

Turinese Stereochemistry: Eligio Perucca's Enantioselectivity and Primo Levi's Asymmetry**

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chirality · circular dichroism · dyes/pigments · enantioselectivity · optical rotatory dispersion

1. A Report in *Nuovo Cimento*, 1919

In 1919, Eligio Perucca (Figure 1) reported anomalous optical rotatory dispersion (ORD) from chiral NaClO_3 crystals that were colored from having been grown from a solution containing an equilibrium racemic mixture of a triarylmethane dye, extra China blue.^[1] In recent decades, this publication has never been cited, except in our review on the dyeing of crystals.^[2] Perucca's chiroptical observations are consistent with a resolution of the propeller-shaped dye molecules by NaClO_3 crystals. This study, if the results are substanti-



Figure 1. Eligio Perucca, 1927, courtesy AIP Emilio Segrè Visual Archives.

ated, produced the first evidence of the enantioselective adsorption of a racemic mixture to an inorganic crystal:^[3] a stereochemical concept that failed to find fertile ground until the 1970s, when crystal–molecule interactions took a prominent place in discussions on the origin of biomolecular homochirality.^[4] Perucca's overlooked publication should concern researchers who study enantioselective catalysis by crystals^[5] and the “spontaneous generation” of chirality and optical activity,^[6] especially in NaClO_3 ,^[7] as well as solid-state CD,^[8] the chiroptics of oriented molecules,^[9] the stereochemistry of adsorption to crystals,^[10] and the history of chiroptics.^[11]

2. Enantioselective Adsorption to Crystals

The discrimination of enantiomers by minerals^[10c–f,12] has been a subject for speculation since Goldschmidt^[13] and Bernal^[14] suggested that quartz or chiral clays may have been responsible for biomolecular homochirality. From 1935

onwards, many scientists claimed to have resolved racemates with *d* or *l* quartz powders;^[15] however, their observations of residual optical activity were deemed experimentally insignificant.^[16,17] Ferroni^[18] and Cini of Florence even claimed to have resolved optical antipodes with NaClO_3 ,^[19] but they made no mention of Perucca's publication.^[1] Their study was discredited,^[20] as were the quartz studies.^[16] Bonner et al. ultimately collected reliable data on asymmetric adsorption to quartz in 1974.^[21]

Perucca's report^[1] on anomalous ORD from dyed NaClO_3 antedates all claims to have resolved racemic mixtures with chiral crystals. Many enantioselective processes on crystal surfaces have since been described.^[3,10,12,22] Recently, the autocatalytic Soai reaction has provided abundant evidence of enantioselective adsorption to a variety of crystals,^[23] including NaClO_3 ,^[7] however, the reactant–crystal interactions have yet to be described.

3. Eligio Perucca

Eligio Perucca (1890–1965) studied in Pisa. In 1911, he became an assistant at the Physics Institute of the University of Turin. Before beginning his independent research on light polarization, he is said to have studied with great care the original works of the pioneers, notably Fresnel, Stokes, and Bravais.^[24] Perucca developed a reputation as an excellent experimentalist. His passion for precision instrumentation is evident in the textbooks and encyclopaedias that he authored.^[25] By 1922 he was full professor of physics at the neighboring Turin Polytechnic, where he taught until 1960.

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As chancellor from 1947 to 1955, he was engaged in rebuilding facilities destroyed during the war. In later years, he was president of the Academy of Sciences of Turin and vice president of the prestigious Lincei National Academy.

Perucca's 1919 publication^[1] was prompted by Dove's claim that amethyst, the purple form of quartz, exhibited circular dichroism (CD) in the visible part of the spectrum.^[26] Perucca concluded that Dove observed the consequences of the interaction of linear dichroism with imperfect circular polarization;^[27] parasitic ellipticities plagued measurements of CD in oriented systems throughout the 20th century.^[28] Perucca then tried to make faux amethyst—NaClO₃ in place of quartz with a triarylmethane colorant—so as to determine whether a simple chiral crystal could induce optical activity in the absorption band of an otherwise optically inactive impurity.

4. Confirmation

We identified aniline blue (**AB**) as the compound most akin to extra China blue, whose constitution Perucca qualified with “*probabilmente*” (probably).^[29] Crystals of NaClO₃ were grown from saturated solutions containing 2.5×10^{-4} M **AB** (diammonium salt, Aldrich, C.I. No. 42780; Figure 2a) by slow evaporation at 5 °C. Large blue cubes were deposited (Figure 2b).

