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Structure as Abstraction

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Abstract

In this paper I argue that structure in chemistry is a creature of abstraction: attending selectively to structural similarities, we neglect differences. There are different ways to abstract, so abstraction is interest-dependent. So is structure. Firstly, there are two different and mutually irreducible notions of structure in chemistry: bond structure and geometrical structure. Secondly, structure is relative to scale (of energy, time and length): the same substance has different structures at different scales, and relationships of structural sameness and difference vary across the scales. However, these facts have no tendency to undermine structure's claim to reality, or its metaphysical seriousness.

1. Introduction

Any philosopher who wishes to engage with chemistry has to engage with structure, which chemists use to individuate and name substances, and to understand their behaviour (see Hendry 2016). But structure is an abstract concept, so it should not be surprising that it covers more than one thing: different parts of physics, chemistry and biology appeal to different kinds of structure exemplified at different scales of energy, length and time. In this paper I identify two distinct kinds of structure at work in chemical explanation: bond structure and geometrical structure. If a structure consists of relations and relata, then bond structure and geometrical structure feature the same relata (atoms and ions), but related in different ways. I then illustrate two distinct ways in which structure is relative to scale: firstly, the very same substance may have different structures at different scales; secondly, the sameness and difference of structures varies with scale. Finally, I argue that recognising that structure is a creature of abstraction makes all this plurality of structures unsurprising, and that this does not undermine the robust reality and metaphysical seriousness of structure.

2. Two Kinds of Structure

2.1. Bond Structure

The International Union for Pure and Applied Chemistry (IUPAC) has developed a systematic nomenclature for organic chemistry, under which the name of a substance is determined by its full structural formula (see Leigh et al. 1998, Chapter 4), which represents what I will call ‘bond structure’. Take for instance 2 4 6-trinitrotoluene, better known as TNT:

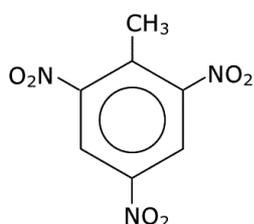


Figure 1. The bond structure of TNT. Positions 3 and 5 are occupied by hydrogen atoms, which are conventionally left out for clarity.

The name ‘2 4 6-trinitrotoluene’ comes from its being regarded as a substituted version of toluene (or methylbenzene), which consists of six carbon atoms bound together in a six-membered structure called a benzene ring, with a methyl (-CH₃) group attached. It is *trinitrotoluene* because it contains three substituent nitro- groups (-NO₂), and it is 2 4 6-trinitrotoluene because these three groups are placed at the second, fourth and sixth places, counting clockwise around the benzene ring, starting from the methyl group as 1.¹ TNT’s

¹ In fact the name ‘2 4 6-trinitrotoluene’ predates the IUPAC nomenclature, but I mention it because it is the origin of the widely-used abbreviation ‘TNT,’ and it too is based on bond structure.

structure provides its name, and explains its chemical and physical properties, including its use as an explosive.

Bond structure was introduced into organic chemistry in the 1860s. During the early nineteenth century chemists had begun to analyse the elemental composition of compound substances, and represent them using chemical formulae. This brought the recognition that it is possible for distinct substances—*isomers*—to have the same chemical composition. Isomerism required a theory of structure, to explain how the same amounts of the same elements might be combined in different ways to form different substances. In the 1860s there appeared a number of different but equivalent ways of representing the bond structure of molecules, employing diagrams on paper or three-dimensional models (see Rocke 1984, 2010). They were equivalent in the sense that the structures they represented, attributed through inferences based on chemical evidence, were identical in respect of the connections they represented between the atoms. They were constructed under rules of valence which determined, for each element, how many atoms of the various other types it could be bonded to in a molecule. By the mid-1870s, graphical formulae came to be understood as embedded in three-dimensional space. The embedding made available new kinds of chemical evidence for distinguishing between structures. Jacobus van't Hoff explained why there are two isomers of compounds in which four different groups are attached to a single carbon atom by supposing that the valences are arranged tetrahedrally: the two isomers are conceived of as mirror images of each other. Adolf von Baeyer explained the instability and reactivity of some organic compounds by reference to strain in their molecules, which meant distortion away from their preferred geometry (Ramberg 2003, Chapters 3 and 4). These stereochemical theories were intrinsically spatial, because their explanatory power depended precisely on their describing the arrangement of atoms in space. From the beginning of the twentieth century, bond structures became dynamic, as chemists and physicists began to develop models of how molecules vibrate and rotate, to explain their spectroscopic behaviour (Assmus 1992). This involved filling out structures with details, such as bond lengths, bond angles and force constants, which had previously been absent.

