

# MOLECULAR TENSEGRITY: PREDICTING 1,3- X - -X DISTANCE IN GAS-PHASE $MX_n$ ( $n \leq 4$ ) COMPOUNDS FROM ATOMIC SIZES

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The Fuller notion<sup>1</sup> of tensegrity structures has structural elements that are held together by compressive and tensile elements that balance each other. Such tensegrity are expected to hold for all length scales, as a general principle. Fuller-Snelson tensegrity structures using (incompressible) struts and (tensile) cables describe well the qualitative features of cell and tissue architecture in complex biological systems<sup>2</sup>. The “molecular tensegrity” that determines, say, the mechanical stability of the structure of isolated gas-phase  $MX_n$  molecules has been elusive. A simplifying feature that we take advantage of is that the energy-minimized, density optimized stationary state is consistent with a free-atom-like  $\mu = 0$  condition<sup>3, 4</sup> such that atoms in molecules may be treated independent of each other. Simple mechanical relationships between atomic sizes contribute to interatomic distances that eventually determine the molecular tensegrity structure *without requiring to know the (quantum) mechanics of the way the  $\mu = 0$  state is reached from a  $\mu \neq 0$  state.*

For an isolated  $MX_n$  molecule, the mutual influences of 1,2-bonded (attractive) M-X distance,  $d_{M-X}$ , and 1,3- non-bonded (repulsive) X - -X distances,  $d_{X-X}$ , is expressed (eqn 3) as a tensegrity factor (similar to the tolerance factor in solids<sup>7, 8</sup>) that forms the quantitative basis for molecular tensegrity. 1,2-interatomic distance,  $d_{MX}^{n0}$ , have been expressed as<sup>3, 5</sup> an universal function of “core” (small compared to interatomic distances) empirical<sup>5</sup> atomic sizes,  $r_G$  as

$$d_{MX}^{n0} = CR_0^+(M)/F_S(M) + CR_0^-(X) + D_0^- \quad (1)$$

with  $CR_0^\pm = C^\pm r_G + D_0^\pm$ , and  $C_0^+ = 2.24$ ,  $C_0^- = 2.49$ ,  $D_0^- = 111$  pm and  $D_0^+ = -37$  pm. The term  $F_S(M) = 1$  ( $n_v = 0$ ) for all M except for transition metal  $MX_3$  ( $n_v = 1$ ) and  $MX_4$  compounds ( $n_v = 2$ ). The superscript,  $\pm$ , refers to charge-transfer states  $CR_0^+$  and  $CR_0^-$  in eqn 1. The size  $CR_0^-(X)$  is close to the ionic radii in solids<sup>5</sup> and is different from the van der Waals’ radius<sup>10</sup>,  $r_{VDW} \neq CR_0^-(X)$ . The non-bonded distance,  $d_{XX}^{00}$  is expected to be

$$d_{XX}^{00} = 2KCR_0^-(X) \quad (2)$$

Unless otherwise mentioned, we take  $K = 1$  hereafter. Eqns 1 and 2 are required to define an ideal “tensegrity” factor<sup>10</sup>,  $t_{n0}^\pm$ , as

$$t_{n0}^\pm = d_{MX}^{n0}/d_{XX}^{00} \quad (3)$$

We now express an experimental quantity  $F_S(\text{obs})$  as

$$F_S(\text{obs}) = d_{XX}(\text{obs})/d_{XX}^{00} \equiv d_{XX}(\text{obs})/2CR_0^-(X) \quad (4)$$

A plot of  $F_S(\text{obs})$  vs  $t_{n0}^\pm$  (Figure 1) for all gas-phase  $MX_2$ ,  $MX_3$  and  $MX_4$  compounds<sup>11, 12</sup> (X = atom of insulating element) two nearly linear relationships of the type

$$F_S(\text{obs}) = A - Bt_{n0}^\pm \quad (5)$$

are obtained (Fig 1) which we refer to as Type I and Type II. In general, Type I  $MX_n$  compounds have M = atom of s-block metal, (met(s) in Figure 1), or transition metal dihalides (TM( $n = 2$ )), while Type II compounds have M as an atom of an insulating element (ins), p-block metal (met(p)) or transition metal  $MX_3$  or

