C_2 IN ALL ITS GUISES

Roald Hoffmann

I love the chemistry that of its own subverts the classical compartmentalization of the molecular science into organic, inorganic, biological, physical and analytical subdisciplines. Here's an example.

C_2 is a simple diatomic molecule. Just two carbon atoms. It's not very stable, quite unlike the familiar O_2, N_2 or F_2. But whenever an arc is struck between two carbon atoms, one gets a little C_2 (and a little soccer-ball shaped C_{60}, buckminsterfullerene. But that's another, marvelous, story). There is also a good bit of C_2 in comets. And C_2 is responsible for the blue light we see in flames.

The C_2 molecule looks like a dumbbell, and the only free geometrical variable it has is the distance between the two carbons. That distance is 1.2425 angstroms in the ground state, the stable form of the molecule.

Any molecule, C_2 as well, also exists transiently in excited states. These result from absorption of light by the molecule, or from the input of energy in other ways. Each excited state is a beast unto itself, with its equilibrium distance different from the ground state. Figure 1 shows some calculated (so this is theoretical chemistry) "potential energy curves." These are plots of how the energy of the molecule varies with internuclear separation—not only for the ground state of C_2, but also for many excited states.

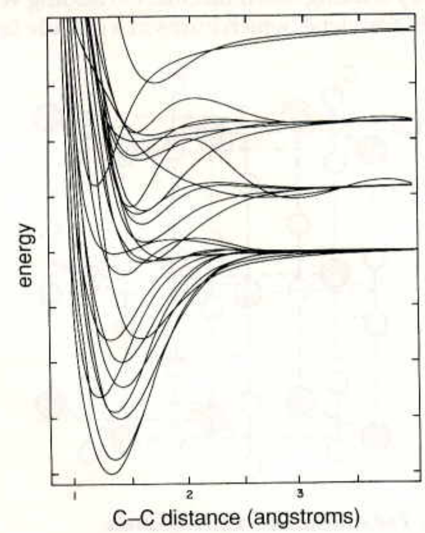

Figure 1: Computed potential energy curves for C_2.

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Of the multitude of these states that are calculated by theory, no less than 13 (the ground plus 12 excited states) have been observed experimentally. Their equilibrium C–C distances are indicated below (the part-Greek name labels are descriptors carrying some information about the state):

State of C_2	C–C Distances (in angstroms)
${}^1\Sigma_g^+$ (ground state)	1.2425
${}^3\Pi_u$, ${}^1\Pi_u$	1.3119, 1.3184
${}^3\Sigma_g^-$	1.3693
${}^3\Pi_g$, ${}^1\Pi_g$	1.2661, 1.2552
${}^3\Sigma_u^+$, ${}^1\Sigma_u^+$	1.23, 1.2380
${}^3\Pi_g$	1.5351
${}^1\Sigma_g^+$	1.2529
${}^3\Sigma_g^-$	1.393
${}^3\Delta_g$	1.3579
${}^1\Pi_u$	1.307

Note the range of C–C distances—from 1.23 to 1.53 angstroms. A chemist reader might also notice a remarkable fact—this molecule has one excited state with a shorter C–C bond than in the ground state! That's extremely rare, but it has its explanation in the electronic motions, the so-called "molecular orbitals," which describe the quantum-mechanical states of the electrons in the molecule. I happen to make a good living calculating these things (if the reviewers of my papers are to be believed) badly.

The study of the excited states of C_2 falls clearly in the realm of physical chemistry. Now let's switch to a group of three molecules representative of much of organic chemistry (and all of which, incidentally, are of commercial importance). These are ethane (C_2H_6), ethylene (C_2H_4) and acetylene (C_2H_2), shown in Figure 2. These molecules contain archetypical C–C single, double and triple bonds. As one might expect, the stronger the bond, the shorter it is. Note the range of C–C bond distances in these molecules, which is just about the complete range of distances in the millions of organic molecules we have wrought—it is between 1.21 and 1.54 angstroms. That's not very different from the repertoire of distances the ground and excited states of C_2 display. Could that be an accident?

It isn't. The bonding in these organic molecules

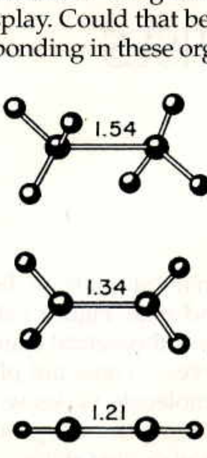

Figure 2: The archetypical organic molecules: ethane, ethylene, acetylene. C–C distances in angstroms = 10^{-8} centimeters are indicated.

can be described by preparing the C_2 portion of the molecule in different ways for bonding with six, four or two hydrogens—one way in ethane, another way in acetylene. The C_2 fragments so prepared may be described by different admixtures of the ground and excited states of C_2.

We move on to organometallic chemistry, a lovely interface between organic and inorganic chemistry that has exploded in the last 40 years. Figure 3 shows one organometallic molecule, made by my Cornell colleague Peter Wolczanski and his

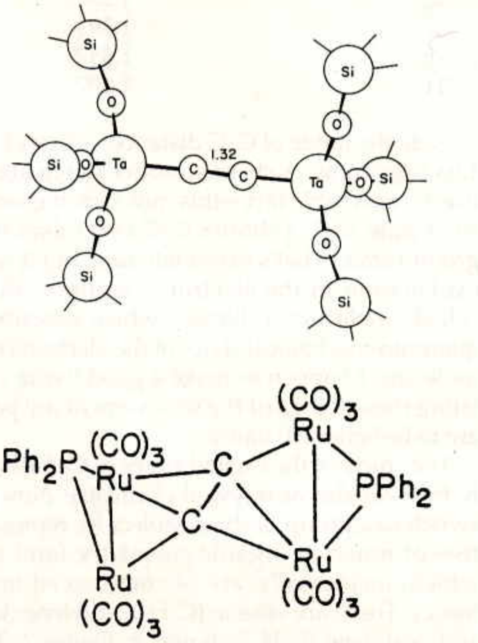

Figure 3: The compound on the top is $[(t\text{-}Bu_3SiO)_3Ta]_2C_2$, $t\text{-}Bu{=}C(CH_3)_3$; the one on the bottom is $Ru_4(C_2)(PPh_2)_2(CO)_{12}$, $Ph{=}C_6H_5$.

