby perpetuating confusion; crystal physicists prefer the more phenomenological noun gyrotropy to the judgmental chiroptics.

A deeper understanding of OR necessitates moving beyond averages. This can be accomplished with measurements of organized media of arbitrary symmetry in which the wave vector can be specified with respect to a molecular coordinate system. Unfortunately, measurements of OR tensors of linearly birefringent media are far more challenging than measurements of specific rotations of isotropic fluids. In Section 4, we discuss the difficulties with such measurements that have hampered the study of the chiroptical properties of achiral media. The OR of achiral compounds is most easily approached computationally, especially with the dramatic advances in the ab initio computation of OR and electronic circular dichroism (ECD) in the past decade.[21]

3. Coupling of Transition Moments

Theoretical specific rotations of chiral compounds are routinely obtained from the trace of computed ***g*** tensors. The trace or average value of the tensor is the only quantity that can be profitably compared with solution measurements of specific rotations or the signs of the Cotton effect. To involve traceless, mirror-symmetric substances in the discussions of OR, the orientational dependence of the rotatory response must be explicitly considered.

Rosenfeld recognized as early as 1928 that the OR tensor for chiral, fluid phases could be calculated as the coupling of the transition electric dipoles and transition magnetic dipoles summed over all the electronic excitations.[22] For an oriented molecule, we must also add the coupling of transition electric dipoles with transition electric quadrupoles. This interaction averages to zero in solution because, for a quadrupole fixed in the xy plane, the interactions of the radiation field with light polarized along the x and y axis have opposite signs; the intensities are zero for light polarized along z.[23] Buckingham and Dunn derived a summation of the terms involving transition magnetic dipole and electric quadrupole moments [Eq. (1)].[24]

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

The OR polarizability tensors $G'_{\alpha\beta}$ [Eq. (2)] and $A_{\alpha\beta\gamma}$[25] [Eq. (3)] are defined as the coupling of transition moments summed over all possible excited states, where μ, m, and Θ are the electric dipole, magnetic dipole, and electric quadrupole[26] operators, respectively.

$$G'_{\alpha\beta} = -2\,\omega \sum_n \mathrm{Im}\frac{\langle\Psi_0|\mu_\alpha|\Psi_n\rangle\langle\Psi_n|m_\beta|\Psi_0\rangle}{\omega^2_{n0}-\omega^2} \qquad (2)$$

$$A_{\alpha\beta\gamma} = 2\sum_n \omega_{n0}\mathrm{Re}\frac{\langle\Psi_0|\mu_\alpha|\Psi_n\rangle\langle\Psi_n|\Theta_{\beta\gamma}|\Psi_0\rangle}{\omega^2_{n0}-\omega^2} \qquad (3)$$

Values of the mixed polarizability tensor elements can be found by using the linear response method[27] embodied in widely available electronic structure programs[28] that circumvent the explicit sum-over-states calculation.[27] In this method the wave functions of the excited states are not explicitly computed. Instead, the poles of the frequency-dependent polarizability are used to determine the electronic energetics.

The sum-over-states can also be avoided by focussing on one excitation. The pioneering quantum mechanical computation of the chiroptical properties of an achiral compound were carried out by Hansen and Bak.[29] They analyzed the response of the lowest π–π* transition of B_2 symmetry in 1,3-butadiene (C_{2v}).

For any one state, the analysis of the rotatory response is straightforward. A sense of the rotatory strength tensor—the tensor governing ECD—for butadiene can be simply obtained by using orbital interaction diagrams, with which all chemists are familiar (Figure 2). Following the qualitative molecular orbital analysis by Snatzke,[30] contributions to OR can be calculated in terms of the moments generated from redistribution of charge in the molecule by orbital overlap between states. Accordingly, the pictorial "product" of the π and π* orbitals of butadiene gives rise to overlap that can be used to establish regions of charge build-up and depletion. These give a net transition electric dipole moment along the y axis and a circulation of charge in the yz plane; the latter

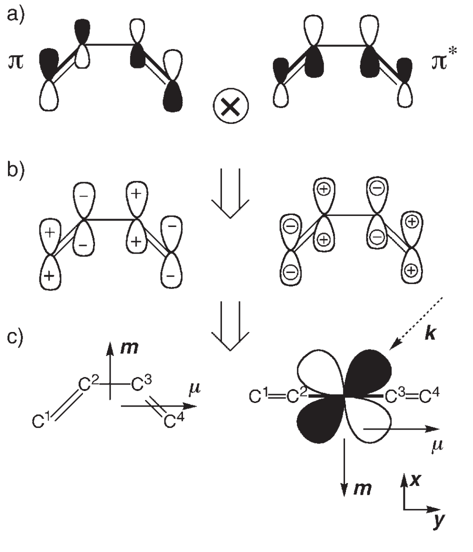


Figure 2. Analysis of the optical rotatory power of the B_2 transition (π→π*) in 1,3-butadiene. a) Schematic representation of the π molecular orbitals. b) Interaction of the orbitals leads to overlap (left) with an associated build-up and depletion of charge density (right). c) Electric and magnetic dipole transition moments as well as the representation surface (right) of OR viewed along the twofold axis with respect to wave vector k. Black (white) is negative (positive). The quadrupole moment is not shown.[29,30]

defines both a transition magnetic dipole moment and an electric quadrupole moment.

In a chiral molecule, transitions occur in which μ and m have components that are parallel or antiparallel: $\mu \cdot m \neq 0$. Parallel moments give rise to clockwise rotation of the electric field (dextrorotation) when viewing the light source, while antiparallel moments lead to anticlockwise rotation (levorotation). In an achiral system, the scalar product of μ and m can be zero. The rotatory response can then only be comprehended by including the role of the wave vector. Although μ and m, generated as described in butadiene, are orthogonal, they make parallel and antiparallel projections onto the wave front for wave vectors that bisect the molecular mirror planes (Figure 2).

Generally speaking, because achiral molecules have fewer unique tensor elements than chiral molecules, theoretical calculations can more clearly focus on trends that relate the calculated property to the electronic structure of the molecule. Kongsted et al. studied the effects of solvent on the rotatory strength tensors of formaldehyde (C_{2v} symmetry) at the coupled cluster level of theory.[31] Since there is only one tensor element, it was comparatively easy to evaluate basis-set effects, variance in electron correlation, and the influence of solvent. Even simpler than formaldehyde is H_2O.

3.1. Example—Water (C_{2v})

In an effort to give the easiest, yet faithful explanation of OR on the basis of molecular electronic structure, ab initio computations of the OR tensor of a single oriented water molecule were carried out.[32] H_2O lends itself to an intuitive understanding because its qualitative wave functions can be easily visualized. An overly simple way to appreciate the origin of OR in water is as such: the three atoms in H_2O define a plane. Viewed obliquely, they trace a helix; mirror-related wave vectors propagate along heterochiral helices. The electric dipole and magnetic dipole transition moments for a C_s- or C_{2v}-symmetric molecule are along the mirror planes (σ and σ') and are perpendicular to one another. Light incident along these mirror planes experiences zero OR. Light incident between the mirror planes, however, experiences the projections of the transition moments on the wave front as parallel or antiparallel. It is this projection, and thus the direction of the incident light, that governs the sign and magnitude of the OR. There is a single unique element $g_{12} = g_{21}$ for C_{2v}-symmetric molecules (Figure 1 d) that fixes the tensor between the molecular symmetry axes (Figure 3 a).

Figure 3 a shows the $1B_2$ transition moments of H_2O. For light incident along $[x,y]$ or $[-x,-y]$, positive OR will be detected as indicated by the white surface along the line of sight. A negative OR of equal magnitude (black surface) will be detected for light incident in the $[x,-y]$ or $[-x,y]$ quadrants.

The transition moments for the prototypical chiral right-handed hexahelicene molecule (Figure 3 b) are parallel for most directions of incident light, which causes a large positive OR when the tensor is averaged over all orientations. As indicated by the small dark disk around the large white lobes of the OR tensor surface, light incident from in-plane directions experiences negative OR from an oriented, right-handed helicene.