2.2. Geometrical Structure

A distinct conception of structure developed quite independently within crystallography. Crystals have been classified on the basis of their shapes and symmetry properties since the eighteenth century, and the general idea that these arise from their internal structure has been widespread since that time. However, the development of X-ray crystallography allowed the integration of structural theory with experimental method.² The structure of a crystal can be specified fully in terms of the (average) relative positions of its constituent atoms and ions, or (more generally) correlations between nuclear centres. This notion of 'structure' may seem strangely inclusive, because even fluids (i.e. liquids and gases) can be said to have structure in this sense: wherever there are physical interactions between the constituent atoms and molecules of a fluid, there will be statistical correlations between their positions.

² See Greenwood 1968, Chapter 1 for a scientist's history of structure in crystallography.

For a more detailed discussion, consider sodium chloride (NaCl), which consists of positively-charged sodium ions and negatively-charged chloride ions in a one-to-one ratio. *Solid* NaCl is composed of ‘two interpenetrating face-centred cubic sub-lattices’ (Greenwood 1968, 48), in each of which a sodium (or chloride) ion is surrounded by six chloride (or sodium) ions arranged octahedrally. The crystal may therefore be considered as a (potentially infinite) array of unit cells, each cell containing four sodium ions and four chloride ions (see Figure 2).³

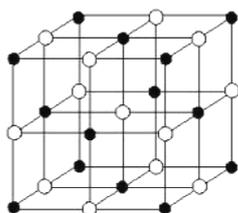


Figure 2. Solid sodium chloride, after Greenwood 1968, 48.

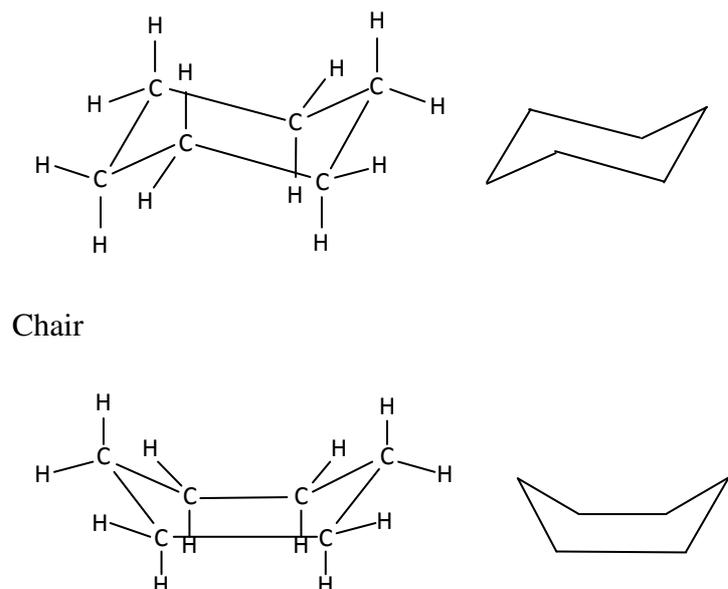
From a theoretical point of view, the structure of an ionic crystal (pretty much) arises from the way its constituent ions pack together so as to maximise interactions between ions of opposite charge, and minimise interactions between those of like charge, given the charges on the ions, the relative size of the ions, and the stoichiometry of the substance (i.e. the compositional ratio). G.N. Lewis (1913) argued that the structure of ionic substances such as potassium chloride (KCl) can be represented without appeal to any bonds between atoms. Lewis considers a proposal to represent ionic bonding in potassium chloride with a directed arrow, as $K \rightarrow Cl$, which would signify that an electron has passed from K to Cl. He argues that this would be misleading, because *even if (per impossibile, given the qualitative identity of electrons), one could tell which electron had come from which potassium atom, the bonding that holds the substance together does not arise from that donation. Rather it arises from attractive forces between the opposite charges that result from that donation.* Furthermore, ‘a positive charge does not attract one negative charge only, but all the negative charges in its neighborhood’ (1913, 1452). In potassium chloride, the bonding is electrostatic and therefore radially symmetrical. An individual ion bears no *special* relationship to any *one* of its neighbours, but the same relationship to each of them. This relationship is non-directional, and so cannot be represented by the lines connecting atoms that appear in structural formulae. So even though, in the representation of the structure of NaCl (Figure 2, above), there are sometimes lines between neighbouring ions, these are merely an aid to the eye in discerning the three-dimensional shape of the unit cell. If Lewis’ argument is accepted, then some substances have geometrical structure but no bonds, and therefore no bond structure. There is bonding, because something or other (to a large extent, electrostatic attraction) holds the ions together in the lattice. There is no bond in the more concrete sense which is important to Lewis’ argument: a localised physical relationship between two atoms or ions, which is represented by the lines between atoms in molecular structure diagrams.