coworkers. It has a C_2 unit neatly bridging two tantalum atoms (Ta), each of which has some bulky molecular shrubbery (not all shown here) around it. Figure 3 also shows another organometallic molecule, one made by Michael Bruce and coworkers in Adelaide. This one has four rutheniums (Ru) caught huddling around a C_2.

We have crossed the bridge to inorganic chemistry, a distinction that seems to matter to some. A group in Milan, Italy, has been prolific at making metal clusters. In Figure 4 you see such a cluster, seven cobalts (Co), three nickels (Ni), many surrounding carbon monoxides. And smack in the middle of the cage is a C_2, with a middling bond length of 1.34 angstroms.

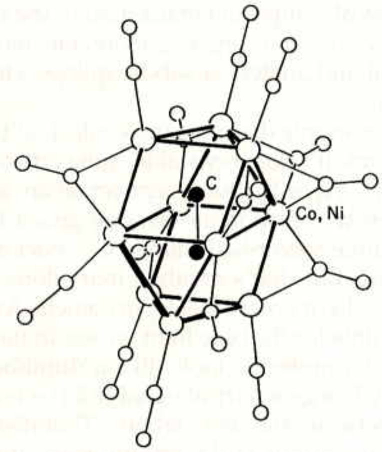

Figure 4: The $Co_3Ni_7C_2(CO)_{15}^{3-}$ cluster.

Once you've lit a carbide lamp, you never forget the smell of wet acetylene. Figure 5 shows the structure of calcium carbide, CaC_2. Union Carbide began by making this molecule. On adding water it yields acetylene, which burns in a carbide lamp.

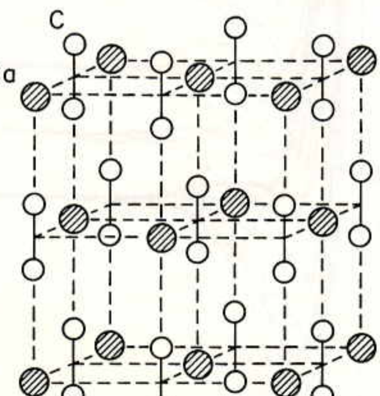

Figure 5: The structure of calcium carbide.

Calcium carbide is called an extended structure, a crystalline solid. It is made of atomic or molecular units, marching off regularly to infinity (or partway there). The C_2 units that you see so clearly in this structure have a very short bond length of 1.19 angstroms.

We have now crossed from inorganic to solid-state chemistry. Here is another typical solid-state structure, made by Arndt Simon and his coworkers in Stuttgart. $Gd_{10}C_6Cl_{17}$ is the kind of molecule we wouldn't *dare* show beginning students in chemistry; we like to shield beginners from such beautiful complexity (Figure 6). The molecule contains no less than seven octahedra of gadolinium (Gd), surrounded by assorted chlorides. Within each and every octahedron nests a C_2 unit!

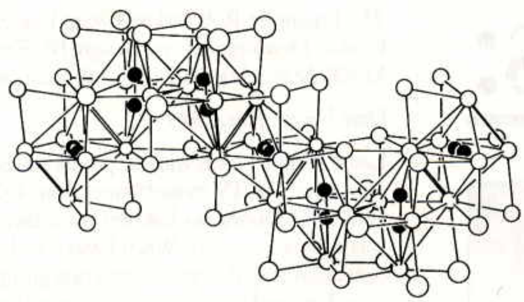

Figure 6: The $Gd_{10}C_6Cl_{17}$ structure.

One more structure. When organic molecules are put down on clean metal surfaces, they are often ripped to pieces. This is not as bad as it sounds, for they may then be reassembled to form other molecules; metal surfaces often act in just this way as commercially important catalysts. On a certain silver surface, Robert Madix and his coworkers at Stanford have found that acetylene, C_2H_2, decomposes to precisely our friend the C_2 unit, which then sits on the surface as shown in Figure 7.

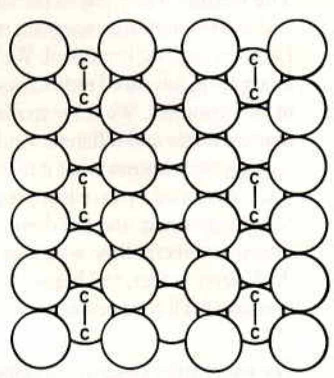

Figure 7: Suggested structure for C_2 on a silver surface.

The structures you've seen in this Marginalium come from different parts of the molecular enterprise: physical, theoretical, organic, organometallic, inorganic, solid state, surface chemistry. I think what nature is saying to us, as clearly as possible through this dazzling richness, is "You guys (now 26 percent of the U.S. Ph.D.'s are women, a major change of the last few years) may chop up chemistry as you wish, but I'm telling you the world is one. There are C_2 molecular units in each of these structures, acting out a dance of varying distances."

I think this is beautiful. And seeing the unity takes nothing away from the diversity.

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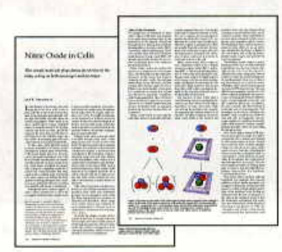

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