Global Molecular Identification from Graphs. IV. Molecules with Four Closed p-Shell Atoms and beyond*

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The identification of main-group molecules having atoms with closed valence p shells, *i.e.*, having atoms with eight valence electrons, is continued into the realm of four-atom molecules. All possible covalently-bonded species, obtained from two independent computer programs, are shown. The method for generalizing to molecules in which some or all atoms have closed valence s shells, *i.e.*, having atoms with two valence electrons, is recalled. A list of all prototype linear/bent four-atom molecules, with dative bonds in addition to covalent and/or van der Waals bonds, is presented (permutations having been culled out). A program code, lists of molecules based on other graphs, and lists of five- and covalently-bonded six-atom species, are available on the Web. For molecules derived from the two other four-vertex graphs, their vast numbers require extensive indexing schemes for the results to be useful. The paper concludes with some preliminary observations concerning the stabilities of four-atom molecules having atoms with closed shells.

Instead of classifying the observed means of knotting neckties, »Physicists Thomas Fink and Yong Mao... set out to learn how many ways you can manipulate a tie... in nine or fewer moves. Mathematical modeling revealed the answer: 85. But only 13, including 9 new ones, were aesthetically pleasing.«
Science News, vol. 158, page 322, 2000;
National Geographic, November 1999, 18th page.

INTRODUCTION

Previous papers have explored the consequences of seeking those molecules with a given structural formula, and specified bonds, that contain closed-shell atoms. This exploration is done with an algebraic procedure and identifies new species, some of which probably exist only under the most unusual conditions. These previous investigations have identified closed-shell species with covalent or van der Waals bonding (with and without additional dative bonds), and ionic bonding (with and without additional dative bonds). The species include neutral and ionized diatomic molecules,[1] neutral diatomic molecules with one or two period-4 transition-metal atoms,[2] and neutral triatomic molecules.[3]

In this paper we begin by identifying all possible four-atom molecules having covalent bonding with two distinct computer programs. These programs identify the molecules, eliminate permutations, identify (one of) the simplest resonant structures, and convert the numerical representations of the atoms to atomic and bond symbols. The rapidly-increasing numbers of graphs for five-atom, six-atom, and more-atom molecules call into question the feasibility of seeking to identify all covalently-bonded species with yet more atoms.

Then we call attention to some four-atom species that also have ionic bonding. Next, we turn to molecules with dative bonds in addition to covalent or van der Waals bonds, and present a sample set of results obtained with the same two computer programs; the sample set consists of linear/bent quadruple-octet molecules. We present observations about isoelectronic and topological aspects of four-atom closed-shell molecules, and explain a graphical scheme in which to arrange data for them. Finally, we conclude with observations about four- and five-atom dative-bonded molecules derived from various graphs.

THEORY

The algebraic identification of molecules proceeds by selecting a graph and the bonds on each edge, writing an appropriate equation for each atom, and solving the resulting system of equations. Each equation states that the number of valence electrons pertaining to an atom before bonding, plus those made available to it in the bonding processes, close its valence shell. A closed p-atom valence shell has eight electrons. (It is assumed that each atom retains its shell structure even when it is contained in a molecule.) Bond-angle issues are not considered in this treatment. Between any pair of atoms, bond orders of one, two, or three are allowed. Since a covalent bond involves two electrons, it follows from the octet rule that at most four bonds may be associated with any given atom, and this can occur only in a molecule with more than two atoms. Solution of the system results in identifying the atoms and the bond orders of the Lewis diagrams.

There are computer applications, such as Chemdraw[TM], which act on-screen as if the codes were solving similar equations; however, no communication with developers has confirmed that such is the case. Numerous tutorials on drawing Lewis structures exist in the literature[4,5] but none has been found that uses such equations. Ugi[6] does begin his work on chemical reactions with representations of octet molecules in matrix form; these matrices are formally equivalent to the equations used in our explorations.[3]

A molecule may have, in addition to its most simple manifestation having no (or, a least number of) dative bonds, a large number of resonance states with (more

complex) dative bonding. A single example, drawn with arbitrary angles and with arrows to indicate dative bonds, is as follows:
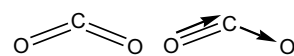

The species with more complex bonds may serve as higher-order configurations, in CI computations, of the experimentally observed molecule; they may be transition states or resonance structures. It seems possible that the larger the number of such resonance states, the greater the stability of the molecule.

