Structural Classification of Polyatomic Molecules Based on Valence-Electron Orbital Radii: AB_3 and A_2B_2 Compounds

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We classify the equilibrium structures of *sp*-bonded tetramers with schemes based on valence-electron orbital radii. Valence-electron orbital-radius plots show the transition from planar to nonplanar geometries, and account for trends in bond angles, thus confirming the success previously obtained by Andreoni, Galli, and Tosi for AB_2 molecules.

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Determination of the equilibrium structure of small atomic aggregates is still a challenging problem for experimental and theoretical physicists as well as for chemists. In the case of crystals, equilibrium structures are known more extensively and more accurately.[1] Also theoretical predictions are rather advanced.[2] In particular, great success has recently been achieved in the classification of a wide class of crystal compounds by means of simple structural parameters derived from quantum parameters of the atomic constituents.[3,4] Such a comprehensive scheme is lacking for polyatomic molecules.

Only very recently have Andreoni and co-workers[5] shown that the same quantum structural parameters which classify *sp*-bonded crystals are able to predict successfully the shapes of AB_2 molecules. In this case, the pertinent question is simple and well defined: Is the molecule linear or bent? Clearly, in the case of polyatomic molecules the number of possible configurations increases and with it the number of questions one should answer. Unfortunately, at the same time, experimental knowledge of the equilibrium structures becomes less accurate, and the statistics less rich. However, it is important to test the transferability of the quantum structural parameters of the crystals to complex molecules within the present knowledge and thus hopefully stimulate further experimental work.

In this Letter we present structural plots for the *sp*-bonded AB_3 compounds in molecular and crystal phases. The structural parameters are derived from the valence-electron orbital radii (VEOR) of the atomic constituents (both pseudopotential and nodal) in full analogy with our previous work on the AB_2 compounds.[5] We show that the same scheme which successfully classifies the main different structures for the solids is able to distinguish planar (2D) from three-dimensional (3D) geometries and also several different distortions of ideal symmetric shapes. In the case of A_2B_2 compounds, we find that for a given family of compounds (the dihalides of alkali metals) with the same structure (D_{2h}), a strong correlation exists between the bond angle and one of our structural parameters, in analogy with our previous findings for double-octet AB_2 molecules.

The structural plots we show in the following use as coordinates either Zunger-Cohen (ZC) elemental coordinates[3] R_σ or compound coordinates (Y,X) derived from nodal radii.[4,5] We remind the reader that for each element E,

$$R_\sigma(E) = S_0(E) + S_1(E),$$

i.e., the sum of the turning points S_l of nonlocal pseudopotentials with $l=0$ or 1; and for each binary compound of elements A and B,

$$Y \equiv N_0(B) - N_0(A) + 3[N_1(B) - N_1(A)],$$

$$X \equiv 3[N_0(B) + N_0(A)] - [N_1(B) + N_1(A)],$$

where N_0 and N_1 are the outermost nodes of the s and p valence wave functions, respectively.

We recall that the most symmetrical structure possible for an AB_3 molecule is planar and corresponds to an equilateral triangle formed by the B atoms with the A atom at the center (D_{3h} symmetry). The long standing arguments of Walsh[6] concern the transition from this planar symmetric shape to the pyramidal one (C_{3v} symmetry or NH_3 type) and consider the number of valence electrons N as the only "structural" parameter. The planar shape is predicted as long as $N \leq N_c = 24$ and for $N=28$, while the pyramidal modification is predicted for $N=25$ and 26. More sophisticated pictures of the molecular bonding[7] agree in identifying a critical number $N_c=24$ for the valence electrons, beyond which distortions from D_{3h} symmetry should occur (either planar or three dimensional). For a few selected species, and in particular for $N>24$, several proposals exist in the literature to figure out which are the electronic proper-

