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Perspective

Chiral Crystals, Jack, Conductivity and Magnetism

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In Memory of *Jack Dunitz*

Recently, the application of magnetic fields to chiral chemical systems has been rewarding. In a forward-looking 1986 paper, 'Chiral Metals?', *Wallis*, *Karrer*, and *Jack D. Dunitz* forecast 'that the limitation to proper symmetry elements in a chiral conductor could be associated with the emergence of new properties, those connected with interactions between applied electric and magnetic fields and their internal counterparts.' This was a prescient remark, but it has become manifest in ways that would not have been foreseen in its details by the authors. Here are reviewed the development of chiral conductors broadly imagined by *Dunitz* and coworkers, based on enantiopure tetrathiafulvalene derivatives that restrict space groups to those that have only symmetry operations of the first kind, as well as the new emergent properties associated with the transport of electrons when magnetic fields are applied to chiral crystals among other systems. These include electrical magnetochiral anisotropy (eMChA), inverse electrical magnetochiral anisotropy (ieMChA), helimagnetism and chirality induced spin selectivity (CISS). The conclusion discussing the circumstances under which achiral TTF crystals becomes chiral, only seems to introduce an oxymoron.

Keywords: chirality, CISS effect, helimagnetism, magnetic field, magnetochiral anisotropy, spin polarization, twisted crystals.

1. Introduction

In one of *Jack D. Dunitz*'s publications, 'Chiral Metals? A Chiral Substrate for Organic Conductors and Superconductors', *Dunitz* and co-authors *Wallis* and *Karrer* faced up to the fact that almost 'nothing appears to be known about the properties of organic conductors or superconductors crystallizing in chiral space groups.'[1] To remedy this situation, the authors prepared the first enantiopure tetrathiafulvalene (TTF) derivative, a bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) with four methyl groups on stereogenic atoms of the ethylenedithio bridges, all with the same configuration (*S*) (*Figure 1,a*). The 2:1 PF_6^- salt of this compound crystallized in the space group *P*1 with a conductivity of $5\,\Omega^{-1}\,cm^{-1}$. While *P*1 is not a chiral space group *per se*, the absence of symmetry is compatible with chiral structures, albeit both enantiomorphs crystallize in *P*1.

The synthesis and structural analysis were aimed to motivate the possibility, as stated above in the abstract, 'that the limitation to proper symmetry elements in a chiral conductor could be associated with the emergence of new properties, in particular those connected with interactions between applied electric and magnetic fields and their internal counterparts.' A full characterization of a variety of salts appeared in the next year with additional contributions of *Hilti*, *Mayer*, *Bürkle*, and *Pfeiffer*.[2] Such was the situation in 1987. This special issue may be a fitting place to ask: Chiral metals, where are we now, especially regarding the reciprocity of the internal fields? It should surprise few reading this special issue that *Jack* seized upon a trenchant intersection of three streams in organic materials science – chirality, conductivity and magnetism – that spilled new and challenging rivulets in the following decades.

2. Chiral Crystal Structures

Wallis, in collaboration with *Martin* and *Akutsu*,[19] continued to prepare conductors made from enantiopure charge transfer salts, and his work in the area has continued until the present day.[20] In this instance just cited, chiral crystal symmetry was ensured by chiral mandelate counterions, but *Wallis* studied many dozens of crystals built from chiral TTF donors, *e.g. Figure 1,i*, derived from the original strategy he pursued with *Dunitz*. This work was reviewed with *Avarvari*,[21] who made equal and independent contributions to the study of conducting chiral crystals, and also collaborated with *Wallis*.[22–24] He continues to push the limits of this field to the present day.[25] *Avarvari* and coworkers well summarized the field in detail rather recently in *Chemical Reviews*[3] and they showcase the ingenuity of the community through the synthesis and resolution of chiral molecules that assemble in crystalline conductors and semiconductors (*Figure 1,b–1,f*). Chirality, conductivity, and ferromagnetism were ultimately combined in a tetramethyl-BEDT-TTF with chromium oxalate counterions.[26] The first benefit of chirality to conductivity arose