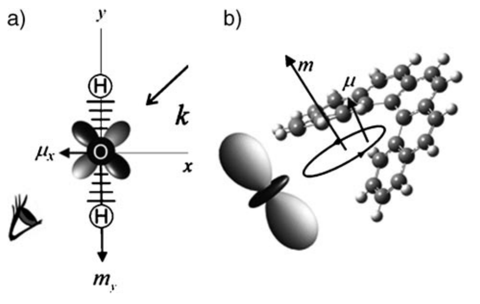


Figure 3. Comparison of the wave-vector-dependent OR for a B_2 transition of an oriented H_2O molecule with the overall response of (+)-[*P*]-hexahelicene. Black (white) is negative (positive) in the representation surfaces. a) The observer sees a positive rotation for a wave vector (k) incident upon H_2O from direction $[x,y]$. μ and m are projected onto the wave vector in parallel. After reflecting the wave vector across the x or y axis, the moments become antiparallel in projection. b) For most directions, μ and m are parallel when projected onto the wave vectors. Thus, the average rotation in solution is large.

The full OR tensor can be understood by examining the coupling of the transition moments in the polarizability summations. The water molecule is small enough that the OR can be built-up state by state with a modest basis set.[32,33] Needless to say, we are not yet able to measure the optical activity of a single oriented water molecule, but given advances in single-molecule spectroscopy, we may be getting close.[34]

Of the 12 oriented water (ice) phases, only the ordered phase of ordinary hexagonal ice (ice XI: space group $Cmc2_1$, point symmetry C_{2v}) has a symmetry compatible with OR.[35] This phase can be crystallized at 70 K. We aim to measure the OR of ice XI by making use of recent advances in chiroptical imaging.[36]

3.2. Counterexample—Ammonia (C_{3v})

H_2O (C_{2v}) is optically active, but NH_3 (C_{3v}) is not. The reason for this distinction is not obvious. The relative disposition of transition moments of a transition with E symmetry in a C_{3v}-symmetric molecule is very similar to that for B-symmetry transitions of a C_{2v}-symmetric molecule. In both kinds of excitations, electric dipole and magnetic dipole transition moments are orthogonal.

The degeneracy of the E transitions, however, creates simultaneous parallel and antiparallel projections onto the wave vector (Figure 4). An E transition may induce OR, but the degenerate transition will induce an equal and opposite response, even when viewed in a projection that appears chiral.

The transformation properties of the coordinate axes and their rotations are specified in precisely the same way for the degenerate E transitions of the D_{2d} and C_{3v} character tables. Yet, degenerate E transitions support optical activity for the point group D_{2d}, but not for the C_{3v} point group. Instead of the

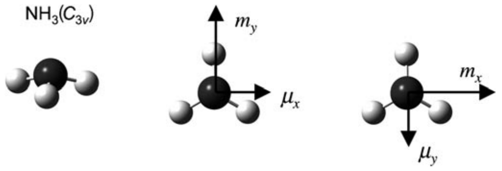


Figure 4. Transition electric and magnetic dipole moments for degenerate *E* transitions of ammonia (C_{3v}).

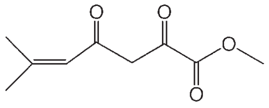
transition moments being perpendicular as they are for C_{3v} molecules, the *E*-symmetry transition electric and magnetic dipole moments in a D_{2d} molecule are parallel along one Cartesian axis and antiparallel along the other, thus creating equal and opposite rotations along these axes. Chiu fully enumerated when and why degenerate states of achiral molecules produce OR.[37]

4. Measurement of Optical Rotation in Achiral Crystals

The effects of OR were evidenced by Arago in 1811 when he passed linearly polarized light along the high-symmetry *c* axis of α-quartz.[38] However, the determination of the anisotropy of the OR of quartz—the complete tensor—by making off-axis measurements was still challenging as late as 1988.[39] This is because linear birefringence ($\Delta n = n_{\parallel} - n_{\perp}$), the ordinary refraction anisotropy for orthogonally polarized rays, is typically three orders of magnitude larger than circular birefringence. The latter condition is a synonym for OR, which expresses the differential refraction of left and right circularly polarized light ($\Delta n = n_L - n_R$). The minor chiroptical perturbation to the polarization state of light in anisotropic media is of the same order of magnitude as parasitic ellipticities from imperfect samples and optical components of the polarimeter. Consequently, we have been handicapped in our ability to make chiroptical measurements in organized systems along directions of low axial (less than threefold) symmetry, where $n_{\parallel} \neq n_{\perp}$. Such measurements had to await advances in polarimetry in the 1980s (see Section 4.2).

4.1. False Start

The first purported evidence of optical activity from an achiral crystal comes from Sommerfeldt, who attributed an anomalous image of crystals made from **1** in conoscopic illumination to the effects of OR. The formula was given as a dimer of **1**, $(C_9H_{12}O_4)_2$, by Federlin,[40] possibly a photodimer as the material was exposed to sunlight. The crystals ostensibly belonged to class C_s on the basis of their morphology.[41] Sommerfeldt's discovery may have been important, but there can be many reasons for strange conoscopic figures.[42,43] Voigt asserted that OR could not have been observed in this case because the optic axes—those directions lacking linear birefringence and thus permitting evidence of OR—were in the plane of symmetry.[44] If the optic axes were perpendicular to the plane of symmetry, then Sommerfeldt could in principle have observed dextrorotation along one optic axis and levorotation along the other.



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This episode amounts to little in light of the report by Rogers that Sommerfeldt's crystals exhibited polysynthetic twinning—thus accounting for the strange conoscopic figure—and that they were centrosymmetric.[45] Crystals cut and polished perpendicular to the optic axis were shown to be devoid of optical activity.[46] "This example," said Rogers, arguing with the force of experiment and theory, "may therefore be rejected, as it neither exhibits optical activity nor is in class C_s (m)," although it is the latter fact that is decisive, as the measured rotation might have been vanishingly small.[15]

4.2. Inorganic Crystals

The confirmation of Gibbs' conjecture that some achiral crystals can be optically rotatory was not established until 1962.[47] Futama and Pepinsky observed opposing signs of rotation along oppositely handed optic axes in $LiH(SeO_3)_2$, a material genuinely belonging to the class C_s. In this case, the optic axes were bisected by the mirror, not contained in it. Hobden measured the first full tensors for an achiral crystal, $AgGaS_2$ (D_{2d}),[48,49] by taking advantage of accidental equivalences of the refractive indices of the ordinary and extraordinary rays ($n_{\parallel} = n_{\perp}$) at particular temperatures and frequencies for wave vectors normal to the high-symmetry direction; given the fortuitous absence of linear birefringence, the OR was easily measured. In the point group D_{2d} there is only one independent tensor element, thus a single measurement defined the whole tensor. The convenient convergence of refractive indices required for Hobden's clever experiment is unfortunately difficult to obtain. Few comparable systems are known,[50] although Hobden also made measurements of $CdGa_2S_4$ (S_4).[51]

In 1969, Hobden wrote of his work optimistically, "It is hoped that this observation will finally eradicate the notion that optical activity is exclusively related to enantiomorphism."[48a] Alas, 30 years later Hansen and Bak lamented, "it is noteworthy that the fact that certain classes of achiral molecules may exhibit optical rotatory power under anisotropic conditions apparently has not attracted much attention in the community of structural chemists, although the phenomenon is part of the general theory of crystal optics."[52]

To measure OR along a general direction of a crystal, one has to understand how the combination of linear birefringence ($\Delta n = n_{\parallel} - n_{\perp}$) and circular birefringence ($\Delta n = n_L - n_R$) affect the polarization state of light. OR in a linearly birefringent crystal plate induces ellipticity in the eigenmodes of anisotropic crystals. Szivessy and Münster[78] showed that the intensity of light passing through a polarizer, optically active anisotropic sample, and analyzer contains all of the necessary information, in principle, for extracting the ellipticity that can in turn be related to OR. The measurement of OR-modulated ellipticity is a key feature of all methods used for the determination of crystalline OR. However, the implementation of this idea prior to the invention of electrophotometry and stable, high-intensity, narrow bandwidth light sources was impractical. In 1983, Kobayashi and Uesu used photon counting techniques, lasers, and computerized modulation of the polarizer and the analyzer orientations to determine OR in crystals for directions off the optic axes.[79] This so-called high accuracy universal polarimetry (HAUP) method benefitted from the suggestion by Bruhat and Grivet[80] that the critical ellipticity could be derived by fitting intensity as a function of polarimetric angles.