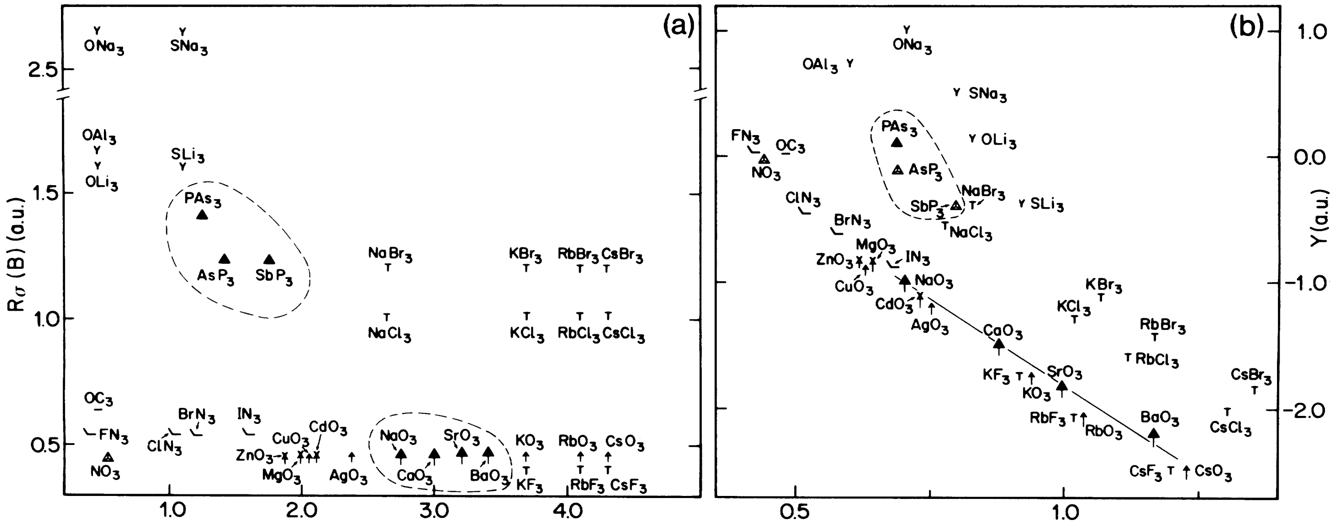

FIG. 1. AB_3 molecules with $N < 24$. Symbols are meant to illustrate the shape whenever possible as mentioned in the text (Y, T, arrow, line, bent chain, equilateral triangle with N in the center for NO_3). Solid triangles indicate 3D structures [pyramidal (triangles) or arrow shaped (large-headed arrows)]. The mixed symbol (Y/arrow) is used when these two isomers have been observed. (a) ZC elemental coordinates, and (b) our compound coordinates.

ties responsible for these distortions.[8] However, according to the present knowledge of molecular shapes, compounds with $N < 24$ are not planar and symmetrical, with the sole exception of NO_3, as indicated by recent infrared laser spectroscopy in the gas phase.[9] The actual geometries are shown in Fig. 1. This collects the few (37) *sp*-bonded AB_3 molecules with $N < 24$ for which equilibrium shapes have been given in the literature, as deduced from either experiment[10] (mostly infrared absorption and Raman spectra in rare-gas matrices) or calculations of the electronic structure.[11] The above-mentioned "distorted geometries" reduce essentially to pyramidal configurations for the compounds of group-V elements, HN_3-type conformations for the halogen azides, T shapes for the alkali trihalides (symmetrical only in the case of trifluorides), Y and arrow shapes for oxides and sulfides. All these structural differences are brought out clearly in our plots. Moreover, it has been suggested[12] that the trioxides of sodium and of alkaline earth elements are nonplanar. This is the only feature not so well resolved in a plot with elemental coordinates derived from nodal radii. Also, we notice that in analogy with AB_2 compounds, ZC compound coordinates are not as successful as the R_σ's in Fig. 1(a).

In full analogy with the case of AB_2 molecules, we find that species with $N = N_c$ and those with $N < N_c$ cannot be placed on the same plot, the former all being planar and symmetrical.