The atoms constituting the molecules are chosen from the second period of the chart of the atoms including He, which is effectively a row-2 atom in group, or column, 0 ($C_{He} = 0$). One or more neighboring atoms may form dative bonds to He using one or more of their electron pairs. Isovalent atoms may be substituted at will for second-period atoms.

## NEUTRAL CLOSED-SHELL FOUR-ATOM MOLECULES WITH COVALENT BONDING

Four-atom molecules can be derived from any one of six graphs, each of which may have a different bond order on its edges: linear/bent, trigonal, kite, cyclic, common-edge bitriangle, and tetrahedral. The rule-of-8 algebra for pure covalent bonding has been given previously[1–3] and can readily be adapted to any of these shapes. Two computer programs, one written in Delphi[TM] and one in C++, produced the results given here. They begin with the 10 identified linear/bent molecules. The angles of the bonds are drawn only so as to separate the species into two groups, the one symmetric with respect to an inversion through the center and the other not symmetric.
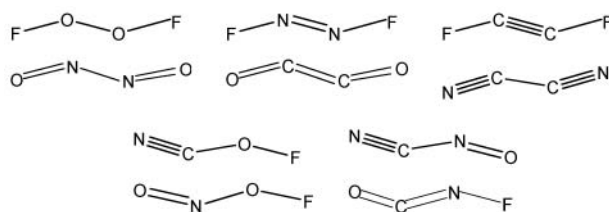

Reading from left to right in successive rows, these molecules have 26, 24, 22, 22, 20, 18, 22, 20, 24, and 22 valence-shell electrons. The two identified trigonal species are as follows:
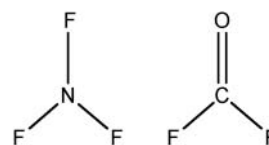
These molecules have 26 and 24 valence-shell electrons. The eight kite-shaped species are arbitrarily shown in one orientation when F is the tail of the kite and the other when O is the tail:
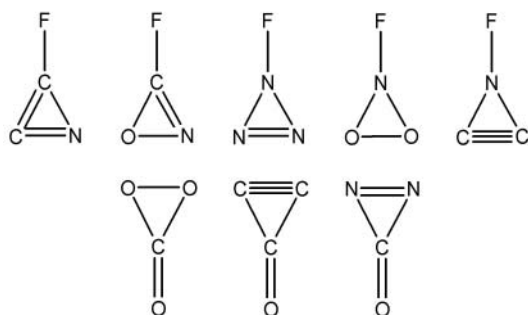
Reading from left to right in the two rows, these molecules have 20, 22, 22, 24, 20, 22, 18, and 20 valence-shell electrons. The nine cyclic molecules include two different C_4 and two different C_2N_2 molecules. The first row contains those with C and N atoms and the second row contains those with oxygen atoms:
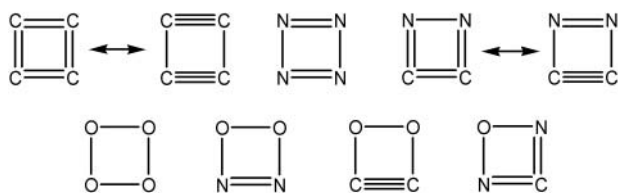
Reading in the usual way, the electron counts are 16, 16, 20, 18, 24, 24, 22, 20 and 20. The species derived from a graph with two triangles sharing a common side are arbitrarily shown with the diagonal bond in one orientation when the atoms are positioned symmetrically with respect to that bond, and in the other direction when they are not:
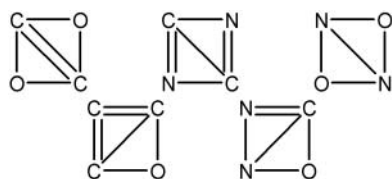
The electron counts are 20, 18, 22, 18, and 20. The last set of molecules is derived from a tetrahedral graph. The homonuclear species and heteronuclear species are drawn with the heavy (near side) lines and the dashed (far side) lines in different orientations. These molecules are subject to enormous steric strain:

The electron counts are 20, 16, and 18.