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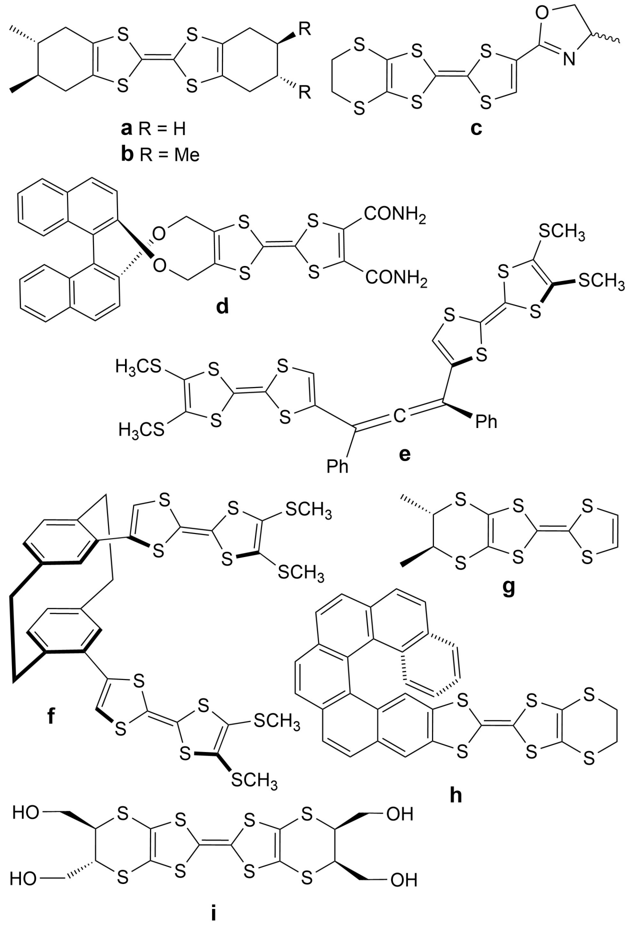

Figure 1. Various chiral tetrathiafulvalene (TTF) derivatives:[3] **a**,[1,2] **b**,[4,5] **c**,[6–8] **d**,[9] **e**,[10,11] **f**,[12,13] **h**,[14,15] **g**,[16,17] and **i**.[18]

merely by precluding occupational site disorder possible in racemic crystals but absent in optically pure materials (*Figure 1,g*).[4–6] It is fair to say that the briefest of papers by *Wallis*, *Karrer* and *Dunitz*[1] *launched 1,000 CIFs*. But the chirality in such derivatives did not capitalize on the 'internal counterparts' to the applied fields. This would come to pass in the discovery of electrical magnetochiral anisotropy (eMChA).

3. Electrical Magnetochiral Anisotropy

Electrical magnetochiral anisotropy (eMChA) is the non-reciprocal charge transport in a chiral system that depends on the scalar product of the electric current **I** and an applied magnetic field, **B**.[27] It was discovered by *Rikken* and coworkers in bismuth wires that were twisted around axes along and against an applied magnetic field (*Figure 2*).[28] The effect has an optical analog originally known as MChA, thus the 'e' for electrical in the acronym above is to distinguish charge transport.

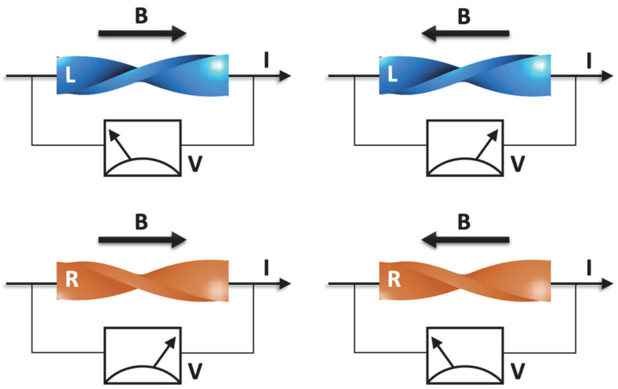

Figure 2. Schematics of the measurement of the electrical magnetochiral anisotropy (eMChA) effect as in a mechanically twisted bismuth wire.[28]

The change in resistivity for opposing applied field directions normalized in the absence of the magnetic field ($\Delta R/R$) is proportional to a magnetochiral anisotropy parameter, $\gamma^{D/L}$. This parameter changes sign for enantiomers/enantiomorphs, $\gamma^{D} = -\gamma^{L}$, where D and L represent right and left-handed configurations of the conductor:

$$\frac{\Delta R}{R} = 2\gamma^{D/L}\mathbf{B}\cdot\mathbf{I}$$

The eMChA effect was confirmed by *Rikken* and coworkers in chiral, single-walled carbon nanotubes[29] and enantiomorphous tellurium metal which crystallizes in the space groups $P3_121$ and $P3_221$.[30] Bismuth is not chiral, crystallizing in the space group $R\bar{3}m$, but a single crystal wire was twisted by 15° over 1 cm. It was thus chiral, but barely so at the atomic level. The anisotropy parameter, $10^{-3}\ \mathrm{T}^{-1}\,\mathrm{A}^{-1}$, was a million times smaller than for nanotubes, $10^{3}\ \mathrm{T}^{-1}\,\mathrm{A}^{-1}$.

