Chemistry: Unusual Structures Predicted for Carbon Compounds

For 102 years, a primary tenet of organic chemistry has been that a carbon atom with four substituents bonded to it prefers a tetrahedral geometry. Since Jacobus H. van't Hoff and Joseph A. Le-Bel first stated this principle in 1874, no fundamental exception, such as an organic compound in which all four substituents lie in a plane, has been discovered. Until now, that is. Recently, a group of investigators headed by Paul von R. Schleyer of the University of Erlangen-Nürnberg in West Germany and John A. Pople of Carnegie-Mellon University have performed some sophisticated molecular orbital calculations and have discovered not just one, but a whole constellation of organic compounds whose preferred conformations are grossly different from the accepted norms. In most cases, furthermore, the new structures belong not to some highly exotic chemicals, but to normally prosaic molecules in which only two elemental substitutions have been made.

Perhaps even more important than the unusual structures whose existence they have predicted is the recognition that quantum chemistry has finally come of age. Ten years ago, the nonempirical calculations—so-called because they use only fundamental constants and mathematical equations—of the type performed by Schleyer and Pople could be carried out only for the very simplest of molecules. Today, the calculations are a thousand times more efficient, and they can be applied to much larger systems.

A factor of 10 in this improvement comes from refinements in digital computers, according to Schleyer. The additional hundredfold improvement in efficiency arose from greatly improved programs written by Pople and his associates. The net result of these improvements is a gross change in emphasis. In the past, such theoretical calculations only provided more information about systems already reasonably well understood. Now, theory can precede experiment and guide the way that a research program should proceed.

The technique used by Schleyer and Pople consists, in essence, of selecting two or more likely geometries for a molecule and then calculating their relative energies. If all the appropriate structures have been included in the calculations, then the geometry with the lowest calculated energy should be the most stable. This approach has been validated for many molecules whose structures are well known.

Consider, for example, methane. The calculated energy for a molecule of methane in which the four hydrogen atoms are arranged tetrahedrally about the carbon atom is about 150 kilocalories per mole lower than the energy calculated for a structure in which all five atoms lie in the same plane. Since the dissociation energy of a carbon-hydrogen bond is only about 104 kcal/mole, planar methane would not be expected to exist under any circumstances. This conclusion is verified by experience. Earlier theoretical work by Roald Hoffman and his associates at Cornell University, however, indicated that the tetrahedral-planar energy difference could be lowered by proper substitution.

Not all carbon atoms are tetrahedral, of course. Compounds in which the carbon atom is double-bonded, as in ethylene, are generally planar; those in which it is triple-bonded, as in acetylene, are generally linear. All known derivatives of these molecules where the hydrogens are replaced by elements important to life—including oxygen, nitrogen, and sulfur—prefer the same basic shapes.

Simple Modifications

What Schleyer and Pople predict is that not only can these three structural precepts be violated, but that they can be violated by very simple modifications, such as substitution of two lithium atoms for two of the hydrogen atoms. In each of these simple molecules, substitution of two lithium atoms produces a change in dimension. Methane is three-dimensional, but dilithiomethane may well be two-dimensional in the sense that the centers of all five atoms may lie in a single plane. Planar ethylene is two-dimensional, but 1,1-dilithioethylene is three-dimensional because the plane of the substituents attached to one carbon is perpendicular to that of the substituents attached to the second carbon. Linear acetylene is one-dimensional, but dilithioacetylene is two-dimensional, with the lithium atoms forming bridges between the two carbon atoms so that the molecule is actually cyclic. Similar effects are observed for many other molecules. In most cases, the energy differences that have been calculated are small, but Schleyer is confident that they are sufficiently large that the molecules will exist in the unusual conformations. One of the molecules that is most stable in the unusual conformation is CF_2Li_2, for which the planar energy is 25 kcal/mole less than the tetrahedral energy.

The investigators found that three effects contribute to stabilization of the unusual conformations. Two of them are delocalization of the lone pair of electrons possessed by planar carbon by conjugation with vacant π orbitals of the substituent and donation of electron density to the carbon atom from σ electrons of the substituent. Both qualifications are met by BH_2, BeH, and, especially, Li; many compounds incorporating them have unusual geometries. The third factor that contributes to stabilization is enforced reduction of the angle around the planar carbon by incorporation of the atom into small rings. A good example of this effect is provided by 1,1-dilithiocyclopropane, which is most stable in the planar conformation.

The predictions of Schleyer and Pople will, of course, require experimental verification. Many of the compounds whose structures they have studied do exist, but their structures have never been examined and published. The structures have not been studied, in part, because previously there had been no reason to expect that their conformations are other than ordinary. Such a study is difficult, furthermore, because many of the compounds, particularly the lithium derivatives, tend to be highly associated in the solid state and highly solvated in solution, which makes examination of structure difficult. It now seems possible that these characteristics may be a reflection of the unusual conformations of the isolated molecules.

The predictions of new structures may not have any immediate practical applications, but they may give a new insight into many chemical problems. The findings are important, Schleyer contends, because chemists learn more about the fundamental nature of matter when accepted rules are broken than when they are obeyed. Even more important, the results indicate that large areas of chemistry that are now completely unknown because experimental methods do not permit easy exploration can be examined by calculation easily, inexpensively, and with increasing accuracy.

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