³ There are four of each kind of ion in a cell because the ions at the corners, edges and faces are shared between appropriate numbers of neighbouring unit cells. Thus for instance ions at the corners count as one eighth.

Although the structure of an ionic substance is characterised by the relative positions of the ions, as represented by distances between the ionic centres (which can be regarded as the sum of two 'ionic radii'), the ions are not static: they vibrate around their equilibrium positions to an extent that is dependent on temperature. Since the structure survives such motions, it must be characterised by small regions around *average* relative positions. At 801°C, however, enough of the constituent ions have enough energy to overcome the forces holding them in the lattice, and the structure begins to break down, forming a liquid consisting mostly of dissociated ions. Since the ions are now free to move under electrical forces, the molten salt is an electrical conductor while the solid is an insulator. Clearly, the geometrical structure of solid NaCl does not survive transition to the liquid phase. Molten NaCl, like other liquids, has its own structure, which can be characterised in terms of radial distribution functions describing the probability density of various molecular or atomic species in terms of their distance from a central atom. Once again, the structure is fully specified by geometrical relations between the constituent ions, and is phase-specific, in that it exists only within a particular state of aggregation. Water is similar. Depending on pressure, ice is described as displaying one of a number of different structures (see Eisenberg and Kauzmann 1969, Chapter 3; Finney 2004), in all of which hydrogen bonds play an essential role, linking together the partial negative charges on oxygen atoms to the partial positive charges of protons on neighbouring H₂O molecules. As in NaCl, this structure breaks down on transition to the liquid phase. It is not that the H₂O molecules cease to form hydrogen bonds with each other, or that these bonds cease to constrain their relative positions and orientations: it is rather that, in this higher temperature range, the H₂O molecules are freer to move around them, and the hydrogen bonds themselves are constantly forming and reforming. So even though, at short range, the structure of liquid water is quite like that of ice, over longer ranges this breaks down, a fact which is evident in the radial distribution functions used to describe its structure (see for instance Eisenberg and Kauzmann 1969, 157). Hence structure also varies with (length) scale. I will return to the relativity of structure to scale in Section 4.

3. The Differences Between Them

The bond structure of a substance, the framework of bonds between its constituent atoms or ions, is quite different from its geometrical structure, if we understand the latter to be constituted by atoms or ions being localised within small regions around fixed relative positions. Consider, for instance, cyclohexane, which is a cyclic alkane with molecular formula C₆H₁₂. Six carbon atoms are bonded together in a ring, and to each is attached two hydrogen atoms. The bond structure of cyclohexane is easily distinguished from its geometry, because the very same bond structure can explore a range of different geometries, or *conformations*. In fact individual cyclohexane molecules are constantly in motion, exploring the different possibilities allowed by its bond structure. Cyclohexane's lowest energy conformation is called the 'chair.' Many thousands of times a second, the molecules flip between the chair and higher energy conformations such as the 'boat' (see Figure 3).



Chair

Boat

Figure 3. Conformations of cyclohexane: in the images on the right, the hydrogen atoms are left out for clarity.

Consider any pair of hydrogen atoms which are attached to the same carbon atom. These two hydrogen atoms may be geometrically adjacent to each other in the sense that they are not far apart, and no other atom is between them. They are in each other's line of sight. But they are not bonded directly to each other, and so are not adjacent in the bond structure. Secondly, the bond structure is compatible with wide variation in the relative positions of the atoms, and hence different geometries. Across all the different conformations, however, one thing remains constant: the pattern of connections between the atoms, including the carbon ring.