SOME FOUR-ATOM MOLECULES ALSO HAVING IONIC BONDING

It was shown in Refs. 2 (Table 3) and 3 [Table I and under Eq. (14)] how diagrams for molecules with ionically-bonded rule-of-2 atoms may be derived heuristically. A fluorine atom attached to a molecule with a single covalent bond may be replaced by a lithium atom and a single-charge ionic bond, an oxygen ligand with its double covalent bond may be replaced by a beryllium atom and a double-charge ionic bond, and a nitrogen atom attached to the rest of the molecule by a triple covalent bond may be replaced by a boron atom and a triple-charge ionic bond. These results are obtained rigorously by using equations tailored for ionic bonding, however for lithium the same result can be obtained by replacing the 8 by 2 in the equations for covalent bonding.[3]

MOLECULES WITH DATIVE BONDS IN ADDITION TO COVALENT BONDS

Allowing for dative bonds complicates the situation because the bond order on any edge of any one of the six graphs for tetra-atomic molecules may have covalent, covalent and dative, or only dative character. (In the last case, the attraction is assumed initially to have been the van der Waals force.) The relevant rule-of-8 algebra for these cases has been given previously.[1–3] Both of the computer programs described above solve the equations effectively. Table I lists the linear/bent four-atom molecules that are identified. The entries are sorted alphabetically, from the last atom working toward the first. The symbols −, =, and ~ stand for single, double, and triple covalent bonds; < and > represent dative bonds contributed by the atom on the right and on the left, respectively; => indicate a double covalent bond and a single dative bond delegated by the atom at the left. Similar tables for molecules based on the five other graphs are available from the authors.

QUADRUPLE-OCTET MOLECULES, ISOELECTRONIC SERIES, AND TOPOLOGY

Isoelectronic Series

The electron counts for all the molecules, given above, indicate that they lie on isoelectronic-series hyperplanes in the chemical space C_1, C_2, C_3, C_4, with the following numbers of valence-shell electrons: 18 (59 states), 20 (56), 22 (39), 24 (13), and 26 (3). It is of interest that these counts include the Walsh boundaries[7] of 22 (beyond which linear A_2B_2 molecules cease to be linear) and 24 (beyond which trigonal AB_3 molecules cease to be planar). A somewhat similar phenomenon was found in triatomic molecules; the linear/bent and cyclic forms lie on isoelectronic-series planes, in their space C_1, C_2, C_3,

TABLE I. Four-atom molecules with closed-shell atoms, having covalent or dative bonds