In the case of A_2B_2 molecules, structural information is available only for about 40 species[13] (infrared absorption and Raman spectra in matrices, electron diffraction, suggestions from thermochemical data, Hartree-Fock calculations). These include alkali dihalides, dioxides of monovalent, divalent, and trivalent ions, plus a few dichalcogenides. They all seem to be planar and to form rings (mostly rhombohedral in shape) apart from C_2N_2 (and probably B_2O_2) which is linear, and N_2O_2 which is bent at both nitrogen atoms. It is not worthwhile showing this map, but it is easy to see that VEOR-based structural parameters separate these three special cases well and confine them to near the origin. Schnuelle and Parr[7] indicated a critical number of valence electrons $N_c = 22$ as marking the border between linear symmetric and other shapes. In fact, in their picture of the electron distribution, $N_c = 22$ corresponds to completed octets at the terminal atoms (say B) plus a triple bond between the two central atoms (say A). This type of bonding, however, is realistic only for covalent species such as C_2N_2 but is unstable against increase of ionicity and also delocalization of the charge density (see, for instance, the case of metal clusters A_4). We find it interesting to look at trends in the values of the bond angles. The statistics are rather poor and only in the case of alkali dihalides can a trend be identified since experimental information[14] can be complemented with the results of ionic models[15] and of self-consisted field (SCF) calculations.[16] In our work on the double-octet AB_2 molecules, Y was found to be related to the tendency to bend, i.e., to the difference $\alpha - \pi$. In the case of tetramers A_2B_2, it is natural to look at the deviation of $\alpha = \angle BAB$ from 90°. Figure 2 indicates that a linear relation exists between the bond angle and our parameter Y: This measures the mismatch of the average core radii of the anion and the cation, and has been related to the ionicity of the com-

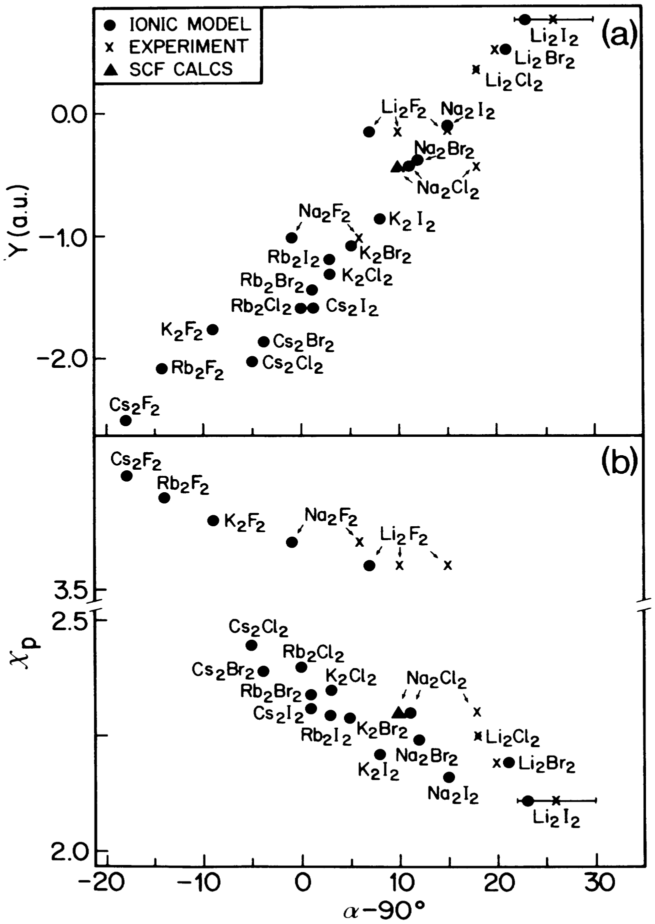

FIG. 2. Relation between structural parameters and bond angle, in (a) our and (b) Pettifor's schemes. For Li_2I_2, the bar indicates the experimental error.

pound.[4] Here, we note that large negative Y values correspond to small BAB angles. This is in agreement with results of our calculations on Na_2Cl_2,[16] where a decrease in α is correlated with an increase of the charge transfer from the cation to the anion. We find that α is also correlated similarly with the ZC coordinate Y_{ZC} and with the difference between the Pauling radii of the two ions.[17] This simple correspondence seems to be lost when we use Pettifor's chemical scale of the elements $\chi(E)$ to construct the structural coordinate $\chi_p \equiv \chi(B) - \chi(A)$ in Fig. 2(b), which singles out the difluorides from the rest of the alkali-halide dimers.

