Controversy in Chemistry I. What Counts as Evidence? Two Studies in Molecular Structure

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An Overview

"The facts speak for themselves." Well … in science as in life, sometimes yes and oftentimes no. The very process of turning scientific data into "facts" can itself be contentious, so that even at this level the "facts" may be far from universally agreed upon. Even when they are, assessing their larger significance is an interpretive process that frequently leads to disagreement or worse. In brief, the normal practice of science provides ample opportunity for controversy; indeed, it is the rare scientist who has not followed, if not participated in, a vigorous scientific controversy that has stretched out for months or even years.

Precisely because controversies are part and parcel of normal science, our colleagues in science studies – historians, philosophers and sociologists of science – have turned increasingly to the study of controversies for what they reveal about the processes of science.[1] Among those colleagues there is a growing consensus that controversy is not only characteristic of science but essential to its development. As practicing chemists we are not surprised, shocked or embarrassed at the role that controversy has played in growth of our discipline. As chemical educators, however, we are disturbed at the way in which this aspect of science has been hidden from our students and even from our peers. It's almost as though there were a "conspiracy" to conceal the fact that chemistry is an open and dynamic network of investigations, and to present it instead as a closed, static body of facts. The naïve student or lay person is often led to envisage science as an imperturbable machine that regularly ejects neatly sealed sausages of imperishable truth, a vision that does not serve them well.[2]

In what follows we explain why this bland, sanitized picture of science does a disservice to students, scientists and science itself, leading up to one possible corrective that we have used: a series of case studies of chemical controversies. The incentive to assemble and coordinate the material described in this and subsequent articles came through developing a course for students majoring in science or engineering.[3] However, the gaps that this material seeks to fill are widespread not only within the university but in the larger educated community as well.

We should point out that a number of articles related to the theme of controversy in chemistry, written by chemists for an audience of chemists, have appeared recently, several in this journal. Just to cite a few examples: a recent book by Jerome Berson that covers a variety of chemical/philosophical controversies;[4] a survey of literary responses to Fritz Haber and his role in chemical warfare;[5] an assessment of credit due for the discovery of ferrocene;[6] and an examination of the role and power of Ockham's Razor in chemistry.[7] The last of these articles has been cited in about 30 research reports, encouraging us in our belief that attention to such considerations can indeed have a positive impact on scientific practice.

Real vs. Idealized Science

There has been a long-standing concern in science policy circles over the small proportion of students who choose science as a profession, as well as over the low level of scientific literacy among the general public. These issues are unquestionably large in scope, yet we believe that *in part* they have a similar origin, namely the way in which science is often taught. Several decades of research have made apparent the discrepancy between the skeletal fiction taught to students as "the scientific method" and actual scientific practice. This discrepancy is not news to practicing scientists, yet the representation of science often fails to match the reality. Thomas Kuhn's characterization of science pedagogy, written 45 years ago, is still appropriate:

"Except in their occasional introductions, science textbooks do not describe the sorts of problems that the professional may be asked to solve and the variety of techniques available for their solution .... Even the most faintly liberal educational theory must view this pedagogic technique as anathema .... and yet we must recognize .... [that] education in the natural sciences .... remains a dogmatic initiation in a pre-established tradition that the student is not equipped to evaluate."[8]

While "facts" are surely central to any discussion of science, context-free presentations which suppress the reality that "science is a complex and messy business"[9] turn many away from science altogether, often at an early stage. As Nobel laureate Dudley Herschbach has noted,

"Many students [in introductory science courses] have told me about a disheartening syndrome: the questions and problems seem to have only one right answer, to be found by some canonical procedure. The student who does not quickly grasp the "right" way, or finds it uncongenial, is soon likely to become alienated from science .... Nothing could be further from what actual frontier science is like."[10]

Steve Weininger has felt this same unease, fed by extensive experience teaching basic organic chemistry. He sees many capable and industrious students become frustrated by their apparent inability to grasp concepts that are typically presented as not only logical but inescapable. Had those concepts been represented as the product of long, collective struggles within the chemical community, and subject to revision or even rejection, many students might have been spared disaffection and self-doubt.