$MX_4$  compounds (TM( $n > 2$ )). The compounds  $BH_2$ ,  $AlH_2$ ,  $MH_4$  (M = Si, Ge, Sn and Pb) and  $SeO_3$  are better described as type I compounds. From the ratios of the two slopes in Fig 1 we find  $F_S(\text{obs})^{(II)}/F_S(\text{obs})^{(I)} \sim 1.12$  for the same  $t_{n0}^\pm$ .

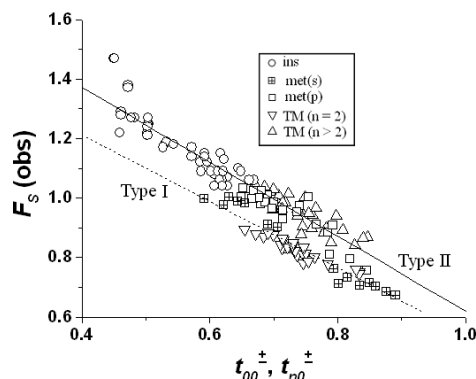


Figure 1. Plot of  $F_S(\text{obs})$  (eqn 4) vs the tolerance factor,  $t_{n0}^\pm$  (eqn 3) for gas-phase  $MX_2$ ,  $MX_3$  and  $MX_4$  compounds. Dotted line: Type I compounds;  $F_S(\text{obs}) = 1.66(0.04)t_{n0}^\pm - 1.12(0.5)$ ;  $R = -0.96$ ,  $SD = 0.03$ . Full line: Type II compounds,  $F_S(\text{obs}) = 1.87(0.02)t_{n0}^\pm - 1.25(0.4)$ ;  $R = -0.96$ ,  $SD = 0.04$ .

The linear relationships in Figure 1 may be understood from Fuller’s original description<sup>1</sup> of tensegrity which considers “continuous, tensional behaviours” as in a stretched membrane of a filled balloon. The “critical proximities that show up physically” are “repellings” which keep the molecular network constituting the balloon membrane stretched outwardly in all directions. The geometrically simplifying Fuller feature of the balloon membrane is the notion of “paired oppositely accelerated molecules” caroming around in “most comfortable great circles”, three of which intersect to give vertices of two spherical octahedral, one octahedron for each opposing direction. The linear relationships (eqn 5) in Figure 1 is understood from the geometrical limits of octahedral structures.

We examine eqn 4 in terms of the ratio of atomic sizes,  $(CR_0^+(M)/CR_0^-(X))$ . The ratio  $CR_0^+(M)/CR_0^-(X) = 0.414$ , geometrically represents the lower limit for stable octahedral coordination in ligand close-packed scenarios quite different from that envisaged by Gillespie *et al*<sup>13, 14</sup>. Writing eqn 3 as  $t_{n0}^\pm \equiv 0.5(CR_0^+(M)/CR_0^-(X) + 1)$  we require from eqn 5  $F_S(\text{obs}) = 1$  when  $t_{n0}^\pm = 1/1.414 = 0.707$  as in the fit for type II compounds in Figure 1. Ideally, we prefer  $F_S(\text{obs}) = (2 - 1.414t_{n0}^\pm)$  and obtain ( $\kappa$  = effective dielectric constant, see eqn 7) from eqns 2, 3 and 5

$$d_{XX}(\text{calcd}) = 2\kappa KCR_0^-(X)/(2 - 1.414t_{n0}^\pm) \quad (6)$$

as an “*ab initio*” quantity dependent only on “portable”<sup>15</sup> core atomic size of M and X atoms (eqn 1). The best fits to plots of

