

Baur W H. Bond length variation and distorted coordination polyhedra in inorganic crystals. *Trans. Amer. Crystallogr. Assoc.* 6:129-55, 1970. [Department of Geological Sciences, University of Illinois, Chicago, IL]

It is shown that the distortions of the coordination polyhedra of atoms around each other in inorganic crystals can, in certain cases, be correlated with the deviations of these atomic arrangements from the postulates of Pauling's second rule. These deviations in turn can be used to predict, with reasonable accuracy, the individual bond lengths among atoms in these coordination polyhedra. [The *SCF*[®] indicates that this paper has been cited in more than 220 publications, making it the most-cited paper published in this journal.]

Predicting Bond Lengths from Bond Strengths

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In my dissertation,¹ I found that, in rutile-type TiO₂, in the coordination octahedron of oxygen atoms around the titanium atom, two of the bond lengths in Ti-O are about 2 percent shorter than the other four Ti-O bonds. This was one of the first crystal-structure determinations sufficiently accurate to establish the experimental validity of such a small difference in bond lengths in an inorganic compound. Unfortunately, I could not explain this result, and, as a matter of fact, it is still difficult to do so to this very day. Papers are still being written on that topic.

About 30 years ago, it was tacitly assumed that coordination polyhedra (octahedra, tetrahedra, etc.) had ideal undistorted shapes. However, I was sensitized to the subject of distortions and watched out for examples in newly determined crystal structures. It seemed to me, even then, that at least some of the observed polyhedral distortions could be rationalized, assuming a violation of Pauling's second rule² (or electrostatic valence principle), which really is a principle of local balancing of electric charges in a crystal

structure. The charge balance is measured by comparing the sum of the bond strengths received by an anion with its formal charge. However, the accuracy of most crystalstructure determinations published 30 years ago was too low to allow firm conclusions.

Bill Busing, of Oak Ridge National Laboratory, invited me to talk at the annual Symposium of the American Crystallographic Association in 1970, in New Orleans, about calculations I had done concerning the experimental findings on rutile. However, I suggested something different. By now there were many well-determined crystal structures available that finally allowed a check of my hunch about deviations from Pauling's second rule causing distortions. I used 2,400 bond distances, from 130 compounds, to establish statistically valid correlations between individual bond lengths and the corresponding sums of the bond strengths received by individual atoms. These correlations could be used to predict bond lengths. This is useful, among other things, for the computer simulation of crystal structures.³ Ironically, this device contributed nothing to the original question about the distortions observed in rutile (because the charges there are perfectly balanced). However, it was the basis for a study about predicting hydrogen bonds.⁴

In any event, it was a thrill to have found something that Pauling had missed in his prediction. Incidentally, my switch in the early 1970s to more theoretical work was prompted by external circumstances. I found that I could not combine a heavy administrative load with the demands of experimental work. But, it was possible to think about things under almost any external circumstances and at any time.

The frequency of citations to this paper must be due to the fact that its approach rationalized a large number of recently obtained accurate, experimental data and showed the way to further studies in a similar vein. Subsequently Brown⁵ and others developed an alternate way to treat deviations from Pauling's rule. Their approach and mine are strictly empirical (and complementary to each other). Thus it is interesting that our empirical studies^{1,5} contributed to falsifying the $d\pi$ - $p\pi$ bonding theory, both proposed and discredited by Cruickshank.⁶

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Received September 1, 1992