The fitting procedure can be made more robust by modulating the birefringence, either by scanning the wavelength,[81] or by tilting the sample. Wavelength scanning has proved less practical because, in the absence of a costly variable wavelength laser system, dispersion of a broadband light source contributes to a loss of intensity that can only be recovered with time. Tilting, akin to the Maker-fringe approach for deriving the *d* coefficients of frequency doubling materials, is faster.[82]

OR has been measured along birefringent directions in over 20 achiral crystals (listed in Table 1). Except for $NaNO_2$ and $LiH(SeO_3)_2$,where the optic axes were isolated, and for $AgGaS_2$ and $CdGa_2S_4$,in which accidental equivalences were exploited, the materials in Table 1 were measured by the HAUP method or one of its variants. In crystal physics, optical activity of non-enantiomorphous crystals is the rule rather than the exception; the anisotropy of OR in achiral crystals has been investigated more frequently than for chiral crystals.

The optical properties of few crystals have been as thoroughly examined as KH_2PO_4 (KDP) because of its ease of growth and utility in ferroelectric and optical applications.[83] Its chiroptical properties are attractive for study because it has a number of isomorphs to which it can be compared. From Table 2 it is hard to discern firm trends among the family of KDP crystals.[19,84]

Crystals can be particularly tantalizing with respect to the determination of structure–property relations because OR can show sharp discontinuities on either side of phase transitions. KH_2PO_4 shows discontinuities at the ferroelectric phase transition linking the D_{2d} and C_{2v} phases.[85] K_2ZnCl_4 likewise shows a sharp break at the ferroelectric phase transition at 145 K (transition between C_{2v} and C_s phases; Figure 5).[63] From the insets of tensor representations, it is clear that the sign of the rotatory power increases dramatically with decreasing temperature and that the direction-specific sign of the effect changes.

As established in Table 1, the great majority of achiral systems for which we have OR data are crystals. At the present time, the quantum chemical computation of the OR of crystals is impractical. However, OR has been computed classically by implementation of the coupled oscillator model, a concept originating with Born.[86] Any interpretation of the OR of crystals requires a method that can accommodate the necessary long-range interactions and convergence in the computation of periodic structures.

Table 1: Measured optical rotation of achiral crystals.

Formula	Point group	Space group	Ref.
$AgGaS_2$	D_{2d}	$P\bar{4}2_1c$	[48, 49, 53, 54]
$BaMnF_4$	C_{2v}	$A2_1am$	[55]
$Ba_2Si_2TiO_8$	C_{2v}	$P2bm$	[56]
$C(CH_2OH)_4$	S_4	$I\bar{4}$	[57]
$CdGa_2S_4$	S_4	$I\bar{4}$	[51]
$Co_3B_7O_{13}I$	C_{2v}	$Pca2_1$	[58]
CsD_2AsO_4, D/H = 0.6	D_{2d}	$I\bar{4}2d$	[59]
CsH_2AsO_4	D_{2d}	$I\bar{4}2d$	[58]
$CsLiB_6O_{10}$	D_{2d}	$I\bar{4}2d$	[60]
$Cu_3B_7O_{13}Cl$	C_{2v}	$Pna2_1$	[57]
$Fe_3B_7O_{13}I$	C_{2v}	$Pca2_1$	[61]
$Gd_2(MoO_4)_3$	C_{2v}	$Pba2$	[62]
K_2ZnCl_4 (300 K)	C_{2v}	$Pna2_1$	[63]
K_2ZnCl_4 (50 K)	Cs	$A1a1$	[63]
KD_2PO_4	D_{2d}	$I\bar{4}2d$	[58]
KH_2PO_4	D_{2d}	$I\bar{4}2d$	[64–67]
$KTiOPO_4$	C_{2v}	$Pna2_1$	[68]
$LiH(SeO_3)_2$	C_s	Pn	[47]
$NaNO_2$	C_{2v}	$Imm2$	[46]
Na_2ZnGeO_4	C_s	Pn	[69]
$(NH_3(CH_3))_5(Bi_2Br_{11})$	C_{2v}	$Pca2_1$	[70]
$NH_4H_2AsO_4$	D_{2d}	$I\bar{4}2d$	[71]
$NH_4H_2PO_4$	D_{2d}	$I\bar{4}2d$	[59, 72]
$(NH_4)_2SO_4$	C_{2v}	$Pmcn$	[73]
RbH_2PO_4	D_{2d}	$I\bar{4}2d$	[65, 74]
$RbTiOAsO_4$	C_{2v}	$Pna2_1$	[75]
$RbTiOPO_4$	C_{2v}	$Pna2_1$	[76]
$Sn(C_6H_5)_4$	D_{2d}	$I\bar{4}2d$	[77]

Table 2: Optical rotation of the KH_2PO_4 family of crystals.

Crystal (deuterium fraction)	ρ [° mm^{-1}] [a,b] Lwiv[59]	ρ [° mm^{-1}] [c] Oxford
$NH_4H_2AsO_4$		25[71]
CsH_2AsO_4	13.54	14[65]
$CsH(D)_2AsO_4$ (0.60)	8.85	
KH_2PO_4	7.42	10[65]
$KH(D)_2PO_4$ (0.71)	7.24	
$KH(D)_2PO_4$ (0.84)	7.09	
$KH(D)_2PO_4$ (0.93)	7.03	7[65]
RbH_2PO_4	8.87	6[72]
$NH_4H_2PO_4$	3.50	

[a] The [010] direction is dextrorotatory according to conventions.[67] [b] Measured at 633 nm. [c] For a better comparison with the HeNe laser results from Ref. [59], the values were scaled assuming a simple square-wavelength dependency.

In the classical model, valence electrons are regarded as being quasielastically bound to equilibrium positions of atoms. These electrons respond as a harmonically oscillating dipole in the presence of an electric field **E**. The interaction of a crystal composed of an infinite number of unit cells with an applied electromagnetic field is described by adding a phase factor of $\exp(i\mathbf{k}\mathbf{r}_s)$ (where $\mathbf{k} = 2p\mathbf{u}/l$ is the wave vector along the propagation direction **u**) to the dipoles $\mathbf{p}_s$ at the atomic positions *s*. The dipole moment $\mathbf{p}_s{}^l$ at atom *s* in unit cell *l* is then given by Equation (4).

$$\mathbf{p}_s{}^l = \alpha_s \sum_{l's'} \mathbf{E}_{s'}{}^{l'}(\mathbf{r}_{s'}{}^{l'}) \tag{4}$$

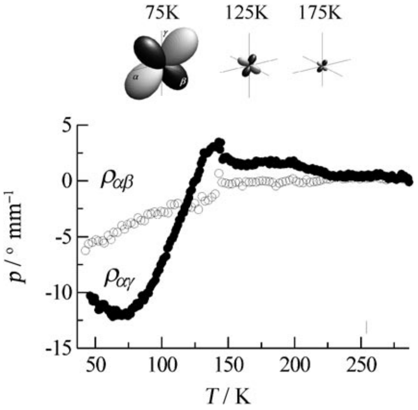

Figure 5. OR tensor elements as a function of temperature in K_2ZnCl_4 as well as the representation surfaces of the tensors. The magnitude and sign changes at the phase transition temperature. The $\rho_{\alpha\gamma}$ element is represented.

Here $\boldsymbol{\alpha}_s$ is the polarizability tensor for atom s and $\mathbf{E}_{s'}^{\,l'}$ is the traveling plane wave generated by all other dipoles at positions $\mathbf{r}_{s'}^{\,l'}$ (Figure 6).