While the eMChA effect is newly discovered and sparingly measured, it is an exacting probe of defect structure as a consequence of sense-dependent electron scattering from chiral defects (*e.g.*, homochiral screw dislocations). The eMChA effect has been observed in metals,[31,32] semiconductors, and superconductors.[33] In 2014, *Rikken* and *Avarvari* brought the effect squarely within the concerns of *Dunitz* and coworkers. They demonstrated the eMChA effect in the $\mathrm{ClO_4}^-$ salt of a chiral TTF derivative (*Figure 1,g*) of configuration (*S,S*) in the space group

$P6_222$ (*Figure 3*).[12] The proportionality constant was on the order of $10^{-2}\ \mathrm{T}^{-1}\ \mathrm{A}^{-1}$.

4. Inverse Electrical Magnetochiral Anisotropy

The eMChA effect is a change in resistivity in a chiral material on directing an applied magnetic field along or against a current in a chiral wire, whether chiral at the level of the space group symmetry or because the sample was twisted as in the case of bismuth.[20] *Wagnière* and *Rikken* made use of symmetry arguments to insist on a reciprocal effect, inverse electrical magnetochiral anisotropy.[34] Here, in a chiral conductor, a current will produce a magnetic field that does not surround a wire as required by *Ampère*, but rather is directed parallel to the current. In other words, a chiral crystal behaves like a solenoid. This was demonstrated in single crystal wires of tellurium. The sign of the induced magnetic field depends on the direction of pulsed current densities of $\pm 82\ \mathrm{A\,cm^{-2}}$ as demonstrated by ± shifts in the chemical shielding of $^{125}\mathrm{Te}$ by nuclear magnetic resonance.[35] It is easy to imagine a comparable experiment executed on a tellurium containing TTF derivative.[36]

5. Helimagnetism

A helimagnet is a crystal in which the magnetic moments are organized helicoidally around an applied magnetic field. Typically, helimagnetic materials have chiral crystal structures as in FeGe, for example.[37] However, in other cases, such as centric MnP, inversion symmetry is broken locally by the canting of the spins to form right-handed or left-handed helices in the presence of an applied magnetic field. The net moment, despite the helicoidal arrangement of spins, is always along the applied field direction. In such a helimagnet, an electric current aligned or anti-aligned with the applied magnetic field can favor one helical sense or the another. Moreover, the net magnetism will also switch with the current direction, somewhat like in a ferroelectric crystal (*Figure 4*).[38] This is yet another new manifestation of the intuition of *Dunitz* and coworkers regarding the interplay of chirality, magnetism and electric conduction,[1] but there remain few examples and none in the domain of molecular crystals.

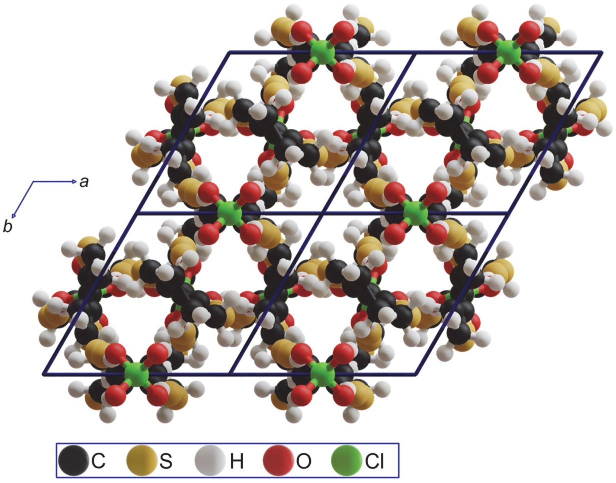

Figure 3. Chiral crystal structure of the $\mathrm{ClO_4}^-$ salt of the (*S*,*S*)-isomer of compound in *Figure 1,g* in the space group $P6_222$.[12]

6. Chiral Induced Spin Selectivity (CISS)

The chiral induced spin selectivity (CISS) effect, discovered in 1999,[39] is a phenomenon in which chiral molecules act as electron spin filters (*Figure 5*).[41] This effect, like magnetochiral anisotropy, is a consequence of an electron moving through a chiral structure to generate a magnetic field:

$$\mathbf{B} = \frac{\mathbf{v}}{c^2} \times \mathbf{E}_{\mathrm{chiral}}$$

Here $\mathbf{v}$ is the electron velocity vector, c is the speed of light, and $\mathbf{E}_{\mathrm{chiral}}$ is the electric field acting on the electron travelling through a chiral molecule, ensemble of molecules, or crystal.[42] The magnetic field generated, $\mathbf{B}$, for which some component is either parallel or antiparallel to the current flow direction,