Of those students who remain in science, many continue to hold a rather distorted idea of what it is really like. Jay Labinger first realized this while reading the student evaluations of an advanced course he taught on catalysis. In courses that cover primarily recent and still ongoing work, Labinger likes to present much of the material in case-study mode. That is, he might describe some of the first experiments on a given topic, explain how they led to a certain conclusion, then show how later work changed the interpretation, and so on. A number of students don't seem to care for this at all. "It's too confusing," one course evaluation read, "why can't you just give us the facts?" Labinger found this response rather surprising, especially from graduate students who would shortly be going out into the real world and engaging in precisely that sort of process themselves. But

perhaps it *isn't* so surprising, if most science education portrays science itself as the unproblematic generation of "facts."

Some readers may feel that the best course of action with respect to many of these controversies would be to ignore them, because bringing them into the limelight would only promote anti-scientific attitudes. While our sample is admittedly small, the reactions of our students do not at all support that view. In fact, the discovery that science is a human enterprise has encouraged some students to believe that ordinary mortals like themselves have a place in science. Furthermore, the realization that chemistry is in fact a dynamic, fluid and occasionally contentious enterprise has made it more appealing for them as a career choice, and we harbor the (perhaps immodest) hope that it will even make them better scientists. As one student wrote,

"I have come to realize that this whole course has changed my outlook on science. I had always assumed that it was straightforward research in black and white that led to definitive answers. I realize in reading all of these articles that it's not as cut and dried .... This has also taught me to see that there is more to science than meets the eye. Although I found it difficult not to take sides on a particular issue that I felt strongly about, I have learned that a critical eye is very necessary in analyzing scientific work."

In our view the problem of science literacy is one that transcends the distinction between scientists and nonscientists. Scientists may have a greater knowledge of scientific facts and techniques, but it is not clear that they enter their careers having a greater sense of the complex reality of science than nonscientists do.

Case Studies of Controversies: A Window on Real Chemistry

An often prescribed antidote for the problems just discussed is the inclusion of historical material in the education of scientists. Over a decade ago the American Association for the Advancement of Science advised the following:

"Science courses should place science in its historical perspective. Liberally educated students – the science major and the non-major alike – should complete their science courses with an appreciation of science as part of an intellectual, social, and cultural tradition .... Science courses must convey these aspects of science by stressing its ethical, social, economic, and political dimensions."[11]

But attempts to implement such recommendations encounter difficulties. To begin with, there seems to be a widely held belief in the science studies community that the history of *chemistry* can yield very few general insights into the fundamental workings of science, a supposition also held by many scientists themselves. For example, the report from the AAAS cites ten "significant discoveries and changes that exemplify the evolution and impact of scientific knowledge" that it recommends for introducing historical perspective into science teaching. Of these only one, conservation of matter, even partly falls into the domain of chemistry.

The challenge then is to use historical material in a way that does justice to the multifaceted reality of chemistry. That certainly cannot be accomplished by augmenting the standard parade of chemical facts and algorithms with an equally uninspiring parade

of names and dates. The aim, rather, must be to emphasize the relevance of chemical developments to larger intellectual issues so that

"... the history of chemistry is no longer seen as a single main line of advance, with regrettable detours like that through the phlogiston theory. Past controversies must be seen as involving choice between live options; theories must be judged according to the information available, and the canons agreed upon, at the time they were proposed."[12]

Our approach to answering this challenge has been to assemble a set of case studies, in this and forthcoming articles, of controversies that have claimed and often continue to claim the attention of both chemists and non-chemists. They span a period from the 18th century to contemporary times, demonstrating that chemical controversy is a special characteristic of neither the past nor the present. We feel it is particularly important to avoid presenting historical issues as somehow *qualitatively* different from contemporary ones – as the old saw goes, history begins with yesterday. Also, we strive to do justice to the technical and contextual aspects alike, and even to question the neat division between science and context. Beyond these goals, it is our hope to recapture the sense of urgency and even drama that permeated those events and made them seem critical to the future development of chemistry and, at times, even the world. These disputes generated extensive investigations and strong passions on the part of many intelligent men and women – it can only benefit our understanding of chemistry to find out why.

