

Marginalia

Molecular Beauty

Roald Hoffmann

Recently my wife and I were on our way to Columbus, Ohio. After I settled on the airplane, I took out a manuscript I was working on—typical for the peripatetic obsessive chemist. Eva glanced over and asked, "What are you working on?" I said, "Oh, on this beautiful molecule." "What is it that makes some molecules look beautiful to you?" she asked. I told her, at some length, with pictures. And her question prompted this column.

Beauty is in the eye of the beholder—who, one might then think, had better be a chemist, a person privy to the codes of molecular structure and function (1). The chemist has gone through a rigorous education and has much experience, and these have prepared him uniquely to appreciate the true loveliness of dodecahedrane or cortisone or $Gd_{12}I_{17}C_6$. Outsiders are excluded.

I refuse to accept that. Aesthetics is deeply rooted in our soul. Our sundry actions touch that core of aesthetics, and draw upon its pleasure-giving principles, in whatever we do. The aesthetic sense is both innate and socially and culturally conditioned. It certainly can benefit from teaching. For instance, scientists tend to go for M. C. Escher, but they need to look and think, and perhaps be guided to ways of looking and thinking, at Carlo Crivelli and David Hockney. So it is with people outside chemistry—I'm sure they can learn what makes a chemist's soul jump with pleasure at the sight of a certain molecule.

In a series of essays I will look at what makes a molecule beautiful. An aesthetic response to a Vivaldi opera or a poem by Pasternak is not likely to be determined by just one factor. It's no different for molecules. They are pleasing to chemists because of their shape or structure, but also they may please because of some complex function they perform; or their internal music—the quantized motions they undergo; or the struggle that may have gone into their creation by man, or the intricacy of their construction by nature; perhaps their pivotal role in world culture; perhaps their economic significance.

Let's begin with the obvious, which was not accessible to us until this century: namely, structure. Molecules have a shape. They are not static at all, but always vibrating. Yet the average positions of the atoms define the shape of a molecule.

That shape can be simple, or it can be exquisitely intricate. Structure 1 is a molecule with a simple shape, dodecahedrane. This $C_{20}H_{20}$ polyhedron (the polyhedron shows the carbons; at each vertex there is also a hydrogen radiating out) was created in 1982 by Leo Paquette and his co-workers (2). It was a major synthetic achievement, many years in the making. The Platonic solid of dodecahedrane is simply beautiful and beautifully simple.



1



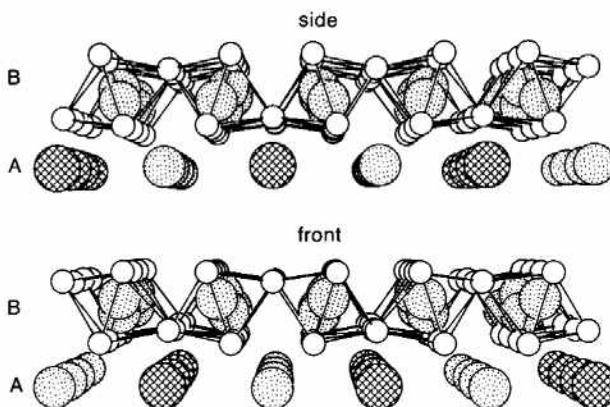
2



3

heide's group (4, 5). All simple, symmetrical, and devilishly hard to make.

Let's try a structure whose beauty is a touch harder to appreciate. Arndt Simon, Tony Cheetham, and their co-workers have recently made some inorganic compounds of the formula $NaNb_3O_6$, $NaNb_3O_5F$, and $Ca_{0.75}Nb_3O_6$ (6). These are not discrete molecules but extended structures, in which sodium, niobium, and oxygen atoms run on in a small crystal, almost indefinitely. Below (drawing 4) is one view of this truly super molecule.



4

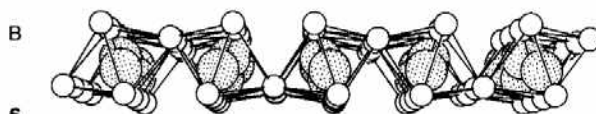
Some conventions: the white balls are oxygen (O), the stippled ones niobium (Nb), the crosshatched ones sodium (Na). The perspective shown chops out a chunk from the infinite solid, leaving it up to us to extend it, in our mind, in three dimensions. That takes practice.