We examined sections of the crystal with a microscope for recording CD.^[30] When viewed normal to a cube face, the crystal sections showed a differential circular transmission in the absorption band of the dye (Figure 2c). The largest values of the differential transmitted intensity of right (I_R) and left circularly polarized light (I_L) divided by the incident intensity ($(I_R - I_L)/I_0$) were ± 0.10 at 515 nm. Adjacent sectors showed opposite signs of CD, a result consistent with the *T* symmetry of NaClO₃ and bisignate CD tensors.

As far as we succeeded in mimicking the chemistry carried out by Perucca, it appears that he observed what he claimed to have: anomalous ORD in the absorption band of the dye. With hindsight, this result could only be the

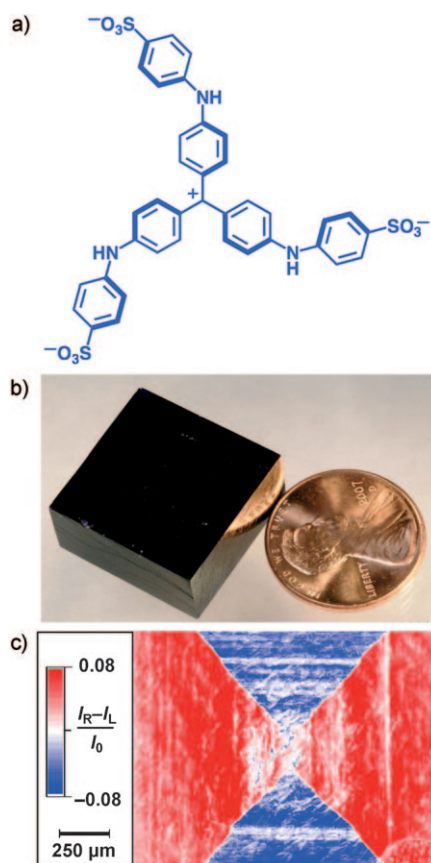


Figure 2. a) Structure of aniline blue (**AB**). b) Photograph of a US penny reflected in an as-grown **AB**-dyed NaClO₃ crystal measuring 4 cm³. c) CD micrograph of a (100) crystal section (500 μm) at 470 nm.

consequence of resolution of the equilibrium racemic mixture of **AB** by the crystal. Perucca's observation serves as evidence of the so-called Pfeiffer effect: the induction of optical activity in an equilibrium racemic mixture by a colorless additive. It antedates the pioneering experiments of Paul Pfeiffer in 1931.^[31,32] Perucca's publication must therefore be viewed as a milestone in chiroptics and enantioselective chemistry. A forthcoming analysis of the data obtained by Perucca will show that he was observing a confluence of optical effects, including anomalous linear birefringence,^[33] linear dichroism, circular birefringence, CD, and anomalous circular extinction.^[34]

5. Did Perucca Know What He Had Achieved?

Yes and no. Perucca did not know, nor could he have been expected to know, given the state of development of conformational analysis in 1919, that solutions of triarylmethyl cations contain equilibrium racemic mixtures of propeller-shaped enantiomers. Not until 1942 did G. N. Lewis first suggest that the aryl rings of triarylmethyl cations cannot be mutually planar owing to steric hindrance.^[35,36] Seel proposed the triphenylmethyl propeller independently.^[37] Evidence for the mutual nonplanarity of the aryl rings of triarylmethyl cations was first provided by IR spectroscopy^[38] and later quantified by X-ray crystallographic analysis.^[39]

Perucca, operating under the assumption that triarylmethanes are achiral, aspired to induce in them a chiroptical response through their noncovalent association within a chiral medium. The study of optical activity induced in planar chromophores began 50 years later, when Blout and Stryer described ORD curves that showed Cotton effects from acridine dyes associated with polypeptides.^[40] With the advent of electro-optic polarization modulation and the production of commercial CD spectropolarimeters, measurements of induced ORD were supplanted by CD spectra.^[41]

Given the equivocal aspects of Perucca's publication, which appeared in a world struggling to regain its own equilibrium in 1919, it is perhaps not surprising that this study went unnoticed. Fortunately, dyed crystals preserve ample optical evidence of their host-guest interactions during growth.^[2] It is from this sort of crystal that we can begin to understand enantioselectivity on catalytic NaClO₃ and other crystals.

6. Perucca and Primo Levi: Turinese Stereochemists

“An apology is in order. This very book is drenched in memory. Thus it draws from a suspect source and must be protected against itself.”^[42]

Perucca was remembered as a *personaggio bizzarro* (eccentric character) in a history of the science faculty of the University of Turin.^[43] In an attempt to

establish the basis of this characterization,^[44] we sought out writings of contemporary Turinese scientists who might have recorded something about Perucca, including the acclaimed author and chemist, Primo Levi.