The nature of evidence and its proper interpretation has always been a major preoccupation of all modern sciences, and chemistry is no exception. In the history of our discipline these problems have generated many intense controversies. Here we explore two cases, well separated in time and *apparently* quite different in character as well — but perhaps not quite so different as appearances might suggest. First we consider the disputes surrounding the birth of stereochemistry, which are not only of major historical interest but also raise issues that are still with us today. Then we turn to a much more recent controversy, the case of bond-stretch isomerism.

Case 1. The Nature and Interpretation of Evidence in the Birth of Stereoisomerism

Justus Liebig's analytical method for determining C and H (1830), Edward Frankland's enunciation of the valency concept (1852), and the reform of atomic weights that took place in the 1860s provided the requisite underpinnings for the structural theory of organic compounds. Grounded in the assumed quadrivalency of carbon and its chain-forming abilities, structural theory allowed the chemist to envisage all the constitutional isomers that could correspond to a given molecular formula. For example, when in 1864 Aleksandr Mikhailovich Butlerov synthesized the previously unknown $C_4H_{10}O$ isomer, tertiary butyl alcohol, he recognized it as a striking confirmation of the structural theory.

By the 1870s the theory was in the ascendant in the major European chemical centers, especially Germany and Britain. As powerful as it was, the theory could only rely on the results of elemental analysis and chemical reactions to verify its conclusions, which were symbolized in structural formulas. And for many chemists, those formulas represented the limit of what chemical methods could reveal about chemical structures. There were few experimental means available to chemists; in particular, there were no techniques

that gave any direct insight into the spatial arrangement of atoms in molecules. So the question posed itself: to what (if any!) extent should inferences from chemical methods, particularly the existence or non-existence of isomers, be taken as acceptable evidence concerning structure?

One might envision the dilemma of structural chemistry by thinking about a sealed power supply which is represented by a circuit diagram (the structural formula). The circuit diagram indicates clearly the *connections* among the components of the power supply (in our case, the atoms) but it doesn't claim to show how they are *actually positioned* with respect to one another. In order to gain any information of that sort the power supply (for us, the molecule) has to be broken apart, which might very well lead to a scrambling of the components. Indeed, the recognition that molecules were dynamic objects undergoing rapid internal motions led many to ask whether it would *ever* be possible to arrive at three-dimensional molecular structures.

The question was of course open to speculation, and some indeed did speculate about molecular arrangements. But that could be unhealthy for one's professional reputation. For many chemists of this period "speculation" was a term of derogation – it raised the specter of the much-despised *Naturphilosophie*. The prevailing atmosphere among chemists in the 1860s and 70s was one in which optimism and caution, a sense of progress and an awareness of limits, were in delicate equilibrium. That equilibrium was soon to be disturbed.

The year 1874 saw the simultaneous and independent publication of two seminal papers, by Joseph Achille Le Bel and Jacobus Henricus van 't Hoff, that came to be the founding documents of stereochemistry.[13] Grounded in different traditions and adopting different approaches, the Dutch and the French chemist nonetheless agreed on one salient point – that the cause of optical activity in organic compounds was molecular asymmetry. Furthermore, they also concurred that the presence of a tetrahedral carbon atom connected to four different substituents would be a sufficient cause of asymmetry. Le Bel, whose approach was geometrical and general, seems to have been somewhat ambivalent about whether optical activity either proved or required the presence of a tetrahedral atom.[14] Van 't Hoff by contrast was a strong realist, both ontologically (he believed in the physical existence of atoms and molecules) and epistemologically (he believed that the three-dimensional arrangements of atoms within molecules could be known). Given the kind of evidence available, Van 't Hoff had to rely on inductive arguments. He pointed out that all naturally occurring, optically active substances whose structures were seemingly secure contained an asymmetric carbon, citing, for example, lactic, malic and aspartic acids and a variety of sugars. Van 't Hoff further noted that if the asymmetry is destroyed (*e.g.* conversion of malic to maleic acid), the optical activity disappears.