Clearly, geometrical structure and bond structure are not the same thing. What is the relationship between them? Is one more basic or fundamental than the other? We saw earlier that some substances have a geometrical structure without a bond structure. Furthermore, every molecule has a geometrical arrangement, in the sense that its parts are distributed somehow in space, and they bear spatial relations to each other. Given that not every substance has a bond structure, this seems to favour geometrical structure over bond structure for the leading role in the relationship between them: geometrical structure is a more general, and so more basic notion, because having a geometrical structure is necessary, even if not sufficient, for having a bond structure. But that would be misleading for two reasons. Firstly, it is not so clear that having a geometrical structure is necessary for having a bond structure, at least in any way that would make it more basic. From a mathematical point of view, a bond structure is a set-theoretic object: if we take the set of a molecule's constituent atoms, a bond structure is some subset of the Cartesian product of this set with itself. This set-theoretic structure is all that is needed to fulfil one important explanatory role for bond structure in chemistry: the combinatorial problem of explaining how many structural isomers may share a particular molecular formula. And from a purely logical point of view, something might have

this set-theoretic structure without it (or its parts) being located in space at all. In fact this is just how the explanatory role of structure may have been seen by one pioneer of structure in chemistry in the 1860s, Edward Frankland (see Hendry 2008). Even though bond structures did eventually come to be regarded as embedded in space, that was an *extension* of the explanatory role of structure to account for specific forms of geometrical and optical isomerism. From a purely mathematical point of view, then, geometrical relationships do not determine bonding relationships. Perhaps bond structure is only contingently embedded in space. But the mathematical point of view is not all there is, and a bond structure is not just a graph: it is a graph generated by a particular *physical* relation, the chemical bond. Is a *bond* structure something that is necessarily embedded in space? To answer that question we need to know more about what a bond is.⁴ Bonds clearly have geometrical constraints: distinct bonds do not overlap or cross, and it may well be that fixing the geometrical configuration *physically* (though not mathematically) determines the bond structure uniquely, in the following way.

In the ‘Atoms in Molecules’ (AIM) programme, Richard Bader and others have sought to recover the traditional bond structure of molecules as a topological feature of a molecule’s electron-density distribution (see Bader 1990; Popelier 2000). From the electron-density distributions for many different molecules can be defined ‘bond paths’ between atoms that generate ‘molecular graphs’ which are strikingly close to the classical molecular structures of those molecules. As Bader puts it, ‘The recovery of a chemical structure in terms of a property of the system’s charge density is a most remarkable and important result’ (1990, 33). This seems to make geometrical structure prior to bond structure. The quantum-mechanical calculations that underlie AIM, like all tractable quantum-mechanical calculations concerning molecules, begin by making the Born-Oppenheimer approximation, which involves separating nuclear and electronic variables, and fixing (or ‘clamping’) the nuclear positions. The electric field due to the nuclei is then used as a constraint on the calculation of a resultant electron density distribution. If the nuclear positions are well chosen (i.e. correspond to the nuclear positions in the molecule’s equilibrium geometry), then from the resulting electron density distribution this procedure allows bond structure to be ‘read off’ nuclear geometry, *modulo* a range of physical laws, plus the separation of nuclear and electronic motions.

Modal and explanatory considerations suggest instead that the bond structure of a substance is something over and above its geometrical structure. Firstly, in molecular substances bond structure may survive phase transitions which geometrical structure cannot. Thus, for instance ice, liquid water and steam all display different geometrical structures, but the bond structure of its molecules, as represented in its structural formula (a central oxygen atom bonded to two hydrogen atoms) remains constant across the different states of aggregation.⁵ Secondly, in the entities that have both, bond structure is explanatorily prior, in the sense that a molecule’s bond structure is compatible with a range of different geometrical arrangements

⁴ That is not merely a rhetorical deferment: the answer is simply unclear. In Hendry 2008, 2010 I discuss two opposed accounts.