Deconstruction aids construction. So let's take apart this structure to reveal its beauty. In drawing 4 we clearly see layers or slabs. One layer, marked A, is shown in structure 5. It contains only niobium and sodium atoms.



5

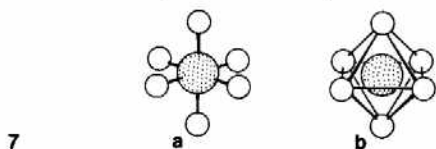
The other layer, B (structure 6), is made up of niobium and oxygen atoms arranged in a seemingly complex kinked latticework. We need to take it apart.



6

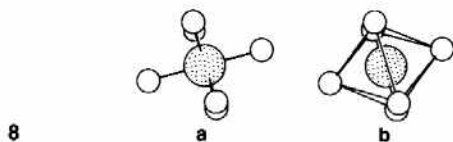
In layer B, the building block of the slab is an octahedron of oxygens around a niobium. One such idealized unit is shown in drawing 7, in two views. In 7a, lines (bonds) are drawn from the niobium to the nearest oxygen. In 7b these lines are omitted, and instead the

oxygens are connected to form an octahedron. Which picture is right? Which is the true one? Sorry—both are. Or, better said—neither is. Three-dimensional molecular models, or their two-dimensional portrayals, which is what we have before us, are abstractions of reality. There is no unique, privileged model of a molecule. Instead, there is an infinite variety of representations, each constructed to capture some aspect of the essence of the



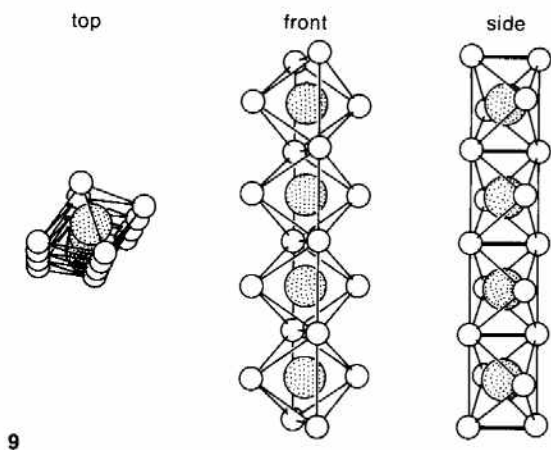
molecule. In 7a the essence is deemed to lie in the chemical bonds, a pretty good choice. These are Nb-O; there are no O-O bonds. Yet portrayal 7b draws lines between the oxygens. This representation seeks after another essence, the polyhedral shapes hiding in the structure. Graphically, forcefully, 7b communicates to us that there are octahedra in this structure.

You may wonder where these octahedra are in the complex structure of NaNb_3O_6 . Well, let's take the octahedra of drawing 7 and rotate them in space, to the viewpoint shown in drawing 8. If you compare 8 with



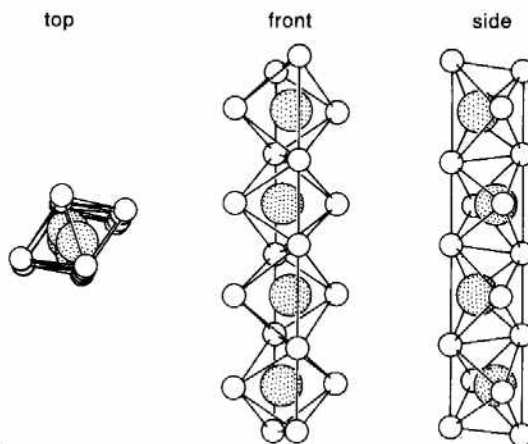
the middle piece of layer B (shown in structure 6), you will see a certain resemblance.

Now consider the structure of the layers. First, many such octahedra are linked into a one-dimensional array by sharing opposite edges. Three views of such an edge-sharing octahedral chain are shown in drawing 9.



One of the three views is from the same vantage point as in 4 or 6. Let's call that "top." The other two views are roughly from the "front" and "side," the viewpoints so marked in the original drawing, 4. The shared edges are emphasized by darker lines in the side view.