Recognizing that inductive arguments are very vulnerable to a single disconfirming case, Van 't Hoff sought to confront those head on. He focused particularly on accounting for those cases in which compounds known to possess asymmetric carbons were nonetheless optically inactive, and offered three possible explanations:

- The compound in question is actually an equimolar mixture of optical isomers that cannot be resolved.

- The inherent optical activity of the compound is small or not easily measured because of solubility problems.

- The presence of an asymmetric carbon may not be sufficient for optical activity, which might also depend on the "character" of the groups attached to the carbon (meso compounds would constitute a clear case, although Van 't Hoff gave no examples).

Van't Hoff also ventured to make a number of predictions based upon his hypothesis – *inter alia* that optically active amyl alcohol must have the structure $C_2H_5(CH_3)CHCH_2OH$ and that 2-butanol was the simplest optically active alcohol. (Chancel's claim to have isolated an optically active propyl alcohol was dismissed as being due to contamination by an impurity. As in so many chemical controversies, questions of sample purity were always present.)[13b]

Van't Hoff's assertions were disputable on at least three grounds: the relevance of evidence put forward to support them; the compatibility of his theory with current ideas about the nature of molecules; and the style of his argument. He thus became the lightning rod in the ensuing controversy. Considering the opposition that his hypotheses eventually aroused it is noteworthy that it took several years before lightning struck. When it did it was accompanied by quite a thunderclap, Hermann Kolbe's notorious diatribe in which he depicted Van 't Hoff as a fantasist having "no taste for exact chemical research", who had spun out his theories on the "chemical Parnassus" whence he had arrived via "Pegasus".[15] Van 't Hoff, who was rather an unknown at this time, was shrewd enough to realize that the immoderate nature of Kolbe's attack would actually serve to publicize his hitherto overlooked hypotheses, and he actually reprinted Kolbe's tirade in the 1877 and later German editions of his pamphlet.

This incident was unfortunate in several ways. For one thing, it gave the impression that Kolbe was "an obscurantist and a fool", which he assuredly was not.[16] More consequentially, it left the impression among many later observers that Van 't Hoff's opponents had no credible grounds for opposing his proposition. That was not the case.

One source of contention was the type of evidence deemed admissible. Charles Gerhardt, the mid-19th century French chemist who contributed greatly to the acceptance of modern atomic weights and the development of notions of valence, wanted to restrict chemists to the use of chemical evidence alone; in his eyes, data derived from such sources as optical rotation measurements were irrelevant to chemistry.[17]

Gerhardt himself eventually relented on this point, and by the last quarter of the 19th-century many chemists were prepared to accept the significance of physical measurements for chemical problems. Indeed, several of Van 't Hoff's most trenchant critics argued that his proposals were flawed *precisely* because they disagreed with current physical theory.[18] For example, physics provided no basis for postulating directed forces such as those that supposedly emanated tetrahedrally from the carbon atom. Marcelin Berthelot criticized stereochemical theory from another angle, for failing to take into account the evidence from physics that pointed to the dynamic character of molecules. This criticism was supported by Victor Meyer's observation that many asymmetric compounds containing hydrogen at the asymmetric carbon, such as $CH_3CH(Br)NO_2$, had never been resolved. Meyer attributed this failure to a very rapid

interchange of isomeric forms resulting from the vibrational mobility of the light H atom.[19]

In pointing out the difficulty of incorporating dynamic considerations into structural hypotheses, critics such as Berthelot drew attention to one of the enduring problems of chemical theory.[20] Van 't Hoff himself had noted that 19th-century chemical theory was incapable of satisfactorily representing either the positions or the intramolecular motions of atoms within molecules. But as one historian has perceptively observed, "[Van 't Hoff's] proposal for a tetrahedral carbon atom solved the first problem at the expense of the second."[21] The attempt to juggle these two incompatible demands resulted in a theoretical flexibility that bordered on self-contradiction. The dilemma is nicely illustrated by Alfred Stewart's treatment of static and dynamic stereochemistry. He begins his exposition of the tetrahedral carbon atom and optical activity in this way:

"The atoms of a molecule may be supposed to be in a state of continual vibration, but this vibration merely carries them to and fro about some fixed points, so that at any time two atoms are within a certain distance of one another, and their movements never withdraw them from each other to any appreciable extent. It is therefore most convenient to neglect these atomic motions, and deal with the molecule as if it were a series of atoms whose positions with regard to one another vary only during the course of intramolecular reactions."[22]

Further on, in the context of an introduction to steric hindrance, Stewart summarizes A. W. Hofmann's work on the reaction of tertiary amines with alkyl iodides, noting that Hofmann's and related results can be explained by assuming "that in any molecule each atom vibrates about a certain centre, *and that the amplitude of vibration is not negligible in comparison with the size of the molecule itself.*"[23] No mention is made of any possible conflict between this hypothesis and the one put forth at the start of the book.

Given that there were serious objections to the basic postulates of stereochemical theory, some of which could not be refuted by its defenders, why did it nonetheless survive and attract ever greater number of adherents? Certainly the theory's ability to explain observations that were essentially inexplicable in any other convincing manner was a primary reason, especially since isomerism was a central concern of organic chemists. And there were numerous experimental results that accorded with prediction; for example, no compound lacking an asymmetric carbon showed optical activity or could be resolved into antipodes. (There were reports of optical activity in symmetric compounds such as styrene, which were eventually disproved. On the other hand, many asymmetric compounds could not be resolved, but these failures were put down to experimental difficulties.)

In addition, stereochemical theory could be extrapolated in new and fruitful directions. Van 't Hoff had already shown how the tetrahedral carbon proposal could be used to rationalize isomerism in unsaturated compounds,[13b] but it was Johannes Wislicenus who systematically applied this model to instances of geometrical isomerism in alkenes, and extended it to speculations about the mechanisms of organic additions and eliminations. This turned out to be "a bridge too far"; through an unfortunate choice of a supposedly paradigmatic addition reaction Wislicenus made a number of incorrect predictions about

the stereochemical outcomes of various reactions, for which he was severely and justly criticized by Arthur Michael.[24] Stereochemistry prospered nonetheless.

What conclusions might be drawn from this recounting? One inescapable conclusion is that, *pace* Karl Popper, an apparently fruitful hypothesis will not be done in by empirical disconfirmations and wrong predictions *alone*. For one thing, the theory can always be adjusted and appeals made to unknown factors. Arnold Eiloart described just such tactics by the adherents of stereochemistry:

"This discussion [of the catalyzed interconversion of maleic and fumaric acids] *illustrates the elasticity of stereochemical theory with regard to these transformations – an elasticity that makes it impossible to crush the theory by the pressure of facts bearing on isolated points, but indicates at the same time a vagueness which only future experiments can diminish. Meanwhile the contest between Wislicenus and his opponents continues."*[25]

As we indicated at the beginning of this article, clashes over the nature and relevance of evidence were very much to the fore in this controversy. At least as important were the interpretations drawn from that evidence. It may be difficult for us today to realize how contentious the atomic theory was in the 19th-century, especially in its physical (i.e. realist) form.[26] Many (although by no means all) stereochemical skeptics were of an older generation,[27] whose concerns about "speculation" and "hypotheses" were really concerns about the character and status of chemistry as a science.