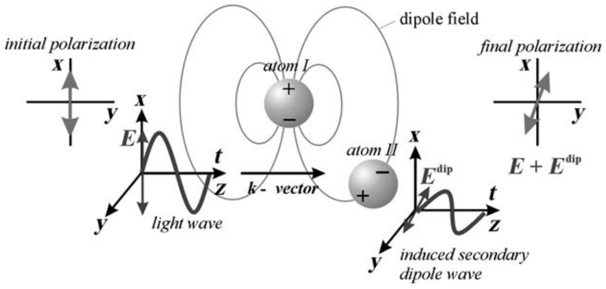

Figure 6. Illustration of the dipole–dipole interaction theory incorporated in the program OPTACT.[88] When an initial wave with polarization *E* passes the first atom at (*x*,0,0) in a Cartesian reference system (light propogation along the *z* direction), a dipole field is created that induces a secondary dipole field in another atom at (0,*y*,*z*). This field oscillates in a direction different from *E* for $y, z \neq 0$. The interference of all induced waves with the initial wave (calculated using an Ewald sum) on passing through the crystal may lead to a rotation of *E*. Reproduced with permission from Ref. [19].

Born realized that the sum of the individual polarizabilities would only give rise to an azimuthally rotated electric field for helical arrangements of interacting, dipolar oscillators. This statement is not incompatible with the rotatory power of water because water is a helix with respect to wave vectors in general directions.

However, the calculation of polarization is not simple for periodic structures and requires Ewald summations. The full calculation was applied by Reijnhart[87] to systems with asymmetric units containing no more than three atoms. In fact, Reijnhart carried out the first OR calculation of an achiral crystal $NaNO_2$.

The classical coupled oscillator model has been incorporated into the program OPTACT by Devarajan and Glazer.[88] After input of the crystal symmetry, unit cell metrics, atom coordinates, and isotropic polarizability volumes α_s for each atom, the OPTACT program returns calculated refractive indices $n^{\alpha/\beta/\gamma}$, anisotropic polarizability volumes, and the optical rotation ρ (° mm^{-1}) along a particular direction.

OPTACT is a tool that researchers have used to evaluate the measured OR of crystals and to establish structure–property relationships. On the basis of the anisotropic polarizability theory of Ramachandran,[89] Glazer and Stadnicka have rationalized the sense of rotation with respect to helical paths of atoms in inorganic crystals.[90] They found that in structures with competing helices, those helices composed of the most strongly polarizable atoms related by the shortest distances and smallest pitch are dominant. Moreover, the sense of rotation follows the helix when the long axis of the polarizability ellipsoids are tangential to the path, whereas the sense of rotation opposes the helix if the largest polarizability is radial to the helix axis.

Calculations and predictions of the KH_2PO_4 family of crystals by employing the dipole–dipole interaction theory and application of the rules outlined by Stadnicka and Glazer, respectively, suggest that OR should decrease with the polarizability of the atoms at the potassium position and should increase with the polarizability at the phosphorus position.[90] Intermolecular interactions are significant as deuteration causes the OR to diminish. However, this effect is considerably stronger in CsH_2AsO_4 than in KH_2PO_4 (Table 2).

The OR of $AgGaS_2$ far from resonance (633 nm) was investigated by using the dipole–dipole interaction model[49] and rationalized on the basis of helical circuits of the most closely bonded, most polarizable atoms. Sulfur atoms are the most polarizable; the inclusion of realistic polarizabilities for Ag^+ and Ga^{3+} made little difference to the result. (Figure 7).[49]

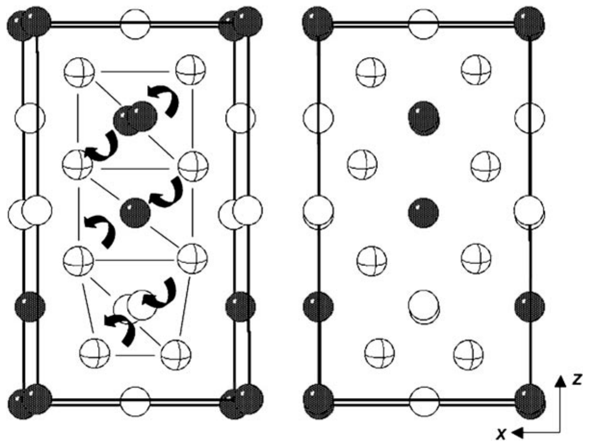

Figure 7. Crystal structure of $AgGaS_2$ (viewed along [010]). Ag ●, Ga ○, S atoms ⊗. Arrows indicate active helices of the S atoms.[49].

4.3. Organic Crystals

4.3.1. Tetraphenylmethane and Isomorphs[57]

Crystals of MPh_4 (M = C, Si, Ge, Sn, or Pb) belong to the tetragonal space group $P\bar{4}2_1c$ in which the molecules sit on the improper fourfold axes. Remarkably, the methane carbon atom in CPh_4 may be replaced with any other Group 14 element, without changing the crystal symmetry.[91] Point symmetry D_{2d} allows only one independent OR tensor element ($g_{11} = -g_{22}$). The OR is of equal magnitude, but of opposite sign along the [100] and [010] directions. This series provides a unique opportunity to explore the variation of OR with the identity of the central atom.

Unfortunately, it is not the {100} but {110} prism faces (perpendicular to optically inactive directions) that are manifest during growth, which complicates the sample preparation required for OR measurements. MPh_4 crystals are very soft, and cut and polished sections never achieved high optical quality. Nevertheless, OR measurements were carried out on $SnPh_4$ crystals by using the tilting method.[82] Although the material is inactive along the optic axis, the OR was assessed at 295 K and 670 nm in plates prepared normal to the optic axis by tilting the crystal into the [100] and [010] directions. The effect amounted to $-300(80)°\,mm^{-1}$ along the [100] direction according to published X-ray coordinates.[92] The error (determined by a least-squares fit), arising from surface roughness, was insurmountably large.

We subsequently applied the dipole–dipole interaction model to the MPh_4 family. The calculated values of OR for homochiral directions with M = C, Si, Ge, Sn, and Pb were +252, +32, −33, −75, and $-40\,°\,mm^{-1}$, respectively (Figure 8). Curiously, the least polarizable derivative (M = C) appears to have the largest OR. This was confirmed semi-quantitatively by polarization microscopy. The possible origin of this trend[93] must be elucidated by quantum chemical analysis.

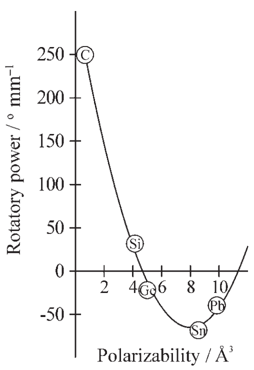

Figure 8. Calculated OR along the [100] direction of MPh_4 crystals at 670 nm as a function of the polarizability of the central atom.

4.3.2. Pentaerythritol[57]

Pentaerythritol ($C(CH_2OH)_4$), like tetraphenylmethane (CPh_4), is a tetrahedral carbon compound with identical substituents. It has four hydroxymethyl substituents that are related to one another by a symmetry operation of the second kind in the point group S_4. The molecules crystallize in the tetragonal space group $I\bar{4}$ and have the full site symmetry of the crystallographic point group. Thus, the crystal tensor may be directly analyzed in terms of its molecular contributions. There are two independent tensor elements, $g_{11} = -g_{22}$ and $g_{12} = g_{21}$, in the point group S_4.

Unlike the group D_{2d}, which governs the physical properties of the tetraphenyl crystals, the maximum values of OR for an S_4-symmetric crystal are not constrained by symmetry to coincide with the principal axes of the crystal, but are offset in the *ab* plane. Multiple measurements at small intervals were therefore required to fix the orientation of the tensor in the plane perpendicular to the optic axis. Pentaerythritol crystals have the advantage of being easily cleaved in the *ab* plane to yield transparent sample slices without further preparation. However, correlating the sign of the OR to metrically degenerate axes of the crystal is complicated by the lack of a heavy atom sufficiently sensitive to the anomalous dispersion of X-ray radiation used routinely for the determination of small-molecule structures. The assignment was ultimately established by using the multiple beam interference technique.[56]

Optical rotation was measured and analyzed by using the tilting method.[82] A sample was mounted on a calibrated, rotating wheel so that the optic axis of the crystal was parallel to both the rotation axis and the wave vector. In this way, data were collected at discrete intervals (θ) as plates were rotated around the [001] direction. The full tensor was compiled by measuring the OR at each orientation by tilting the crystal into the *bc* or *ac* plane around an axis perpendicular to the direction of the wave vector.