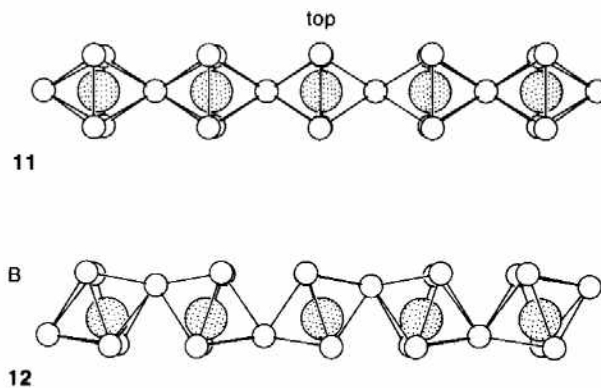
If you compare the top view of one of these infinite chains in 9 with the view in 6, you will see a difference: the niobiums are receding from you in a neat straight line in 9, but are "staggered" in pairs in 6. Indeed, drawing 9 is an idealization. One of the stacks in the real structure is carved out in drawing 10, shown in the same top view as in 6, but also from the front and the side. The



motion of the niobiums off the centers of the oxygen octahedra, and an associated asymmetry of the oxygens, are clearly visible.

Would you like to know why there occurs this departure from ideality? So did we, and a piece of the answer is to be found in a paper that Maria José Calhorda and I have written (7). For the moment, let's accept this symmetrical asymmetry as one of those complexities that makes life interesting.

Next, the one-dimensional chains of octahedra combine to generate the full B layers by sharing two opposite vertices with identical chains. They could have done so in a nice "straight" way (see drawing 11, a top view of a line of such vertex-sharing octahedra). But they don't;



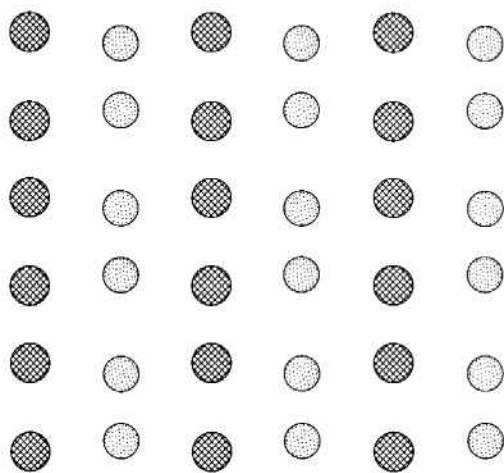
they "kink" (drawing 12) in a less straightforward but still symmetrical way. One gets the feeling that nature is insubordinate. What really is going on, though, is that we, in the weakness of our minds, fix on the first, most symmetrical suggestion of how things might be.

We now have layer B, this fantastic slab (repeated

Roald Hoffmann is professor of chemistry at Cornell University.

over and over in the crystal) of infinite, one-dimensional, edge-sharing octahedral chains, in turn stitched up to a two-dimensional slab by sharing vertices. What about layer A?

Drawing 4 shows that layer A is made up of needle-like lines of sodium and niobium. We might think that these atoms are equally spaced, but this molecule has another surprise in store for us, as the front view of A (in drawing 13) indicates. Whereas the sodiums are approxi-

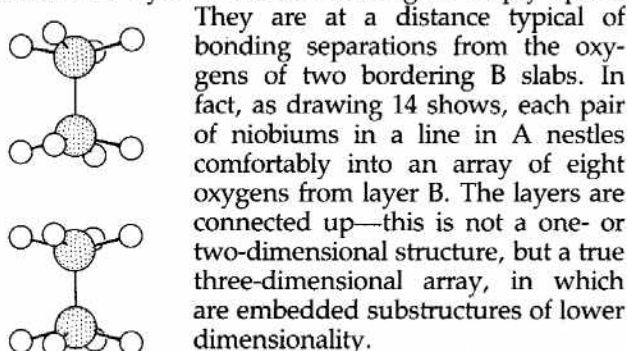


13

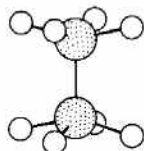
mately equally spaced, the niobiums clearly are not. They pair along the vertical direction (this pairing is obscured from the "top" vantage of 4 or 5), so that there are distinct short (2.6 Å) and long (3.9 Å) Nb...Nb separations. The short one is very short, substantially shorter than in pure niobium metal.