$d_{XX}(\text{obs})$  vs  $d_{XX}(\text{calcd})$  ( $\kappa = 1$  in eqn 6) in more than 160 gas-phase  $\text{MX}_2$ ,  $\text{MX}_3$  and  $\text{MX}_4$  compounds give ( $R > 0.99$ )  $d_{XX}(\text{obs}) = 1.19d_{XX}(\text{cal}) - 15.8(9.2)$  for type I compounds and  $d_{XX}(\text{obs}) = 1.04d_{XX}(\text{cal}) - 6.7$  for Type II compounds. The improvement in the R factor of the fits as compared to that in Figure 1 attests to the goodness of the model (eqn 6), especially considering that the gas-phase distances are obtained at various conditions of measurement, temperature and pressure and without a substantial theoretical basis for the “core” atomic sizes.

The finite intercepts of the best fits using eqn 6 highlights the uncertainty in the way the effective dielectric constant,  $\kappa$ , of eqn 6 varies with atomic size (as it should because of changes in polarizability with size). We have varied  $\kappa$  as  $\kappa = 1 + (Ld_{MX}^{00})^2$  such that the intercept of the best fit is zero. We find that  $L \sim 0.001$  (for  $d_{MX}^{00}$  in pm) is empirically required for all compounds. We thus write

$$d_{XX}(\text{calcd}) = 2\{1 + (0.001d_{MX}^{00})^2\}KCR_0(X)/(2 - 1.414t_{00}^{\pm}) \quad (7)$$

The best fits to plots of  $d_{XX}(\text{obs})$  vs  $d_{XX}(\text{calcd})$  using eqn 7 then requires with  $K(\text{Type I})/K(\text{Type II}) \approx 1.08$  (Fig 2). The standard deviation is 8 pm for type II and 13 pm for type I which is comparable to calculated values<sup>11</sup> employing latest theoretical methodologies

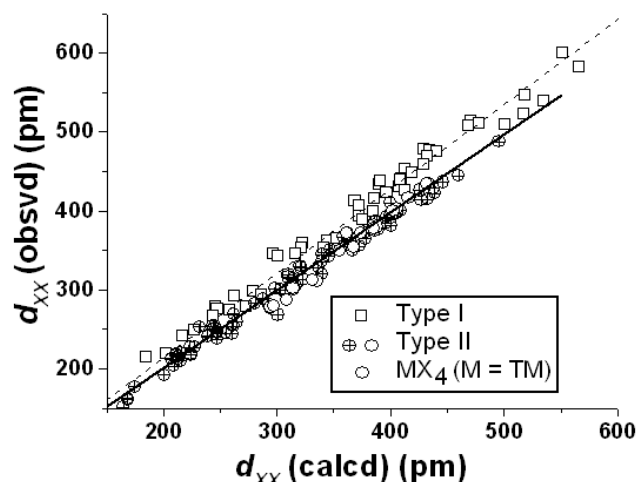


Figure 2. Plots of  $d_{XX}(\text{obs})$  vs  $d_{XX}(\text{calcd})$  using eqn 7 (except transition metal tetrahalides for which we take  $\kappa = 1$ ). The best fits ( $R > 0.993$ ) give  $d_{XX}(\text{obs})$  vs  $1.07d_{XX}(\text{calcd})$  for type I compounds and  $d_{XX}(\text{obs})$  vs  $0.99d_{XX}(\text{calcd})$  for type II compounds

The size  $2CR_0(X)$  ( $K = 1$  in eqn 2) is close to the negatively charged ionic radii of atoms in solids while the size  $2 \cdot 1.08 \cdot CR_0(X)$  ( $K = 1.08$  in eqn 2) could be close to the so-called van der Waals' radii<sup>10</sup>,  $r_{VDW}$ . For example, the ratio of the Bondi radii<sup>10</sup> of  $r_{VDW}$  for C, N, O, F to the corresponding values of  $CR_0(X)$  is close to 1.09. The nearest-neighbour interatomic separation of Ne, Ar, Kr and Xe in their crystals<sup>18</sup> when given by  $2 \cdot 1.08 \cdot CR_0(X)$  could require  $r_G$  values of 0.27, 0.51, 0.61 and 0.74 (a. u.), respectively, which is close to that expected (e.g., from the Zunger-Cohen valence  $s$ -electron radii<sup>6</sup> of 0.22, 0.46, 0.65 and 0.75 (a. u.)).