The spatial variation of OR corresponding to the tensor $g_{11} = -g_{22} = -5.9(0.2)\,°\,mm^{-1}$ and $g_{12} = g_{21} = 2.6(0.2)\,°\,mm^{-1}$ is plotted in Figure 9. A maximum of $-6.4(0.2)\,°\,mm^{-1}$ was obtained for an azimuthal angle θ of 78° from the crystallographic axes. Unlike the case of water, a state-by-state analysis was not possible for pentaerythritol.

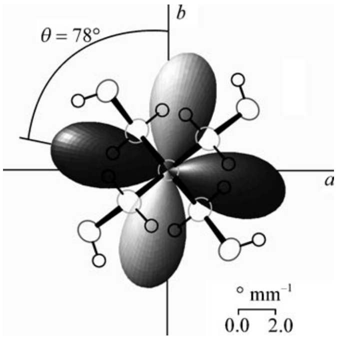

Figure 9. OR power ρ as a function of the azimuthal rotation θ of a pentaerythritol crystal about the wave vector *k* and the corresponding representation surface (black (white): negative (positive)). Reproduced from Ref. [57] with permission from the ACS.

In crystals, OR is a natural consequence of the atomic configuration in the molecules and ions as well as their arrangement in the lattice.[94] We are now faced with parsing the intra and intermolecular contributions to OR. In our publication on pentaerythritol, we reported that the computed rotation for isolated molecules was six times larger than that measured for crystals. In fact, because of an arithmetic error, it is only twice as large.[57]

5. Liquid Crystals

Cholesteric liquid crystals manifest the most spectacular chiroptical responses by virtue of the helical precession of layers whose pitch matches the wavelength of visible light.[95] Naturally, cholesteric liquid crystals have little place in the context of this Minireview that focuses on non-enantiomorphous systems. Nevertheless, any liquid crystal with the symmetry of one of the non-enantiomorphous, optically active point groups should be optically rotatory. Indeed, OR from macroscopically racemic bent-core liquid crystals with C_{2v} symmetry was recently predicted by Hough and Clark.[96] The measurement of this effect is a challenge for the future.[97]

6. Outlook

"Of all the natural phenomena observed in nature", begins Liehr in his massive treatise on the chiroptical properties of metal complexes with three bidentate ligands, "none has had so profound an effect on chemical thought as that of natural optical rotatory power."[98] Irrespective of whether this extraordinary statement is true or not, and forgiving its "natural" redundancies, Liehr surely makes one pause: One is compelled by his claim to conjure up counterexamples. Combustion has probably done more for chemistry than OR, yet qualitative observations of the latter surely have been of great influence in the development of structural chemistry. Still, the orientational dependence of OR in molecules and crystals, an essential aspect of any quantitative understanding, has resisted measurement and computation for many generations. At the same time, an entire subset of optically active compounds, the achiral compounds, has been comparatively neglected. By embracing achiral triatomic species, our understanding of OR is sure to grow because it is these compounds that are far and away the easiest to parse state by state. Combined with advances in both the measurement and computation of chiroptical properties of oriented systems in the past decade, there is finally cause for optimism regarding our comprehension of structure/chiroptical property relationships.

Appendix: What's So Special About D_{2d} and its Non-Enantiomorphous Subgroups?

We are frequently asked, "Why can achiral molecules or crystals with S_4 symmetry such as pentaerythritol be optically active but not those with, say, C_{4v} symmetry?" Why C_{2v} but not C_{3v} symmetry, as in the distinction between H_2O and NH_3 described in Section 3? One can choose an achiral, acentric molecule and falsify the possibility of OR as was done for NH_3 in Section 3.2. A general answer requires an analysis of the way that symmetry operations behave under the transformation rules of the tensors describing OR.

Tensors must be equivalent in all orthogonal reference frames. This requirement is expressed as the invariance to a coordinate transformation. Thus, axes of unit length (u_1, u_2, u_3) can be transformed into another set of axes (u_1', u_2', u_3') with a common origin by a 3×3 direction cosine matrix l_{ij}. Accordingly, polar tensors (T_{ij}) of second rank, denoted by the superscript p, must have the transformation properties give by Equation (5). The definition of axial tensors in Equation (6) must include the determinant of the transformation matrix to accommodate a change in sign upon inversion of the reference frame, where the superscript a denotes an axial tensor.

$$T_{ij}^{p'} = \sum_{k,l=1}^{3} l_{ik} l_{jl} T_{kl}^{p} \quad (i,j = 1,2,3) \tag{5}$$

$$T_{ij}^{a'} = \det|l_{ij}| \sum_{k,l=1}^{3} l_{ik} l_{jl} T_{kl}^{p} \quad (i,j = 1,2,3) \tag{6}$$

By using the symmetry operations as the transformation matrices in the definition of a tensor, the nonzero tensor elements for each crystal class may be deduced. The presence of an inversion center in crystals is the most important symmetry to be considered since it governs the existence of polar and axial tensors of various rank.

The inversion operation ($l_{ij} = [-1\ 0\ 0,\ 0\ -1\ 0,\ 0\ 0\ -1]$) gives elements for polar p and axial a second rank tensors T_{ij} as shown in Equation (7), where the expression for the T_{11} element is derived explicitly.

$$\begin{array}{ll}
T_{ij}^{p'} = l_{ik} l_{jl} T_{kl} & \\
T_{11}^{p'} = & l_{11} l_{11} T_{11} + l_{12} l_{11} T_{21} + l_{13} l_{11} T_{31} \\
 & + l_{11} l_{12} T_{12} + l_{12} l_{12} T_{12} + l_{13} l_{12} T_{32} \\
 & + l_{11} l_{13} T_{13} + l_{12} l_{13} T_{23} + l_{13} l_{13} T_{33} \\
= & l_{11} l_{11} T_{11} = (-1)(-1) T_{11} \\
= & T_{11}^{p} \\
 & \vdots \\
T_{ij}^{a'} = \det(l_{ij}) l_{ik} l_{jl} T_{kl} & \\
T_{11}^{a'} = & -1(l_{11} l_{11} T_{11}) = (-1)(-1)(-1) T_{11} \\
 & = -\mathrm{T}_{11}^{a}
\end{array} \tag{7}$$

Here, the Einstein convention is invoked (where the summation over 1, 2, 3 is implied by the repeated indices). When the exercise is extended to each element in the matrix, only those persist for which $T_{ij}' = T_{ij}$, according to the definition of a tensor. $T_{ij}' = -T_{ij}$ is satisfied only if both elements are zero. Accordingly, neither polar tensorial properties of odd rank nor axial tensorial properties of even rank exist for crystals with inversion symmetry.

Following the procedure outlined above, determinations of the elements present for second-rank axial tensors in non-centrosymmetric materials with C_{2v} and C_{4v} symmetry are provided. The point group C_{2v} has three symmetry elements besides the identity (E): a twofold rotation axis parallel to the z direction (C_2), a mirror in the xz plane ($\sigma_v(xz)$), and a mirror in the yz plane ($\sigma_v'(yz)$). The twofold rotation $l_{ij}(C_2) = [-1\,0\,0,\ 0\ -1\ 0,\ 0\ 0\ 1]$ with $\det(l_{ij}) = +1$ around the z axis converts x into $-x$ and y into $-y$.