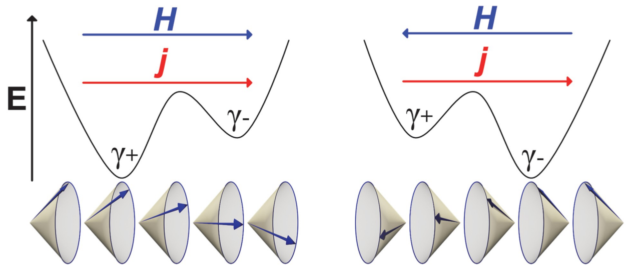

Figure 4. Helimagnetism. The relative senses of magnetic fields and electric currents will favor either right-handed helicoidal spins (left) or left-handed helicoidal spins (right), where $\gamma_\pm$ represents the twist sense. This figure follows very closely that in ref. [37] with the components redrawn and reorganized for compactness. *H* is the applied magnetic field, *j* is the current.

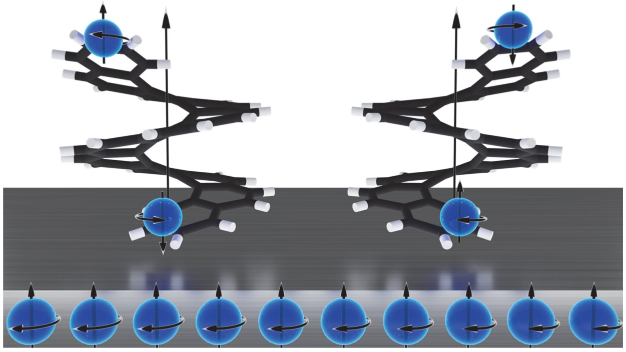

Figure 5. Chiral induced spin selectivity. Electrons (blue spheres) moving through a molecular solenoid, the helicene shown here, and also aligned in a magnetic substrate in the row at bottom, to which an electric field (large vertical arrow) is applied. This illustrates, phenomenologically, how the molecular handedness differentially interacts with electrons of opposing spin states. This Figure is modeled after ref [40]. For a pair of enantiomers on a ferromagnetic substrate the configurations of the spins will be high spin (right) or low spin (left) depending upon the polarization of the substrate and the chirality of the enantiomers. The electric field drives spin-selective electron displacement that results in a transient spin polarization at the poles at the ends of the helices.

splits electron energies based on their spin state, resulting in the preferential propagation of electrons of a given spin state through one enantiomer or enantiomorph.

The CISS effect was first observed in the spin-dependent transmission of electrons through L- or D-stearoyl monolayers[30] and has since been observed in a number of crystals including perovskites,[43–45] metal organic frameworks,[46] metal oxides and sulfides.[47–53] In these systems, electron spin polarization can be induced by generating current flow through chiral structures in an applied electric field, but can also manifest as spin dependent charge reorganization.[54] In the latter scenario, interactions between two chiral molecules generate charge polarization, which in turn induces a transient spin polarization in chiral molecules.[55] A mechanistic understanding remains incomplete because most theoretical models fail to capture the magnitude of the CISS effect observed experimentally.[56]

To the best of our knowledge, the CISS effect has not been observed in a molecular crystal such as a TTF derivative. However, it has been observed in crystals described as chiral molecular intercalation superlattices, where two dimensional atomic crystals such as TaS_2 and TiS_2 are layered with enantiomers ((*R*/*S*)-α-methylbenzylamines).[57]

7. Can Any Molecular Crystal Be Chiral?

Of the 230 *Fedorov–Schönflies* space groups with three-dimensional periodicity, 65 are restricted to translational symmetry, proper rotations, and their combinations. These so-called *Sohncke* groups[58] are those that admit chiral crystal structures. These groups are in the minority and moreover they are less well populated than those compatible with achiral structures. Only 16% of the entries in the Cambridge Structural Database are chiral.[59] Even if we double the number of chiral structures, because a significant portion of the enantiomorphous structures are not determined, the fraction of chiral structures is still lower than one third.