A point of importance is the relative insensitivity of non-bonded X - -X distances to the deviation (Fig 3) of bonded M-X distances from the calculated value of  $d_{MX}^{n0}$  (using eqn 1). This is consistent with early seminal observations of Bartell<sup>16</sup>, re-emphasized by Gillespie and coworkers<sup>13, 14</sup>. The invariance of 1,3- non-bonded distances may be regarded as struts and the more variable 1,2- distances as tensile elements in molecular tensegrity structures of gas-phase  $\text{MX}_n$  compounds. Our methodology is

applicable to terminal linkages in gas-phase dimers (such as those in  $\text{M}_2\text{X}_6$  dimers,  $\text{M} = \text{Al}, \text{Ga}$ ,  $\text{X} = \text{halogen}$ ) or organic compounds but not to the bridged linkages (showing effects due to a transition to a condensed state). The main exceptions (not shown) are the linear compounds  $\text{KrF}_2$  and  $\text{XeF}_2$  (not shown) and the axial non-bonded F - -F distances in T-shaped molecules,  $\text{BrF}_3$  and  $\text{ClF}_3$ . The understanding of non-bonded X---X distance using eqn 5 for these and other  $n > 4$   $\text{MX}_n$  compounds requires more elaboration.

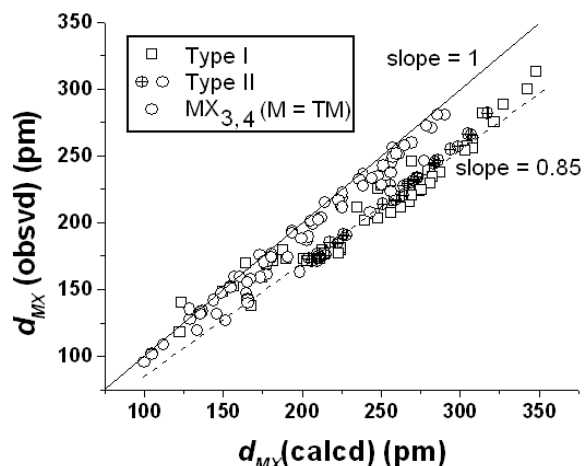


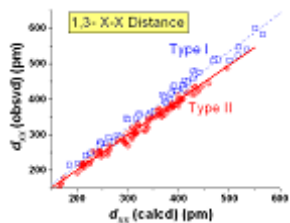
Figure 3. Plots of  $d_{MX}(\text{obs})$  of gas-phase  $\text{MX}_n$  compounds ( $n \geq 4$ ) (Refs 11, 12) versus  $d_{MX}^{n0}$  (calculated) using eqn 1.

In conclusion, we find that molecular tensegrity seems to be a powerful concept for molecular structure. Our methodology does not require prior knowledge of ionic character of M-X bond, nor the full weight of quantum chemical complications, given a core atomic size.

The author thanks the Council of Scientific and Industrial Research for an emeritus sustenance grant.

**Supporting Information Available:** Table of observed and calculated distances for  $\sim 160$  gas-phase  $\text{MX}_n$  compounds, a figure showing the nature of fit obtained from eqn 6..

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- see Hargittai, M., *Chem. Rev.* **2000**, *100*, 2233-2301 and references therein for a comprehensive review.
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ABSTRACT This article describes a methodology for obtaining quantitatively the 1,3-non bonded distances in gas-phase  $MX_n$  compounds ( $n \leq 4$ ) of nearly 160 inorganic compounds (including those of transition metal elements). The simple principles behind its methodology (involving only linear equations), its quantitative character, its transparency, its portability and its generality have not been noticed before. There is no dependence on the “ionic character” of the M-X bond, nor on complex calculations using molecular wave functions, once the atomic size is given.

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