⁵ With one proviso: that in liquid water a small proportion of H₂O molecules dissociate into protons and hydroxyl ions. In contrast, liquid cyclohexane is a more neatly molecular substance.

of its parts, and determines which arrangements it may have. Consider once again the conformations of cyclohexane. In that case, the bond structure is a constant while the molecule moves between quite different geometrical configurations. Indeed the persistent bond structure *explains* the energetic ordering of the various conformations. The chair is the lowest-energy conformation because in that geometry the bond structure experiences the least strain: that is, the arrangement of bonds around individual carbon atoms is closest to tetrahedral, and the hydrogen atoms are less crowded, reducing their mutual (repulsive) interactions.

4. Structure and Scale

We saw earlier that the structure of an ionic solid such as NaCl is constituted by the *average* relative positions of the atoms or ions. It follows that structure in this sense must depend on the energy range and timescale over which that average is taken. The structure of solid NaCl, as we saw, breaks down above its melting point, and so if we choose a wide enough energy range, the long-range geometrical order of solid NaCl is lost. Similarly, ice, liquid water and steam differ in the way that H₂O molecules interact and aggregate within them, but count as the *same* substance because each is formed from populations of H₂O molecules, their distinct structures arising from interactions among those populations.

Once it is acknowledged that even in the solid state, atoms and ions are constantly in motion, it becomes clear that structure varies with timescale too. Eisenberg and Kauzmann (1969, 150-2) provide an elegant argument illustrating this. H₂O molecules in ice undergo vibrational, rotational and translational motions, the molecules vibrating much faster than they rotate or move through the lattice. At very short timescales (shorter than the period of vibration), the structure of ice is a snapshot of molecules caught in mid-vibration. It will be disordered because different molecules will be caught in slightly different stages of the vibration. As timescales get longer, the structure averages over the vibrational motions, and then (at yet longer scales) the rotational and translational motions. This yields successively more regular but diffuse structures. None of this should be surprising: different kinds of structural feature persist over different energy ranges and timescales, and when ice interacts with other physical processes, such as electromagnetic radiation from different parts of the frequency spectrum, they will interact in ways that are characteristic of that frequency range. The fact that other things are going on at some other frequency range is often simply irrelevant. I conclude that the ice has different structures at different scales, and see no particular reason to privilege any scale.

A second aspect of the scale-relativity is that relationships of structural sameness and difference vary across different scales. This variation can occur at two different levels: in the way that molecules interact to form macroscopic substances, and in the structural distinctness of the molecules themselves. At the level of the substances, consider Louis Pasteur's achievement in separating, by hand, crystals of the L- and D- forms of sodium ammonium tartrate, obtained from a racemic solution (an equal mixture of the two). This is a famous

exemplar of structural explanation in science, and its experimental demonstration, for the L- and D-forms are enantiomers: structures which are mirror images, but which cannot be superimposed on each other. It is less well known that had Pasteur attempted the separation at a higher temperature than he did, he would likely have failed, because above 26°C the L- and D-salts form a single racemate (Kauffman and Myers 1975).⁶

At the level of the sameness and difference of molecular consider substituted biphenyls, which contain pairs of benzene rings connected by a single bond (see Figure 4).

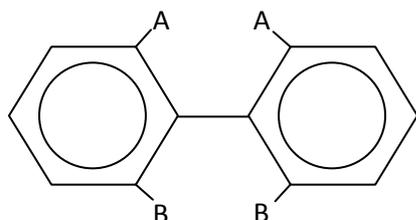


Figure 4. Substituted biphenyls.

When the rings are substituted by functional groups A and B in the four positions shown, the possibility of a new form of stereoisomerism arises—the molecule can in principle exist in two enantiomeric forms—but the isomerism is interestingly temperature dependent. Other things being equal, single carbon-carbon bonds, like the one connecting the two benzene rings, allow free rotation of the groups they connect. If the groups A and B are relatively small (e.g. single atoms such as hydrogen or fluorine), then that rotation will be relatively unrestricted. In such cases the two enantiomers will not be separable at room temperature because they will readily interconvert, or if they can be separated then they will racemize rapidly. However, as the groups A and B increase in size they will increasingly hinder the rotation. Where A and B are both bulky groups such as $-\text{NO}_2$, or $-\text{COOH}$, the two enantiomers will be separable and will racemize only slowly. So for any given substituent groups A and B, the physical distinctness of the enantiomers disappears above a characteristic temperature. Hence structural sameness and difference is a temperature- (and therefore energy-) dependent phenomenon.