The numerous 19th-century quarrels about induction vs. hypothesis were more about rhetoric than about how chemistry was actually done.[28] But such verbal volleys should never be dismissed as "mere" rhetoric, because they provide invaluable insight into chemists' understanding of their science and of their self-understanding. In fact, an increasing number of them began to publicly laud the value of hypotheses, among whom were some prominent stereochemists. In defending his assumptions against the criticisms of Wilhelm Lossen, Wislicenus asserted that "a speculative discussion … could bring more clarity than the certain, admittedly long, path of empirical research."[29] And Van 't Hoff chose the theme "Imagination in Science" for his inaugural address at the University of Amsterdam.[30]

"Speculation" is no longer a *casus belli* in chemistry, and a great deal of the "vagueness" in stereochemical theory has been removed with the aid of numerous and sophisticated theoretical and physical tools. It might thus be fair to ask whether the issues raised in this controversy have been laid to rest. Our answer would be – not quite. For example, on the theoretical side there have been intense discussions about whether it is meaningful to speak of the chirality of isolated molecules.[31] And in the experimental realm, despite the abundance of methodology, we still often surprise ourselves — as we see in the next case.

### Case 2. Bond-stretch Isomerism: Some Evidence is More Equal than Others

We jump forward in time, about a century, to the bond-stretch isomerism controversy. At first glance this story might not seem in any way comparable to the preceding one, particularly in terms of significance — interest was pretty much limited to inorganic

chemists, with virtually no awareness in the rest of the chemistry community, let alone the scientific community at large. Nonetheless, we feel there are some important lessons here, concerning the nature of acceptable evidence and the settling of controversies thereby, that intriguingly resonate with the earlier story.

The controversy basically turns on the question of whether two different isomers of a molecule, differing essentially *only* in the length of one of the bonds, might both be sufficiently stable (thermodynamically and kinetically) to be isolated. This is an issue of potentially wide-ranging scope,[32,33] but we focus here only on its application to a particular class of species, metal-oxo (or metal-sulfur, in a couple of examples) coordination complexes. A detailed history was published a few years ago by Parkin;[34] following is a much briefer summary.

In 1970 Chatt reported a series of oxomolybdenum complexes, all giving acceptable elemental analyses for the formula $MoOX_2L_3$, but either blue or green depending on the phosphine ligand L and the halide (or pseudohalide) ligand X, assumed to be geometric isomers.[35] In one case, for L = PMe_2Ph and X = Cl, *both* blue and green products could be isolated, depending upon conditions. The two species in solution exhibited identical electronic and ^1H NMR spectra (solutions of the green compound rapidly changed to blue) but did show different IR bands (for crystalline samples as Nujol mulls), at 943 and 954 cm^{-1} for green and blue, respectively.

The crystal structure of the blue isomer revealed that it had the <u>cis</u>, <u>mer</u> configuration Ia; initially it was suggested that the green isomer was <u>trans</u>, <u>mer</u> II.[36] However, the crystal structure of green $MoOCl_2(PEt_2Ph)_3$ (suitable green crystals of the PMe_2Ph analog were not obtained), determined the next year, showed the same <u>cis</u>, <u>mer</u> configuration (Ib) as blue $MoOCl_2(PMe_2Ph)_3$.[37] Comparing the two molecular structures, the Chatt group found i) the rotational orientation of the organic groups on the phosphine ligands was quite different; and ii) the Mo=O bond distance was considerably shorter for blue Ia than for green Ib — 1.676(7) vs. 1.801(9) Å, with smaller differences in the Mo-Cl distances and some bond angles. They proposed that this represented "a new type of isomerism, involving two equilibrium arrangements of ligands, which differ in the distortions of the highly strained co-ordination polyhedron of the metal" — in other words, that non-bonded interactions involving the phosphine ligand substituents were primarily responsible — for which they offered the term "distortional isomerism."
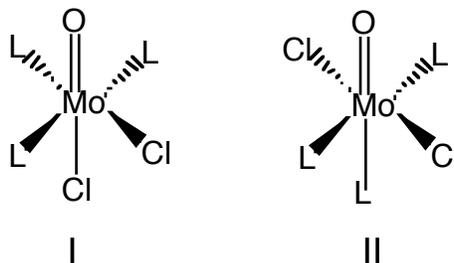
a, L = PMe_2Ph
b, L = PEt_2Ph