The nonzero tensor elements generated by the twofold rotation around the z axis must contain products of the diagonal terms only. Furthermore, combinations of the $l_{11}l_{33}$ and $l_{22}l_{33}$ terms give elements (T_{13}, T_{23}, T_{31}, T_{32}) of the type given in Equation (8). The tensor elements allowed for a twofold rotation around the z axis are shown explicitly in Equation (9).

$$T_{ij}{}^{a'} = -T_{ij}{}^{a'} = 0 \tag{8}$$

$$\begin{aligned}
T_{11}{}^{a'} &= (+1)[l_{11}l_{11}T_{11}{}^{a}] = (+1)[(-1)(-1)T_{11}{}^{a}] = T_{11}{}^{a}\\
T_{22}{}^{a'} &= (+1)[l_{22}l_{22}T_{22}{}^{a}] = (+1)[(-1)(-1)T_{22}{}^{a}] = T_{22}{}^{a}\\
T_{33}{}^{a'} &= (+1)[l_{33}l_{33}T_{33}{}^{a}] = (+1)[(+1)(+1)T_{33}{}^{a}] = T_{33}{}^{a}\\
T_{12}{}^{a'} &= (+1)[l_{11}l_{12}T_{12}{}^{a}] = (+1)[(-1)(-1)T_{12}{}^{a}] = T_{12}{}^{a}\\
T_{21}{}^{a'} &= (+1)[l_{22}l_{11}T_{21}{}^{a}] = (+1)[(-1)(-1)T_{21}{}^{a}] = T_{21}{}^{a}
\end{aligned} \tag{9}$$

A mirror in the xz plane converts y into $-y$ according to the transformation matrix $l_{ij}(\sigma_v(xz)) = [1\ 0\ 0,\ 0\ -1\ 0,\ 0\ 0\ 1]$ with $\det(l_{ij}) = -1$. By similar computation, the only elements that can be nonzero are T_{12}, T_{21}, T_{23}, and T_{32}. Tensor elements allowed for a mirror in the xy plane are T_{12}, T_{21}, T_{13}, and T_{31}. The only elements of a second-rank axial tensor that are allowed for all symmetry operations within the point group C_{2v} are T_{12} and T_{21}.

In addition to the symmetry elements in C_{2v} (E, C_2, and σ_v), the point group C_{4v} also possesses a fourfold rotation axis around the z direction (C_4) and mirrors along the body diagonals (σ_d). A (counterclockwise) fourfold rotation around z transforms x into y and y into $-x$, as expressed by the matrix $l_{ij}(C_4(xz)) = [0\ 1\ 0,\ -1\ 0\ 0,\ 0\ 0\ 1]$ with $\det(l_{ij}) = +1$.

Since it has already been established that T_{12} and T_{21} are the only elements that persist for the symmetry operations explored above, they will be the only ones evaluated explicitly for the remaining two symmetry operations. The general expressions for the existence of tensor elements T_{12} and T_{21} are given in Equations (10) and (11). Transforming the elements T_{12} and T_{21} by a fourfold rotation around z, gives the relationships shown in Equation (12).

$$\begin{aligned}
T_{12}{}^{a'} = \det(l_{ij})[&l_{11}l_{21}T_{11}{}^{a} + l_{11}l_{22}T_{12}{}^{a} + l_{11}l_{23}T_{13}{}^{a} +\\
&l_{12}l_{21}T_{21}{}^{a} + l_{12}l_{22}T_{22}{}^{a} + l_{12}l_{23}T_{23}{}^{a} +\\
&l_{13}l_{21}T_{31}{}^{a} + l_{13}l_{22}T_{32}{}^{a} + l_{13}l_{23}T_{33}{}^{a}]
\end{aligned} \tag{10}$$

$$\begin{aligned}
T_{21}{}^{a'} = \det(l_{ij})[&l_{21}l_{11}T_{11}{}^{a} + l_{21}l_{12}T_{12}{}^{a} + l_{21}l_{11}T_{13}{}^{a} +\\
&l_{22}l_{11}T_{21}{}^{a} + l_{22}l_{12}T_{22}{}^{a} + l_{22}l_{13}T_{23}{}^{a} +\\
&l_{23}l_{11}T_{31}{}^{a} + l_{23}l_{12}T_{32}{}^{a} + l_{23}l_{11}T_{33}{}^{a}]
\end{aligned} \tag{11}$$

$$\begin{aligned}
T_{12}{}^{a'} &= (+1)[l_{12}l_{21}T_{21}{}^{a}] = (+1)[(+1)(-1)T_{21}{}^{a}] = -T_{21}{}^{a}\\
T_{21}{}^{a'} &= (+1)[l_{21}l_{12}T_{12}{}^{a}] = (+1)[(-1)(+1)T_{21}{}^{a}] = -T_{12}{}^{a}
\end{aligned} \tag{12}$$

Therefore, in the point symmetry C_{4v}, a further condition is imposed on the extant elements. Second-rank axial tensors for C_{2v} and C_{4v} thereby have the forms given in Equations (13) and (14).

$$T_{ij}^{a}(C_{2v}) = \begin{bmatrix} 0 & g_{12} & 0 \\ g_{21} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{13}$$

$$T_{ij}^{a}(C_{4v}) = \begin{bmatrix} 0 & g_{12} & 0 \\ -g_{12} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{14}$$

Despite the fact that all elements are not zero, the opposite signs of the off-diagonal elements in C_{4v} preclude azimuthal rotation (see Ref. [16] and compare with Figure 1 d).

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[1] R. T. Morrison, R. N. Boyd, *Organic Chemistry, 2nd ed.*, Allyn and Bacon, New York, **1973**, p. 123.

[2] Throughout, “optical activity” will be used synonymously with optical rotation. This is colloquial usage, and we recognize that this might be a source of confusion. Literally, optical activity may refer to any optical response. Optically active nonlinear materials are often said to be optically active irrespective of whether or not they rotate the azimuth of linearly polarized light. Optical activity is also used to specifically distinguish the polar longitudinal effect from natural OR; see Ref. [6d].

[3] L. D. Barron, *Molecular Light Scattering and Optical Activity*, Cambridge University Press, Cambridge, **2004**.

[4] K. O’Loane, *Chem. Rev.* **1980**, *80*, 41–61.

[5] A. Hansen, *Monatsh. Chem.* **2005**, *136*, 253–273.

[6] a) M. A. Osipov, B. T. Pickup, D. A. Dunmur, *Mol. Phys.* **1995**, *84*, 1193–1206; b) N. A. Cherepkov, V. V. Kuznetsov, *J. Chem. Phys.* **1991**, *95*, 3046–3052; c) J. Schellman, H. P. Jensen, *Chem. Rev.* **1987**, *87*, 1359–1399; d) J. Jerphagnon, D. S. Chemla, *J. Chem. Phys.* **1976**, *65*, 1522–1529; e) S. Bhagavantam, D. Suryanarayana, *Acta Crystallogr.* **1949**, *2*, 21–26.

[7] Monographs: J. F. Nye, *Physical Properties of Crystals*, Oxford University Press, Oxford, **1957**; G. N. Ramachandran, S. Ramaseshan in *Handbuch der Physik*, *Vol. XXV/1* (Ed.: S. Flügge), Springer, Berlin, **1961**.

[8] L. Sohncke, *Entwickelung einer Theorie der Krystallstruktur*, Teubner, Leipzig, **1879**.

[9] J. W. Gibbs, *Am. J. Sci.* **1882**, *23*, 460–476.

[10] A. M. Glazer, K. Stadnicka, *Acta Crystallogr. Sect. B* **1989**, *45*, 234–238. They write: “The existence of chiral arrangements within classes that are normally called ’achiral’ is strictly analogous to the existence of polar directions in non-polar classes. In both cases, more than one chirality or polarity exists within the same crystal and occurs in all of the non-centrosymmetric classes.”.

[11] J. H. van’t Hoff, *Bull. Soc. Chim. Fr.* **1875**, *23*, 295–301.

[12] T. M. Lowry, *Optical Rotatory Power*, Dover, New York, **1964**, p. 337.

[13] F. Pockels, *Lehrbuch der Kristalloptik*, Teubner, Leipzig, **1906**; G. Szivessy, C. Münster in *Handbuch der Physik* (Eds: H. Geiger, K. Scheel), Springer, Berlin, **1928**, pp. 20, 822.

[14] Trivial null values may occur at particular temperatures and wavelengths; see: K. Mislow, P. Bickart, *Isr. J. Chem.* **1977**, *15*, 1–6.

[15] K. Mislow in *Topics in Stereochemistry*, *Vol. 22* (Ed.: S. E. Denmark), Wiley, New York, **1999**.

[16] Fedorov predicted a kind of optical activity, called the polar longitudinal effect, associated with crystals having *C3v*, *C4v*, and *C6v* symmetry. In such crystals, linearly polarized light is reflected with an orthogonal component and hence becomes elliptical. For further details see Refs. [4] and [6d].