Ne>>>Be>O>>>Be	F->N>N->>B	N-<F>>C>>C	F-N=O>>C	F->>B>B~N
F->>B>O>>>Be	C=<O>N->>B	N-<F>C=>C	F-N<O=>C	O=>C>B~N
O=>C>O>>>Be	O=O>N->>B	F-F>>C>>C	C=<O>O>>C	Ne>>C>>B->N
Ne>>C>O>>>Be	Ne>O>N->>B	F-F>C=>C	O=O>O>>C	Ne>>C>B~N
N~N>O>>>Be	B-<<F>N->>B	C<<Ne>>C>>C	O<O=O>>C	N~N>B~N
F->N>O>>>Be	N-<F>N->>B	C<<Ne>C=>C	O<O<O=>C	F->N>>B->N
C=<O>O>>>Be	F-F>N->>B	O<Ne>>C>>C	Ne>O>O>>C	F->N>B~N
O=>O>O>>>Be	C<<Ne>N->>B	O<Ne>C=>C	N-<F>O>>C	O=O>>B->N
Ne>O>O>>>Be	O<Ne>N->>B	Ne>>>Li-N=>C	F-F>O>>C	O=O>B~N
B-<<F>O>>>Be	Ne>>>Li-O->>B	F->>Be-N=>C	C<<Ne>O>>C	Ne>O>>B->N
N-<F>O>>>Be	F->>Be-O->>B	O=>B-N=>C	O<Ne>O>>C	Ne>O>B~N
F-F>O>>>Be	O=>B-O->>B	Ne>>B->N>>C	Ne>>>Li-F>>C	N-<F>>B->N
Be<<<Ne>O>>>Be	Ne>>B-O->>B	Ne>>B-N=>C	Ne>>Li-<F>>C	N-<F>B~N
C<<Ne>O>>>Be	N~C-O->>B	N~C-N=>C	F->>Be-F>>C	F-F>>B->N
O<Ne>O>>>Be	F->C-O->>B	F->C->N>>C	F->Be-<F>>C	F-F>B~N
Ne>>>Li-F>>>Be	C=<N-O->>B	F->C-N=>C	O=>B-F>>C	O<Ne>>B->N
F->>Be-F>>>Be	O=N-O->>B	C=<N-N=>C	O=B-<F>>C	O<Ne>B~N
O=>B-F>>>Be	Ne>N-O->>B	O=N->N>>C	Ne>>B-F>>C	Ne>>>Li-C~N
Ne>>B-F>>>Be	B-<<O-O->>B	O=N-N=>C	Ne>B-<F>>C	F->>Be-C~N
N~C-F>>>Be	N-<O-O->>B	Ne>N->N>>C	N-<C-<F>>C	O=>B-C~N
F->C-F>>>Be	F-O-O->>B	Ne>N-N=>C	N~C-F>>C	Ne>>B->C->N
C=<N-F>>>Be	C<<F-O->>B	N-<O->N>>C	F->C-F>>C	Ne>>B-C~N
O=N-F>>>Be	O<F-O->>B	N-<O-N=>C	F-C-<F>>C	N~C-C~N
Ne>N-F>>>Be	Ne>>>He<F->>B	F-O->N>>C	O<N-<F>>C	F->C->C->N
B-<<O-F>>>Be	F->>Li<F->>B	F-O-N=>C	O=N-F>>C	F->C-C~N
N-<O-F>>>Be	O=>Be<F->>B	C<<F->N>>C	Ne>N-F>>C	O=N->C->N
F-O-F>>>Be	Ne>>Be<F->>B	C<<F-N=>C	N-<O-F>>C	O=N-C~N
Be<<<F-F>>>Be	N~B<F->>B	O<F->N>>C	F-O-F>>C	Ne>N->C->N
C<<F-F>>>Be	F->B<F->>B	O<F-N=>C	C<<F-F>>C	Ne>N-C~N
O<F-F>>>Be	C=<C<F->>B	Ne>>>He<O=>C	O<F-F>>C	N-<O->C->N
Ne>>>He<Ne>>>Be	O=C<F->>B	F->>Li<O=>C	Ne>>>He<Ne>>C	N-<O-C~N
F->>Li<Ne>>>Be	Ne>C<F->>B	O=>Be<O=>C	Ne>>He<<Ne>>C	F-O->C->N
O=>Be<Ne>>>Be	N-<N<F->>B	Ne>>>Be>O>>C	F->>Li<Ne>>C	F-O-C~N
Ne>>Be<Ne>>>Be	F-N<F->>B	Ne>>Be>O>>C	F->Li<<Ne>>C	O<F->C->N
N~B<Ne>>>Be	C<<O<F->>B	Ne>>Be<O=>C	O=>Be<Ne>>C	O<F-C~N
F->B<Ne>>>Be	O<O<F->>B	N~B<O=>C	O=Be<<Ne>>C	Ne>>>He<N~N
C=<C<Ne>>>Be	Ne>>>Be>C=>C	F->>B>O>>C	Ne>>Be<Ne>>C	F->>Li<N~N
O=C<Ne>>>Be	F->>B>C=>C	F->B=O>>C	Ne>Be<<Ne>>C	O=>Be<N~N
Ne>C<Ne>>>Be	O=>C>C=>C	F->B<O=>C	N-<B<<Ne>>C	Ne>>>Be>N->N
B-<<N<Ne>>>Be	Ne>>C>>C>>C	O=>C>O>>C	N~B<Ne>>C	Ne>>Be>N->N
N-<N<Ne>>>Be	Ne>>C>C=>C	O=C=O>>C	F->B<Ne>>C	Ne>>Be<N~N
F-N<Ne>>>Be	N~N>C=>C	O=C<O=>C	F-B<<Ne>>C	F->>B>N->N
C<<O<Ne>>>Be	F->N>>C>>C	Ne>>C>O>>C	O<C<<Ne>>C	F->B=N->N
O<O<Ne>>>Be	F->N>C=>C	Ne>C=O>>C	O=C<Ne>>C	F->B<N~N
Ne>>>Be>N->>B	C=<O>C=>C	Ne>C<O=>C	Ne>C<Ne>>C	O=>C>N->N
F->>B>N->>B	O=O>>C>>C	N~N>O>>C	N-<N<Ne>>C	O=C=N->N
O=>C>N->>B	O=O>C=>C	N-<N=O>>C	F-N<Ne>>C	O=C<N~N
Ne>>C>N->>B	Ne>O>>C>>C	N-<N<O=>C	O<O<Ne>>C	Ne>>C>N->N
N~N>N->>B	Ne>O>C=>C	F->N>O>>C	Ne>>>Be>B~N	Ne>C=N->N
Ne>C<N~N	F->N>Be=<O	O=O>>C>O	F-N<O=O	Ne>N->Be-<F
N~N>N->N	O=O>>Be=O	O<O=>C>O	O=O>O>O	Ne>N-Be-<<F
F->N>N->N	O=O>Be=<O	O<O<C=<O	Ne>O>O>O	F-O->>Be-F
F-N=N->N	Ne>O>>>Be>O	O=O>C=O	F-F>O>O	F-O->Be-<F
F-N<N~N	Ne>O>>Be=O	O<O=C=O	O<Ne>O>O	F-O-Be-<<F