Interest in this phenomenon was not really fired until Wieghardt reported, in 1985, that salts of the cationic complex $[CnWOCl_2]^+$ (Cn = κ^3-N,N',N''-trimethyl-1,4,7-

triazacyclonanone) could be crystallized in two different forms, again one blue and one green. In contrast to $MoOCl_2(PMe_2Ph)_3$, the two forms each appeared to be indefinitely stable in solution (acetonitrile), although addition of water to the green solution caused an immediate color change to blue. The IR spectra differed only in the position of the peak assigned to W=O stretching (980 and 960 cm^{-1} for blue and green respectively). The elemental analyses agreed well with each other and the nominal formula. Most intriguingly, the molecular structures of the two apparent isomers were identical in *all* respects except for the W=O bond lengths (blue, 1.72(2); green, 1.89(2) Å) and, to a lesser degree (possibly below statistical significance), the W-N distance trans to O (blue, 2.37(2); green, 2.32(2) Å).[38]   This finding appeared to exclude Chatt's interpretation, as there are no differences in ligand orientation, steric effects, packing, or anything of that nature — just a difference in bond length. A number of other examples (see Parkin's review[34] for specifics) from several different labs around the same time also suggested that M=O distance, not ligand orientation, was central to this form of isomerism.

Two papers by Hoffmann and collaborators appeared in 1988, reporting calculations suggesting that it might indeed be possible to have a double minimum along a coordinate essentially representing one bond distance.[39,40] They proposed the term "bond-stretch isomerism" as a more appropriate descriptor for this behavior, borrowing from earlier work on quite different classes of molecules.

By this point, with a number of apparently solid examples and a plausible theoretical framework in hand, bond-stretch isomerism began to be seriously discussed at meetings, as well as in reviews, monographs and even textbooks — although often hedged with a degree of residual doubt. For example:

"To our knowledge this is the only suggestion that molecules of any kind have two stable structures with substantially different bond distances. Therefore, if distortional isomerism is a real phenomenon and not an artifact of some kind, it has significant implications beyond metal-ligand multiple bonding".[41]

However, in 1991 Parkin showed that the crystallographic support for bond-stretch isomerism, at least in the $MoOCl_2L_3$ class of complexes, was indeed an artifact.[42] Crystals of green $MoOCl_2(PMe_3)_3$ (which had previously been found in both blue and green forms) contained two independent molecules in the asymmetric unit, with quite different Mo=O bond lengths, 1.698(8) and 1.866(7) Å. On the other hand, the crystals exhibited only a single IR band in the Mo=O stretching region. Crystallography on a crystal from a different batch yielded two *different* Mo=O distances (1.772(12), 2.154(8) Å). Clearly these could not all be real, stable molecules.

The anomaly results from contamination with $MoCl_3L_3$, which can co-crystallize with $MoOCl_2L_3$ in almost any proportion. Since substitution of $MoCl_3L_3$ for $MoOCl_2L_3$ effectively puts a Cl where an O is supposed to be, the calculated structure (based on the assumption that one is dealing with pure $MoOCl_2L_3$) will have an apparently long Mo=O distance, as Mo-Cl is longer than Mo=O. Since the electron density of Cl is much higher than that of O, even relatively small amounts of contamination can cause a significant perturbation. Furthermore, contamination of blue $MoOCl_2L_3$ by yellow $MoCl_3L_3$ gives a green sample; and the contaminant is paramagnetic, so it will not show up in the NMR except as broad, substantially shifted signals — which were observed, once looked for.

A series of samples of $MoOCl_2L_3$ deliberately contaminated with increasing amounts of $MoCl_3L_3$ showed a steady increase in the apparent Mo=O bond distance, along with the apparent degree of green-ness.