We now turn briefly to the classification of AB_3 crystals. In the recent literature, we mention in particular those due to Villars[18] and to Pettifor[19] which have been rather successful. However, neither of the above schemes seems to be useful for AB_3 molecules. In fact, Villars's scheme requires very large statistics to have a sufficient number of compounds at each value of N, while Pettifor's scheme does not give such an accurate account of the structures of the molecules in Fig. 1 [see also Fig. 2(b)].

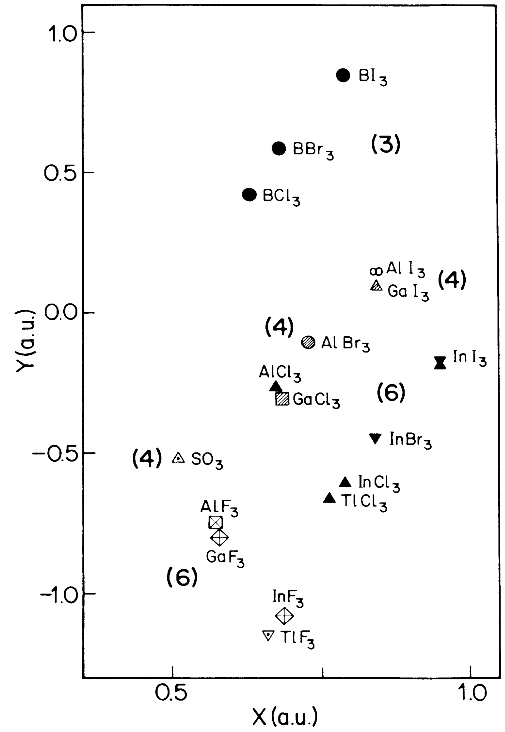

FIG. 3. AB_3 solids with $N=24$. Different symbols indicate different structures (see Ref. 20), which can be grouped as 3D (open), layer (filled) and "intermediate" (hatched). Also the CN of A is reported in brackets.

Once more, we treat separately compounds with $N=24$ from those with $N<24$. Among the former, only 17 compounds of nontransition elements are structurally determined. These are essentially halides of trivalent cations. As indicated in Fig. 3, they appear in different domains depending on whether or not the atomic configuration is layered (solid/open symbols) and on the coordination number (CN). Hatched symbols label compounds with a kind of "intermediate" structure.[20] A similar distinction is achieved with both ZC and our elemental coordinates. The situation appears to be more complicated for $N<24$. Once we have eliminated nonstoichiometric phases as well as polyanion compounds, we are left with about 50 intermetallic compounds with $6 \leq N \leq 10$. In either VEOR scheme, we encounter some difficulties with elements such as Pb, Hg, and Cu, in analogy with our previous findings for AB_2 compounds.[4,5] In spite of the existence of some overlap between different domains (e.g., $AuCu_3$ and β-Cu_3Ti), we distinguish groupings of structures with high (≥ 9) and low (≤ 6) CN.[21] In the same plot, we can also consider Au trihalides ($N=22$), which are well separated and have layer-type structures with CN = 3 or 4.[20] We note that mixing exists also in Pettifor's plots, and believe that the superiority of Villars's scheme for the intermetallics is due to introduction of the third parameter N.

In conclusion, we have shown that quantum structural parameters derived from VEOR can be transferred from solids to small molecules. A larger basis of experimental data is still needed to test these schemes better, and to extend them to more complex molecular aggregates.

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