(cont.)

O=O>N->N
O<O=N->N
O<O<N~N
Ne>O>N->N
N-<F>N->N
F-F>N->N
O<Ne>N->N
Ne>>>Li-O->N
Ne>>Li-<O->N
F->>Be-O->N
F->Be-<O->N
O=>B-O->N
O=B-<O->N
Ne>>B-O->N
Ne>B-<O->N
F->C-O->N
F-C-<O->N
O<N-<O->N
O=N-O->N
Ne>N-O->N
N-<O-O->N
F-O-O->N
O<F-O->N
Ne>>>He<F->N
Ne>>He<<F->N
F->>Li<F->N
F->Li<<F->N
O=>Be<F->N
O=Be<<F->N
Ne>>Be<F->N
Ne>Be<<F->N
F->B<F->N
F-B<<F->N
O<C<<F->N
O=C<F->N
Ne>C<F->N
F-N<F->N
O<O<F->N
Ne>>>Be>Be=<O
F->>B>Be=<O
O=>C>Be=<O
Ne>>C>>Be=O
Ne>>C>Be=<O
F->N>>Be=O
Ne>>Li-<O-F
Ne>Li-<<O-F
Ne>>B-O-F
Ne>B-<O-F
Ne>N-O-F
F-O-O-F
Ne>>>He<F-F
Ne>>He<<F-F