Levi was born in Turin in 1919—the place and time associated with Perucca's publication on NaClO_3 ^[1]—into a middle-class Jewish household. He enrolled at the University of Turin in 1937 to study chemistry, but racial prohibitions precluded an experimental thesis. In his story “Potassium” in *The Periodic Table*,^[45] which was named by the Royal Institution in London as the best science book ever written,^[46] Levi recalled his days as a chemistry student. To Levi, the preparation of the dye methyl violet (a congener of **AB**) was merely “amusing”. The following of seemingly arbitrary recipes was unsatisfying to a young man who sought a firm foundation in an increasingly unstable Italian society. Levi fondly recalled his exercises in physics—“simple measurements of ... rotatory power, and such”—and consequently sought a mentor among the physics faculty. Might Levi have approached Perucca, the expert in Turin on optical activity? Levi writes, “I made desperate attempts [in 1941] to be taken on as a student assistant by this or that professor. Some of them snidely or even arrogantly told me that the racial laws prohibited it; others fell back on hazy or flimsy excuses.” Levi does not reveal whether “eccentric” Perucca was among the snide or arrogant. However, in her biography of Levi, Anissimov identified Perucca as one of the contemptuous professors.^[47]

We considered it unlikely that Perucca could have been one of the professors who rebuffed Levi. For a student at the University of Turin to have approached a professor at the wholly independent Turin Polytechnic would have been a rather exceptional event. For this reason, we sought out independent recollections of the relationship, if there was one, between Eligio Perucca and Primo Levi. We interviewed Perucca's nephew Giovanni Perucca and his onetime assistant Professor Radicati di Brozolo, among others. By general consensus, Perucca was well known to be an antifascist. This sentiment was colorfully confirmed by

Angiola Maria Sassi Perino,^[24b] who recalled her teacher in an essay, “A Fascinating and Terrifying Teacher”, published in a celebration of *A Half Century of Physics for Engineers Taught by Eligio Perucca at the Turin Polytechnic*. Sassi Perino tells of Perucca receiving Mussolini on an official visit to Turin in 1939. Perucca deliberately turned up for the encounter in fancy, ceremonial dress, rather than in a “black shirt”, the expected concession to *Il Duce*.

We also interviewed Levi's sister Anna Maria Levi, his son Renzo Levi, and his university contemporary Giovanna Rava. They did not recall Primo Levi mentioning Perucca's refusal and considered it very unlikely that Levi and Perucca would have had any contact. Rava did recall that she and Levi used the physics textbook written by Perucca^[25b] as students. Most salient are the recollections of Renato Portesi, who worked for more than a decade with Levi at the SIVA paint factory. Once, when Portesi had occasion to take some samples to the Polytechnic, Levi remarked that as a student he had attended some of Perucca's lectures because they were very clear and peppered with antifascist allusions.

Anissimov also identified Giacomo Ponzio and Mario Milone, both chemists at the University of Turin, as scientists who turned Levi away.^[47] Levi's other biographers, Thompson^[48] and Angier,^[49] agree that both Ponzio and Milone refused to accept Levi and other Jewish students as *interni* (research assistants). Neither makes any mention of Perucca. Ponzio and Milone ultimately approved the thesis and subthesis,^[50] respectively, that Levi prepared. Owing to racial prohibitions, neither investigation included experiments.

The thesis approved by Ponzio was an analysis of Walden inversion. The heuristic theme of “inversion” and a specific interest in stereochemistry recur throughout Levi's writings.^[51] In a 1984 essay, *L'asimmetria e la vita (Asymmetry and Life)*, he weighed various theories of biogenesis.^[52] He writes, “asymmetry, so jealously transmitted by the living cell, is difficult to obtain and easy to lose”, a reflection on his undergraduate report. Indeed, we observed that NaClO_3 grown with **AB** at room temperature is barely circularly dichroic,

and modest heating of crystals that have grown cold prompts the racemization of **AB** with dispersive kinetics (details to be published).^[53]

Eligio Perucca was a pioneer of stereochemistry. Primo Levi was a stereochemist never to be. Perucca was an intimidating teacher,^[24b,44] but his intellectual rigor and razorlike wit inspired Levi, a soon-to-be partisan. We have no evidence that Perucca encouraged the misfortune of Levi^[54] or the misfortune of others like him.

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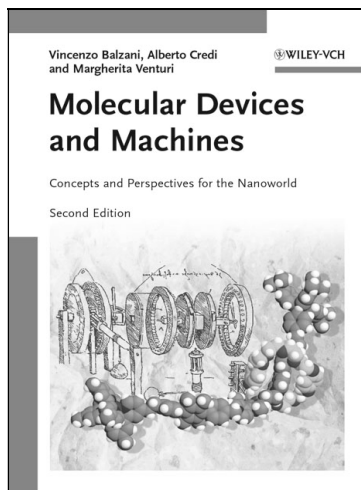
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