[17] A solidus (slash) indicates that the symmetry elements have an arbitrary relationship, a colon indicates that the symmetry elements are orthogonal, and a dot indicates that the symmetry elements have a common axis.

[18] I. S. Zheludev, *Sov. Phys. Crystallogr.* **1957**, *2*, 202 – 210; see also: W. Kaminsky, B. Kahr in *Symmetry 2000*, Wenner-Gren Foundation, Stockholm, **2001**, pp. 309 – 316.

[19] For exceptions, see the following reviews: a) W. Kaminsky, *Rep. Prog. Phys.* **2000**, *63*. 1575 – 1640; b) R. Kuroda in *Circular Dichroism*: *Principles and Applications* (Eds.: N. Berova, K. Nakanishi, R. Woody), Wiley-VCH, Weinheim, **2000**, pp. 159 – 183; c) H.-G. Kuball, T. Höfer in *Circular Dichroism*: *Principles and Applications* (Eds.: N. Berova, K. Nakanishi, R. Woody), Wiley-VCH, Weinheim, **2000**, pp. 133 – 156.

[20] The pitfall of studying averages was acknowledged in the earliest studies of OR. Herschel remarked, "There may possibly exist in every molecule, a direction or axis in which the force of rotation is a maximum, and others in which it is nothing or even negative. … In liquids, in which the axes of the particles have every possible direction, the rotatory force resulting from their joint action will be an average or mean among all the values it is susceptible of." J. F. W. Herschel, *Trans. Cambridge Philos. Soc.* **1822**, *1*, 43 – 51.

[21] P. L. Polavarapu, *Mol. Phys.* **1997**, *91*, 551 – 554; R. K. Kondru, P. Wipf, D. N. Beratan, *Science* **1998**, *282*, 2247 – 2250; K. Yabana, G. F. Bertsch, *Phys. Rev. A* **1999**, *60*, 1271 – 1279; P. J. Stephens, F. J. Devlin, J. R. Cheeseman, M. J. Frisch, *J. Phys. Chem. A* **2001**, *105*, 5356 – 5371; P. L. Polavarapu, *Chirality* **2002**, *14*, 768 – 781; P. J. Stephens, F. J. Devlin, J. R. Cheeseman, M. J. Drisch, O. Bortolini, P. Besse, *Chirality* **2003**, *15*, S57 – S64; P. J. Stephens, D. M. McCann, J. R. Cheeseman, M. J. Frisch, *Chirality* **2005**, *17*, S52 – S64; M. Pecul, K. Ruud, *Adv. Quantum Chem.* **2005**, *50*, 185 – 212; T. D. Crawford, *Theor. Chem. Acc.* **2006**, *115*, 227 – 245.

[22] L. Rosenfeld, *Z. Phys.* **1928**, *52*, 161 – 174.

[23] E. Charney, *The Molecular Basis of Optical Activity*, Wiley, New York, **1979**.

[24] A. D. Buckingham, M. B. Dunn, *J. Chem. Soc. A* **1971**, 1988 – 1991.

[25] While $G'_{\alpha\beta}$ and $A_{\alpha\beta\gamma}$ are dependent on the choice of molecular origin, there combination is not. This interdependence underscores the necessity of considering electric dipole–electric quadrupole contributions; see Ref. [3], and M. Krykunov, J. Autschbach, *J. Chem. Phys.* **2006**, *125*, 034102.

[26] Buckingham's traceless quadrupole operator: A. D. Buckingham, *Adv. Chem. Phys.* **1967**, *12*, 107 – 142.

[27] J. Olsen, P. Jørgensen, *J. Chem. Phys.* **1985**, *82*, 3235 – 3264; P. Jørgensen, H. J. A. Jensen, *J. Chem. Phys.* **1988**, *89*, 3654 – 3661; J. Olsen, D. L. Yeager, P. Jørgensen, *J. Chem. Phys.* **1989**, *91*, 381 – 388; K. L. Bak, A. E. Hansen, K. Ruud, T. Helgaker, J. Olsen, P. Jørgensen, *Theor. Chim. Acta* **1995**, *90*, 441 – 458.

[28] T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, J. Olsen, K. Ruud, H. Ågren, A. A. Auer, K. L. Bak, V. Bakken, O. Christiansen, S. Coriani, P. Dahle, E. K. Dalskov, T. Enevoldsen, B. Fernandez, C. Hättig, K. Hald, A. Halkier, H. Heiberg, H. Hettema, D. Jonsson, S. Kirpekar, R. Kobayashi, H. Koch, K. V. Mikkelsen, P. Norman, M. J. Packer, T. B. Pedersen, T. A. Ruden, A. Sanchez, T. Saue, S. P. A. Sauer, B. Schimmelpfennig, K. O. Sylvester-Hvid, P. R. Taylor, O. Vahtras, *Dalton, a molecular electronic structure program*, Release 1.2, **2001**.

[29] A. E. Hansen, K. L. Bak, *J. Phys. Chem. A* **2000**, *104*, 11362 – 11370.

[30] G. Snatzke, *Angew. Chem.* **1979**, *91*, 380 – 393; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 363 – 377; G. Snatzke in *Circular Dichroism: Principles and Applications*, *2nd ed.* (Eds.: N. Berova, K. Nakanishi, R. W. Woody), Wiley-VCH, New York, **2000**, pp. 1 – 28.

[31] J. Kongsted, T. B. Pedersen, A. Osted, A. E. Hansen, K. V. Mikkelsen, O. Christiansen, *J. Phys. Chem. A* **2004**, *108*, 3632 – 3641.

[32] C. Isborn, K. Claborn, B. Kahr, *J. Phys. Chem. A* **2007**, *111*, 7800 – 7804.

[33] K. B. Wiberg, Y. G. Wang, S. M. Wilson, P. H. Vaccaro, J. R. Cheeseman, *J. Phys. Chem. A* **2006**, *110*, 13995 – 14002.

[34] R. Hassey, E. Swain, N. I. Hammer, D. Venkataraman, M. D. Barnes, *Science* **2006**, *314*, 1437 – 1439.

[35] H. Fukazawa, A. Hoshikawa, H. Yamauchi, Y. Yamaguchi, Y. Ishii, *J. Cryst. Growth* **2005**, *282*, 251 – 259; H. Fukuzawa, A. Hoshikawa, Y. Ishii, B. C. Chakoumakos, J. A. Fernandez-Baca, *Astrophys. J.* **2006**, *652*, L57 – L60.

[36] W. Kaminsky, K. Claborn, B. Kahr, *Chem. Soc. Rev.* **2004**, *33*, 514 – 525.

[37] Y.-N. Chiu, *Phys. Rev. A* **1985**, *32*, 2257 – 2269.

[38] F. Arago, *Mem. Inst. Fr.* **1811**, *1*, 93 – 134.

[39] J. Kobayashi, T. Asahi, S. Takahashi, A. M. Glazer, *J. Appl. Crystallogr.* **1988**, *21*, 479 – 484.

[40] W. Federlin, *Justus Liebigs Ann. Chem.* **1907**, *356*, 251 – 280.

[41] E. Sommerfeldt, *Phys. Z.* **1909**, *7*, 207 – 208; 266 – 269.

[42] V. B. Tatarskii, *Sov. Phys. Crystallogr.* **1964**, *9*, 377 – 379.

[43] A. Shtukenberg, Y. Punin, *Optically Anomalous Crystals* (Ed.: B. Kahr), Springer, Dordrecht, **2007**.

[44] W. Voigt, *Ann. Phys.* **1905**, *18*, 645 – 694.

[45] D. Rogers, *Nature* **1953**, *171*, 929.

[46] M.-J. Chern, R. A. Phillips, *J. Opt. Soc. Am.* **1970**, *60*, 1230 – 1232; M.-J. Chern, R. A. Phillips, *J. Opt. Soc. Am.* **1970**, *60*, 1542A.

[47] H. Futama, R. Pepinsky, *J. Phys. Soc. Jpn.* **1962**, *17*, 725.