5. What is Structure?

If chemists appeal to two mutually irreducible kinds of structure, and a single substance may have more than one structure, doesn't that make structure oddly perspectival, or interest-dependent? There is nothing odd as long as we understand structure to be a creature of abstraction: relationships among a substance's parts (at the atomic scale) which remain invariant over specific ranges of physical conditions. Imagine some chemical substance S within some range of physical conditions C. Let R be the relationships among its parts which survive across C. Over a wider range of physical conditions, some subset of R will be maintained. The weakest structure we can specify for a substance is the set of relationships

⁶ I would like to thank John Hudson for the reference.

among its parts that survive across the full range of conditions under which it exists. More can be said about shared structure over narrower ranges of conditions, but we need to find the right level of generality or scale to find commonality among a diverse group of things: right from the point of view of understanding what the substance can do, what it can have done to it, and what it can survive. In short, we obtain structures by abstraction, a form of partial consideration, or selective attention (see Heil 2003, 172). This undermines neither the reality nor the metaphysical seriousness of structure, for we are selectively attending to (and also abstracting away from) genuine physical properties and relations such as charge, mass and spatial proximity. Even the chemical bond can be regarded as a topological feature of a molecule's electron density distribution. These are all genuine properties and relations, rather than (monadic or polyadic) predicates, because they are directly causally efficacious: charges and masses interact via well-known physical laws in ways that depend on spatial proximity, and crystallographers bounce X-rays off electron density. It is the *selection* which is interest-dependent, and therefore plural, but we are selecting only among the real.

I will conclude by emphasising two consequences of thinking about chemical structure in this way. Firstly, the structures *in re* that we have been exploring in this paper should be distinguished from the structures of structural realism. That position is sometimes motivated by the thought that we can know the mathematical structure of phenomena, but not the nature of the things that generate them. In chemistry there should be no distinction between structure and nature, quite the reverse: there are good reasons to think that the nature of a substance is simply its structure.⁷ Although this is not the place to pursue a detailed argument for microstructural essentialism, here is a sketch of how I think the argument should go. Nancy Cartwright has defended the idea that we can know the (Aristotelian) natures of things through what she calls '*the analytic method in physics*' (1992, 49):

[T]o understand what happens in the world, we take things apart into their fundamental pieces; to control a situation we reassemble the pieces, we reorder them so they will work together to make things happen as we will. You carry the pieces from place to place, assembling them together in new ways and new contexts. But you always assume that they will try to behave in new arrangements as they have tried to behave in others. They will, in each case, act in accordance with their nature. (1992, 49)

Chemical structures are very concrete examples of this. If we wish to employ the capacities and susceptibilities of some chemical substance, we must assemble it in the right way from its microstructural parts, or bring it ready made. What is it that carries the capacities and susceptibilities of a substance from place to place, or underpins their coming into being if we have to assemble it *in situ*? Its structure.

⁷ The story of the chemical bond might seem to provide more fertile ground for structuralism. Here is a relation whose existence is hypothesised in the 1860s, but whose nature is unknown at that time. But the *nature* of the chemical bond is an ongoing foundational issue in theoretical chemistry. A bare structuralism, in which we regard the bond simply as whatever generates molecular graphs, would be an abdication of this foundational enquiry.

Another consequence is that if chemical classification is based on structure, and there is more than one way to abstract from the structure of a given substance, then the requirement that schemes of classification should be hierarchical *must* be wrongheaded.⁸ One would in general expect just the opposite. Take NaCl: it shares structural features with diverse groups of substances: abstracting away from its chlorine content it contains sodium, which it has in common with (for instance) sodium bromide; abstracting away from its sodium content it contains chlorine, which it has in common with potassium chloride and carbon tetrachloride; abstracting away from its elemental components entirely, it is a face-centred cubic crystal, a structure it shares with most of the alkali-metal halides, alkaline-earth metal oxides and many other ionic substances. The different sets of substances which share different aspects of its structure overlap: why shouldn't they? In so far as structure underwrites chemical classification, the hierarchy condition must fail.

⁸ For defence of the hierarchy requirement see Ellis 2001. For critical attention see Khalidi 1998, Tobin 2010 and Hendry 2016.

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