Nevertheless, we now can say confidently that one third to one half of molecular crystals that melt can be made to grow with helicoidal morphologies, irrespective of their space group symmetry.[60–65] Thus, many molecular crystals, chiral or otherwise at the level of its space group symmetry can be chiral. This includes TTF.[66]

TTF crystallizes in three known phases, the α form ($P2_1/c$) and the β and γ forms ($P\bar{1}$), all of which are centrosymmetric and non-enantiomorphous.[67–69] However, when 1–2 mg of TTF powder (*Sigma* 99%, $T_m = 115\,^\circ C$) was mixed with a natural resin such as Canada balsam (15 wt-%) and melted between a glass slide and a cover slip, the subsequently cooled film displayed striking textures between crossed polarizers that indicated that twisted of fibrous crystals formed on the mesoscale (*Figure 6*). They are of the β-form. Spherulitic growth of crystals from the melt shoots fibers radially from common nucleation centers with optical textures showing rhythmic precessions of interference colors. Bands of constant refractivity recur with spacings (half-pitches) on the scale of tens of microns. All helicoids are chiral and can be right-handed or left-handed. Typically, one side of a TTF spherulite spins out crystals that twist to the right while the other spins out crystals that twist to the left. This is ultimately determined by the sense of the enantiopolar faces of the crystal that served as the nucleus.[70–72]

Twisting necessarily introduces chirality to organized systems – even in crystallographically centrosymmetric crystals – resulting in unique interactions with light, including strong circular retardance and circular extinction (the differential refraction and scattering of left and right circular polarizations).[60,73–75] The manner in which mesoscale twisting affects optoelectronic processes is an open question. Twisted crystals may

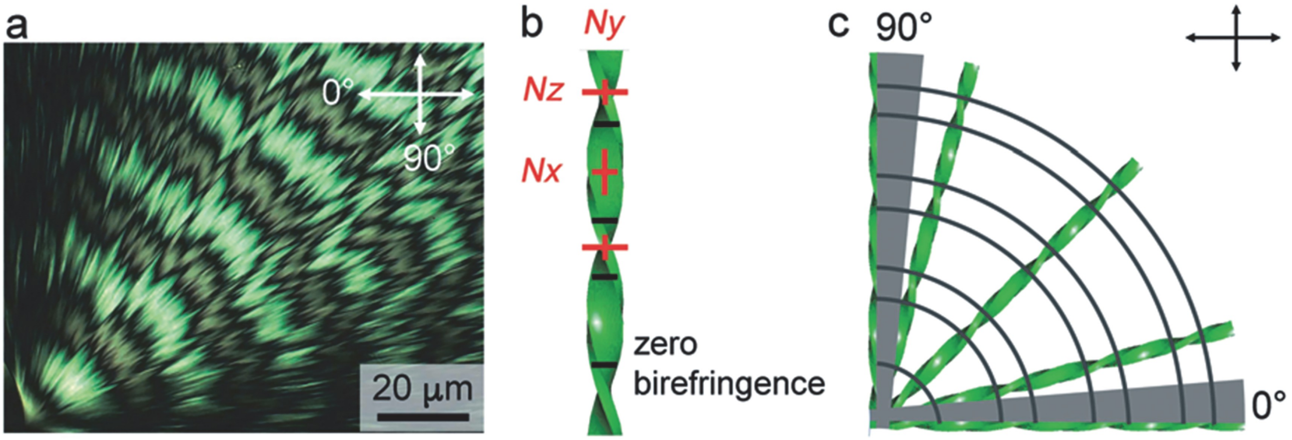

Figure 6. a) Optical micrograph of one quarter of a twisted TTF spherulite between crossed polarizers. b) Model for the structure of a fiber with N_x, N_y, and N_z corresponding to orientation of the smallest, intermediate, and the largest principal refractive indices. c) Illustration of assembled fibers in banded spherulites. Zero birefringence bands are shown as black arcs, while areas of extinction are shaded in grey. Figure is adapted with permission from Reference [66]. Copyright 2022 *The Royal Society of Chemistry* and *IChemE*.

well be burdened with chiral defects depending on the handedness of twisting. These chiral defects can have magnetic-field dependent interactions with charge carriers. We aspire to study the effect of chiral defects on charge transport in twisted crystals by measuring the impact of external magnetic fields on twisted organic semiconductor crystal-based field effect transistors as a function of pitch and direction.

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Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Author Contributions Statement

B. K. conceived of the essay in response to the invitation from *Helv. Chim. Acta* and wrote a first draft. *A. S.* and *S. L.* revised the manuscript. *Y. Y.* and *S. J. W.* performed the experiments previously published and *S. J. W.* and *Y. Y.* made the new graphical content.

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