Ne>O>Be=<O
F-F>>>Be>O
F-F>>Be=O
F-F>Be=<O
O<Ne>>>Be>O
O<Ne>>Be=O
O<Ne>Be=<O
Ne>>>Li-B=<O
F->>Be-B=<O
O=>B-B=<O
Ne>>B->B=O
Ne>>B-B=<O
F->C->B=O
F->C-B=<O
O=N->B=O
O=N-B=<O
Ne>N->>B>O
Ne>N->B=O
Ne>N-B=<O
F-O->>B>O
F-O->B=O
F-O-B=<O
O<F->>B>O
O<F->B=O
O<F-B=<O
Ne>>>He<C=<O
F->>Li<C=<O
Ne>>>Be>C=O
Ne>>Be<C=<O
Ne>>Be=C=O
F->>B>C=O
F->B<C=<O
F->B=C=O
O=>C>C=O
Ne>>C>>C>O
Ne>C=>C>O
Ne>>C>C=O
Ne>C<C=<O
Ne>C=C=O
F->N>>C>O
F-N=>C>O
F->N>C=O
F-N<C=<O
F-N=C=O
Ne>He<<<F-F
Ne>>Be<F-F
Ne>Be<<F-F
Ne>C<F-F
Ne>>>Be>He<<<Ne
Ne>>C>>He<<Ne
Ne>>C>He<<<Ne
Ne>O>>>He<Ne

Ne>O>>C>O
Ne>O>C=O
F-F>>C>O
F-F>C=O
O<Ne>>C>O
O<Ne>C=O
Ne>>>Li-N=O
Ne>>Li-<N=O
F->>Be-N=O
F->Be-<N=O
Ne>>B->N>O
Ne>B~N>O
Ne>>B-N=O
Ne>B-<N=O
F->C->N>O
F-C~N>O
F->C-N=O
F-C-<N=O
O=N->N>O
Ne>N->N>O
Ne>N-N=O
F-O->N>O
O<F->N>O
O<F-N=O
Ne>>>He<O=O
Ne>>He<<O=O
F->>Li<O=O
F->Li<<O=O
Ne>>>Be>O>O
Ne>>Be=O>O
Ne>Be=<O>O
Ne>>Be<O=O
Ne>Be<<O=O
F->>B>O>O
F->B=O>O
F-B=<O>O
F->B<O=O
F-B<<O=O
Ne>>C>O>O
Ne>C=O>O
Ne>C<O=O
F->N>O>O
F-N=O>O
Ne>O>>He<<Ne
Ne>O>He<<<Ne
Ne>>>Li-Li<<<Ne
Ne>>B->Li<<Ne
Ne>>B-Li<<<Ne
Ne>N->>Li<Ne
Ne>N->Li<<Ne
Ne>N-Li<<<Ne

Ne>>>Li-F>O
Ne>>Li-<F>O
Ne>Li-<<F>O
F->>Be-F>O
F->Be-<F>O
F-Be-<<F>O
Ne>>B-F>O
Ne>B-<F>O
F->C-F>O
F-C-<F>O
Ne>N-F>O
F-O-F>O
O<F-F>O
Ne>>>He<Ne>O
Ne>>He<<Ne>O
Ne>He<<<Ne>O
F->>Li<Ne>O
F->Li<<Ne>O
F-Li<<<Ne>O
Ne>>Be<Ne>O
Ne>Be<<Ne>O
F->B<Ne>O
F-B<<Ne>O
Ne>C<Ne>O
F-N<Ne>O
Ne>>>Be>Li-<<F
F->>B>Li-<<F
Ne>>C>>Li-<F
Ne>>C>Li-<<F
F->N>>Li-<F
F->N>Li-<<F
Ne>O>>>Li-F
Ne>O>>Li-<F
Ne>O>Li-<<F
F-F>>>Li-F
F-F>>Li-<F
F-F>Li-<<F
Ne>>>Li-Be-<<F
F->>Be-Be-<<F
Ne>>B->Be-<F
Ne>>B-Be-<<F
F->C->Be-<F
F->C-Be-<<F
Ne>N->>Be-F
Ne>>>Be>Be<<Ne
Ne>>C>>Be<Ne
Ne>>C>Be<<Ne
Ne>C<Be<<<Ne
Ne>C=>Be<Ne
Ne>C=Be<<Ne
Ne>O>>Be<Ne
Ne>O>Be<<Ne