At about the same time, Enemark reexamined both the Chatt and Wieghardt complexes by chromatography and spectroscopy, and found decisive evidence for mixtures.[43, 44] And higher-level theoretical work indicated that the proposed mechanism(s) would *not* produce energy differences, along a single stretching coordinate, sufficiently large to permit two isomers to exist as stable species.[45]

General consensus that the controversy was over was quickly reached,[46, 47, 48] making it appear that this was a rather straightforward case with little in the way of take-home lessons, besides perhaps being more careful with crystallographic results. In fact, though, we believe the controversy represents another illustration of the fundamental issue here — what counts as evidence — and in particular the dominant status that is (unconsciously?) granted to crystallographic evidence in structural investigations. Here is a typical quote (from a book written by spectroscopists!):

"X-ray crystallography is the ultimate arbiter of chemical structure .... Spectra and chemical reactions alone can never tell you the structure of a compound. All they can do is give you pieces of information".[49]

At the same time, routine crystallography has become so automated — "black-boxed", to apply a term from science studies[50] — that there is a tendency to accept the semi-automated process leading to the structure solution without question, in the absence of any obvious difficulty. As noted just above, there is also a tendency to ignore discordant findings from methods considered less reliable, such as spectroscopy, in the face of an "ultimate" answer from crystallography. So crystallography becomes a particularly privileged form of evidence — results are difficult to challenge on either intrinsic or extrinsic grounds — while all other forms are heavily discounted or even ignored.

We can see this playing out over the course of the bond-stretch story. Hints that something might be wrong were available from the very beginning. For example, in the original Chatt work, the identical electronic and NMR spectra of the two "isomers" as well as higher Cl content in the elemental analyses for the green form might have argued against simple isomerism. In Wieghardt's tungsten case, differing electronic spectra for the "isomers" can (in retrospect) clearly be seen to be due to superposition, while the color change on addition of water seems much more indicative of a chemical reaction than an isomerization. But none of these anomalies raised any concern about possible crystallographic errors — even among trained crystallographers. Only a clear red flag *within* crystallography— four different apparent Mo=O bond lengths for a single complex — triggered Parkin's systematic reinvestigation.

Even after the controversy seemed to be settled to the satisfaction of most of the community, we can still see the effects of privileging evidence. Note that the differing IR bands assigned to Mo=O stretching were *not* accounted for by the contamination explanation, as the contaminant contains no Mo=O bond! Commentators either ignored this[42] or attributed it to an error in the initial report.[43] This brings us full circle in the consideration of crystallography as privileged evidence. Initially, contrary evidence from any other source had little or no impact on the acceptance of crystallographic evidence

supporting bond-stretch isomers, while the IR findings appeared to be generally consistent with the crystallography. As soon as the crystallography was found to point the other way, the IR evidence was no longer consistent; but even though unexplained, it was completely discounted.

The IR problem was resolved for the $MoOCl_2L_3$ system only later, when Gibson[51] found that blue Ia can be obtained in two different crystalline forms that exhibit the two different IR stretching bands reported by Chatt. The IR differences disappear in solution, so this is a consequence of crystal packing — a familiar phenomenon. On the other hand, the complex $NbSCl_3(PMe_3)_3$ has been obtained in two crystalline forms, orange-yellow and green, that exhibit different apparent Nb=S bond lengths and stretching frequencies; the latter difference persists in solution, apparently ruling out a solid-state effect explanation.[52, 53] But this residual unexplained discrepancy does not attract much if any attention (it isn't even mentioned in the recent review cited above[33]). In the presence of crystallographic results, no "lower" form of evidence counts for much of anything.

One might well be tempted to view this story as of a quite different nature from the preceding one. In Kuhnian terms, the birth of stereochemistry looks much more like a fundamental, even revolutionary development in the history of chemistry, as opposed to the apparently puzzle-solving, normal science of the birth and demise of bond-stretch isomerism. Such a conclusion, however, depends heavily (and unfairly) on hindsight. While it was going on, the controversy over bond-stretch isomerism seemed to have considerable potential as a fundamental change in chemical understanding. Also, of course, it is very difficult to characterize a controversy while one is in the middle of it. All one can really do then is consider the evidence — and as we have tried to show, the question of which evidence merits consideration was central to *both* cases.

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[2] Others have recognized this inadequacy as well; there are already imaginative efforts underway to repair it, aimed at children in elementary and secondary schools, *e.g.*, Project SCOPE <http://scope.educ.washington.edu>, retrieved 24 December 2002 from the World Wide Web.

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