[48] a) M. V. Hobden, *Nature* **1967**, *216*, 678; b) M. V. Hobden, *Acta Crystallogr. Sect. A* **1968**, *24*, 676 – 680.

[49] J. Etxebarria, C. L. Folcia, J. Ortega, *J. Appl. Crystallogr.* **2000**, *33*, 126 – 129.

[50] R. J. Lingard, A. R. Renshaw, *J. Appl. Crystallogr.* **1994**, *27*, 647 – 649.

[51] M. V. Hobden, *Nature* **1968**, *220*, 781; M. V. Hobden, *Acta Crystallogr. Sect. A* **1969**, *25*, 633 – 638.

[52] A. E. Hansen, K. L. Bak, *Enantiomer* **1999**, *4*, 455 – 476.

[53] W. J. Anderson, P. W. Yu, Y. S. Park, *Opt. Commun.* **1974**, *11*, 392 – 395.

[54] O. G. Vlokh, V. A. Grabovsky, *Opt. Spektrosk.* **1988**, *64*, 1307 – 1312.

[55] T. Asahi, M. Tomizawa, J. Kobayashi, W. Kleeman, *Phys. Rev. B* **1992**, *45*, 1971 – 1987.

[56] T. Asahi, T. Osaka, J. Kobayashi, S. C. Abrahams, S. Nanamatsu, M. Kimura, *Phys. Rev. B* **2001**, *63*, 094104.

[57] K. Claborn, J. Herreros Cedres, C. Isborn, A. Zoulay, E. Weckert, W. Kaminsky, B. Kahr, *J. Am. Chem. Soc.* **2006**, *128*, 14746 – 14747.

[58] N. Takahashi, M. Tomizawa, J. Kobayashi, *Jpn. J. Appl. Phys. Part 1* **1992**, *31*, 3209 – 3211.

[59] Y. Shopa, L. Lutsiv-Shumskiy, R. Serkiz, *Ferroelectrics* **2005**, *317*, 271 – 274.

[60] J. Herreros Cedres, C. Hernández-Rodríguez, W. Kaminsky, *J. Appl. Crystallogr.* **2005**, *38*, 544 – 554.

[61] M. Tomizawa, H. Sugiya, J. Kobayashi, *Jpn. J. Appl. Phys. Part 1* **1991**, *30*, 2419 – 2422.

[62] O. Vlokh, Y. Shopa, M. Kravchuk, *Ferroelectrics* **1997**, *203*, 107 – 111.

[63] D.-Y. Kim, W. Kaminsky, A. M. Glazer, *Phase Transitions* **2001**, *73*, 533 – 563.

[64] J. Kobayashi, T. Takahashi, T. Hosokawa, *J. Appl. Phys.* **1978**, *49*, 809–815.
[65] S. D. Arzt, DPhil Thesis, University of Oxford, **1995**.
[66] C. Hernández-Rodríguez, P. Gómez-Garrido, S. Veintemillas, *J. Appl. Crystallogr.* **2000**, *33*, 938–946.
[67] W. Kaminsky, E. Haussühl, L. D. Bastin, J. A. Subramony, B. Kahr, *J. Cryst. Growth* **2002**, *234*, 523–528.
[68] P. A. Thomas, I. J. Tebbutt, A. M. Glazer, *J. Appl. Crystallogr.* **1991**, *24*, 963–967.
[69] S. P. Kozyrev, A. B. Gil'varg, B. N. Grechushnikov, N. V. Belov, *Sov. Phys. Crystallogr.* **1974**, *18*, 813.
[70] R. J. Lingard, DPhil Thesis, University of Oxford, **1994**.
[71] S. D. Arzt, A. M. Glazer, *Acta Crystallogr. Sect. B* **1994**, *50*, 425–431.
[72] K. Stadnicka, A. Madej, I. J. Tebbutt, A. M. Glazer, *Acta Crystallogr. Sect. B* **1992**, *43*, 319–325.
[73] T. Asahi, R. Ikeda, M. Nakamura, T. Morikawa, M. Higano, H. Suzuki, J. Kobayashi, *Ferroelectr. Lett. Sect.* **1996**, *21*, 47–53.
[74] O. G. Vlokh, N. I. Klepach, Y. I. Shopa, *Kristallografiya* **1986**, *31*, 195–197.
[75] W. Kaminsky, P. A. Thomas, A. M. Glazer, *Z. Kristallogr.* **2002**, *217*, 1–7.
[76] I. J. Tebutt, DPhil, The University of Oxford, **1991**.
[77] K. Claborn, B. Kahr, W. Kaminsky, *CrystEngComm* **2002**, 252–256.
[78] G. Szivessy, C. Münster, *Ann. Phys.* **1934**, *20*, 703–736.
[79] J. Kobayashi, Y. Uesu, *J. Appl. Crystallogr.* **1983**, *16*, 204–211; J. Kobayashi, Y. Uesu, H. Takehara, *J. Appl. Crystallogr.* **1983**, *16*, 212–219.
[80] G. Bruhat, P. Grivet, *J. Phys. Rad.* **1935**, *6*, 12–26.
[81] J. R. L. Moxon, A. R. Renshaw, *J. Phys. Condens. Matter* **1990**, *2*, 6807–6836.
[82] W. Kaminsky, A. M. Glazer, *Ferroelectrics* **1996**, *183*, 133–141.
[83] J. J. De Yoreo, A. K. Burnham, P. K. Whitman, *Int. Mater. Rev.* **2002**, *47*, 113–152.
[84] I. V. Stasyuk, S. S. Kotsur, R. Y. Stetsiv, *Ferroelectr. Lett. Sect.* **1988**, *8*, 71–74.
[85] W. Kaminsky, unpublished results.
[86] M. Born, *Phys. Z.* **1915**, *16*, 251; M. Born, M. Goeppert-Mayer, *Handb. Physik* **1933**, *24*, 623–794.
[87] R. Reijnhart, *Classical calculations concerning the double refraction, optical rotation and absolute configuration*, Delftsche Uitgevers Maatschappij N. V., Delft, **1970**.
[88] V. Devarajan, A. M. Glazer, *Acta Crystallogr. Sect. A* **1986**, *42*, 560–569; A. M. Glazer, *J. Appl. Crystallogr.* **2002**, *35*, 652.
[89] G. N. Ramachandran, *Proc. Indian Acad. Sci. A* **1951**, *33*, 217–227; G. N. Ramachandran, *Proc. Indian Acad. Sci. A* **1951**, *33*, 309–315; G. N. Ramachandran, *Proc. Indian Acad. Sci. A* **1951**, *34*, 127–135.
[90] A. M. Glazer, K. Stadnicka, *J. Appl. Crystallogr.* **1986**, *19*, 108–122.
[91] W. H. George, *Proc. R. Soc. London Ser. A* **1926**, *113*, 585–593; P. C. Chieh, *J. Chem. Soc. Dalton Trans.* **1972**, 1207–1208; H. W. Newkirk, *J. Chem. Soc. Dalton Trans.* **1973**, 12–14.
[92] P. C. Chieh, J. Trotter, *J. Chem. Soc. A* **1970**, 911–914; L. M. Engelhardt, W.-P. Leung, C. L. Raston, A. H. White, *Aust. J. Chem.* **1982**, *35*, 2383–2384; V. K. Belsky, A. A. Simonenko, V. O. Reikhsfeld, I. E. Saratov, *J. Organomet. Chem.* **1983**, *244*, 125–128.
[93] K. Claborn, PhD Thesis, University of Washington, **2006**.
[94] R. W. Munn, *J. Chem. Phys.* **1994**, *100*, 6203–6209.
[95] P. Ostwald, P. Pieranski, *Nematic and Cholesteric Liquid Crystals*, CRC, Boca Raton, **2005**.
[96] L. E. Hough, N. A. Clark, *Phys. Rev. Lett.* **2005**, *95*, 107802.
[97] L. E. Hough, C. Zhu, M. Nakata, N. Chattham, G. Dantlgraber, C. Tschierske, N. A. Clark, *Phys. Rev. Lett.* **2007**, *98*, 037802.
[98] A. D. Liehr, *J. Phys. Chem.* **1964**, *68*, 665–772.