Ne>>>He<B-<<F
Ne>>>Be>B-<F
Ne>>Be<B-<<F
Ne>>Be=B-<F
F->>B>B-<F
Ne>>C>>B-F
Ne>>C>B-<F
Ne>C<B-<<F
Ne>C=>B-F
Ne>C=B-<F
F->N>>B-F
F->N>B-<F
F-N<B-<<F
F-N=>B-F
F-N=B-<F
Ne>O>>B-F
Ne>O>B-<F
F-F>>B-F
F-F>B-<F
Ne>>>Li-C-<F
Ne>>Li-<C-<F
Ne>>B->C-F
Ne>>B-C-<F
Ne>B-<C-<F
Ne>B~C-F
F->C->C-F
Ne>N->C-F
Ne>N-C-<F
F-O->C-F
F-O-C-<F
Ne>>>He<N-<F
Ne>>He<<N-<F
Ne>>>Be>N-F
Ne>>Be<N-<F
Ne>Be<<N-<F
Ne>>Be=N-F
Ne>Be=<N-F
Ne>>C>N-F
Ne>C<N-<F
Ne>C=N-F
F->N>N-F
Ne>O>N-F
F-F>N-F
Ne>>>Li-O-F
Ne>>B->B<Ne
Ne>N->B<Ne
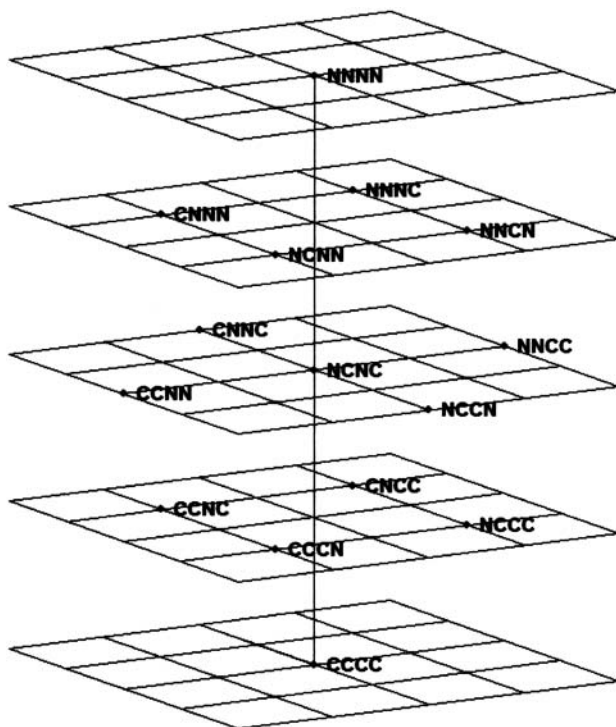Ne>N-B<<Ne
Ne>>C>C<Ne
Ne>O>C<Ne
Ne>N-N<Ne

Figure 1. Molecules formed from carbon and nitrogen in the octahedral coordinate system. The molecule CNCN resides along with NCNC at the center. Beautiful symmetry is encountered in moving from C4 to N4: point, square, cross, square, and point. In the central plane, the molecular formulae bear interesting relations to each other. The formulae in the second and fourth planes are also related to each other in an intriguing fashion.

with 12, 14, 16, 18, and 20 valence-shell electrons, and 16 is the Walsh boundary beyond which non-hydride molecules cease to be linear.[3]

Cyclomatic Numbers

The cyclomatic number (also denoted by C, but with no subscript) of a graph is its number of independent cycles, or, the minimum number of cuts that must be made to reduce the graph so that it has no cycles.[8,9] For example, a tretrahedron has $C = 3$. The values of C for the linear/bent and trigonal, the cyclic and kite, the common-side bitriangle, and the tetrahedral graphs are 0, 1, 2, and 3, respectively. The maximum numbers of valence-shell electrons for molecules derived from these four graphs are 26, 24, 22, and 20, respectively.