Why do the niobiums pair? In the study we've done of the way electrons move in these compounds, we find that the pairing is driven by a desire-cum-necessity to form the Nb-Nb bonds along the needle (7). There are even Nb-Nb bonds, not shown here, between the niobium atoms of stacks A and B.

Other links stitch up the layers. For instance, the niobiums in layer A are not floating in empty space.



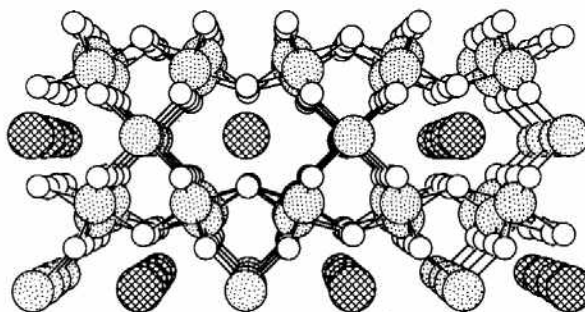
They are at a distance typical of bonding separations from the oxygens of two bordering B slabs. In fact, as drawing 14 shows, each pair of niobiums in a line in A nestles comfortably into an array of eight oxygens from layer B. The layers are connected up—this is not a one- or two-dimensional structure, but a true three-dimensional array, in which are embedded substructures of lower dimensionality.



14

Now we've toured the structure. And just as you settle back to contemplate it, let me remind you again of the ambiguity of the basic representation. Drawing 15 is the same structure, but without any oxygen octahedra; instead it shows the short Nb-O bonds. It takes a while to see

that it's the same molecule as the one in drawing 4. The relationship between 15 and 4 is the same as that



15

between 7a and 7b, two different aspects of the same octahedron.

Either way, the molecule is a highly aesthetic object. Its beauty is in its structure, which is at once symmetrical and unsymmetrical. The beauty is in the incredible interplay of dimensionality. Think of it: two-dimensional slabs are assembled from infinite one-dimensional chains of edge-sharing octahedra around niobiums, which in turn share vertices. These two-dimensional slabs interlink to the full three-dimensional structure by bonding with one-dimensional needles of niobium and sodium. And then, in a final twist of the molecular scenario, these one-dimensional needles pair up niobiums, declining to space equally. The NaNb_3O_6 structure self-assembles, in small black crystals, an aesthetic testimonial to the natural forces that shape the molecule, and to the beauty of the human mind and hands that unnaturally brought this structure into being (8).

References

1. The phrase "Beauty is in the eye of the beholder," according to *The Macmillan Book of Proverbs, Quotations, and Famous Phrases* (Macmillan, 1948), derives from Margaret Hungerford's *Molly Bawn* (1878). David Hume, in *Essays Moral and Philosophical* (1742), says: "Beauty in things exists merely in the mind which contemplates them."
2. R. J. Ternansky, D. W. Balogh, and L. A. Paquette, 1982, *J. Am. Chem. Soc.* 104:4503; L. A. Paquette, R. J. Ternansky, D. W. Balogh, and G. Kentgen, 1983, *J. Am. Chem. Soc.* 105:5446. Dodecahedrane was recently synthesized in a very different way by Horst Prinzbach, Paul von R. Schleyer, and their co-workers, 1987, *Angew. Chem. Int. Ed. Engl.* 26:452.
3. M. Doyle, W. Parker, P. A. Gunn, J. Martin, and D. D. MacNicol, 1970, *Tetrah. Lett.* 3619.
4. Y. Sekine, M. Brown, and V. Boekelheide, 1979, *J. Am. Chem. Soc.* 101:3126.
5. For an immensely enjoyable tour of the coined landscape of chemistry, see A. Nickon and E. F. Silversmith, *Organic Chemistry: The Name Game* (Pergamon Press, 1987). Structures 1-3 are drawn after this source.
6. J. Kohler and A. Simon, 1986, *Angew. Chem. Int. Ed. Engl.* 25:996; S. J. Hibble, A. K. Cheetham, and D. E. Cox, 1987, *Inorg. Chem.* 26:2389.
7. M. J. Calhorda and R. Hoffmann, unpubl.
8. In the preparation of this essay I was helped by Maria José Calhorda and Arndt Simon, who provided some essential drawings. I thank them both. The ink drawings were beautifully done, as always, by Elisabeth Fields and Jane Jorgensen.