PLOTTING DATA FOR TETRA-ATOMIC MOLECULES

This research has forecasted a large number of molecules for which it will be of interest to plot computed (or even experimental) properties. An efficient way to plot data for four-atom species derived from a given graph is to use an octahedral coordinate system. Its axes are defined

by the edges of an octahedron placed with one vertex at the origin, with the opposite vertex on the z axis, and with planes containing the non-horizontal edges oriented such that they also contain the x and y axes. The displacements from the origin to each of the four non-axial vertices of the octahedron define the coordinates (Figure 1). Neglecting normalization, they are

$$x_1 = x + y + z$$
$$x_2 = x - y + z$$
$$x_3 = -x - y + z$$
$$x_4 = -x + y + z$$

As an example, let C_4 be placed at the origin, and consider the species C_nN_m, where $n + m = 4$. Changing the first C to an N moves the molecule one step along the x_1 axis, and similarly for the other carbons, hence NCCC, CNCC, CCNC, and CCCN are found at $x + y + z$, $x - y + z$, $-x - y + z$, and $-x + y + z$. Coordinate positions add tail to head, so that NNCC, NCNC, NCCN, CCNN, CNCN and NCNC, and CNNC are found at $2x + 2z$, $2z$, $2y + 2z$, $-2x + 2z$, $2z$, and $-2y + 2z$, respectively. Two more such steps lead to NNNN at $4z$.

It can be seen that the z direction is an important axis; all isoelectronic molecules reside at the same value of z. For example, FB_3 has the same number of valence-shell electrons as C_4. A handy way to find its location is to start with B_4, at $-4z$, and to move from there in the x_1 direction four units (boron to fluorine) to $-4z + 4(x + y + z) = 4x + 4y - 0z$.

DISCUSSION

Either of the computer programs can determine molecules with five and more closed-shell atoms. One of the codes, a list of all four- and five-atom species, and a list of six-atom covalent-bonded molecules, are available on the Web.[10] The lists are sorted by structure, as represented by the adjacency matrices.

Table I, and the entries in Ref. 10, show that computation-time and indexing problems are encountered in this work. Penta-atomic species are derived from not six but from 21 graphs, each of which may have different bond orders, formed of either covalent or dative bonds or both, on its edges; six- and seven-atom molecules are derived from 112 and 583 graphs![8,10] It is a consequence of the assumptions stated in the Introduction that no atom can bind to more than four others; it follows that for molecules with six atoms, species derived from the maximally-connected graph cannot exist. For species with still larger numbers of atoms, more and more of the rapidly increasing numbers of graphs can be excluded. These considerations are of little comfort because even main-group atoms from rows beyond period 2 can bind to more than four others (*e.g.*, SF_6) and because the

numbers of graphs not excluded still climb rapidly. However, a modification of one or both of the programs might make it possible to find the one or more structures that, for a given molecular formula, allows each atom to have a closed shell.

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SAŽETAK

Globalna molekularna identifikacija pomoću grafova. IV. Molekule izgrađene od atoma s četiri zatvorene p-ljuske

Chris J. Walters, Ken Caviness i Ray A. Hefferlin

Identifikacija molekula koje se sastoje od atoma sa zatvorenim valentnim p-ljuskama, tj. koje imaju atome s osam valentnih elektrona, proširena je na molekule s četiri atoma. Prikazane su sve moguće kovalentne specije, koje su dobivene pomoću dva neovisna kompjutorska programa. Autori su podsjetili na metodu za identifikaciju molekula u kojima imaju neki ili svi atomi zatvorene s-ljuske, tj. koje imaju atome s dva valentna elektrona. Dana je lista svih prototipova linearnih i savijenih molekula s četiri atoma. Na web-u je dostupan program, liste molekula temeljene na drugim grafovima i liste kovalentnih molekula s pet i šest atoma. U slučaju molekula izvedenih iz drugih dvaju grafova s četiri vrha, njihov je broj ogroman te da bi primjena u kemiji imala smisla zahtjeva proširenje sheme indeksiranja. Članak završava s preliminarnim rezultatima o stabilnosti molekula s četiri atoma koji imaju zatvorene ljuske.