Molecular geometry from molecular tensegrity: A case study of gas-phase MX_2 compounds

Parthasarathy Ganguly

Physical Chemistry Division, National Chemical Laboratory,
Pune 411 008, India

We define a tensegrity factor, $t_{00}^{\pm}$, for X–M–X linkages of gas-phase MX_n compounds (X is an atom of an insulating element) that is a measure of the matching of 'ideal' 1,2-(single-bonded) M–X distance, d_{MX}^{00}, to the 'ideal' (non-bonded) 1,3-X---X distances, d_{MX}^{00}. The actually observed 1,3-distance, d_{XX} is given (within 1% error) by $2CR(X)/F_S$, where F_S ($= 2$–$1.41_{00}^{\pm}$) is shown to be an *ab initio* quantity with no adjustable parameter, no dependence on actual M–X distance or bond order and with $2CR(X)$ depending only on whether M is an atom of an insulating element ($2CR(X) \equiv d_{XX}^{00}$) or whether M is metallic ($2CR(X) = 1.1d_{XX}^{00}$). This is illustrated for gas-phase MX_2 compounds.

Keywords: Gas-phase, molecular geometry, MX_2 compounds, tensegrity.

IN current descriptions of molecular structure, geometry of a molecule at rest is determined by the balance between attractive and repulsive forces between charges. Such electrostatic forces may be viewed as the electrostatic equivalent of the balance between compressive and tensile elements that define stable engineering tensegrity structures[1]. The fundamental Fuller–Snelson notion is that counteracting forces stabilize a structure consisting of structural tension elements (continuous cables) and discontinuous compression elements (struts) to stabilize itself. The struts act in concert when loaded with the tension elements, efficiently dispersing loads around a structure. Such considerations could be used to define a 'molecular tensegrity' that accounts for molecular shape at the simplest level without requiring, say, the time-consuming computations of *ab initio* energy-landscape scenarios or even force-field methodologies. We find that consideration of just a two-dimensional X–M–X structure is sufficient, with a single strut determining the 1,3-X---X distance, while the M atoms provide the load that changes this distance. A case study is made of gas-phase MX_2 compounds in this communication.

Quantitative descriptions from a model of tensile integrity structures are expected from a mechanical model[2] for such molecules. A mechanical model is available from the justification of a 'ball-and-stick' description[3,4] of interatomic distances using a principle of maximum mechanical hardness. The basic tenet of such a model is that

for an energy-minimized, density-optimized molecule at rest, the chemical potential $\mu = 0$, as in a free atom[3]. Interatomic (1,2-bonded) distances may then be expressed as a simple (mechanical) function of 'core' atomic sizes which are consistent with the $\mu = 0$ condition[4]. Since the balance of opposing forces determines the stable structure, interatomic distances are a measure of this balance. The way the 1,2-(M–X) and 1,3-(X—X) distances accommodate themselves in an X–M–X linkage would then form the basic ingredients of the molecular tensegrity. We avoid thereby complex energy-minimizing computations in quantum methodologies or their force field approximations that start with a $\mu \neq 0$ state.

We use the empirical atomic size (from ref. 3), r_G, consistent with the $\mu = 0$ condition. A rigorous justification of this size is not necessary for the present illustrative purposes. We have shown[3,4] that a 'single-bond' M–X distance, d_{XX}^{00} (the superscript, 00 or subscript, 0, used for future continuity, refers to a 'single' bond for which there are no 'unsaturated', or 'extrabonding' valence electron, $n_v = 0$) may be written in terms of a core atomic size, r_G as (the + and – signs refer to the sign of the charge associated with the atoms in brackets):

$$d_{XX}^{00} = CR_0^+(M) + CR_0^-(X)$$

$$= \{ C_0^+ r_G(M) + C_0^- r_G(X) \}_{\text{`ball'}} + [D_0^+ + D_0^-]_{\text{`stick'}} \quad (1)$$

$$= \{ 2.24 r_G(M) + 2.49 r_G(X) \}_{\text{`ball'}} + 74 \text{ pm } (d_{H-H}) \quad (2)$$

$$\equiv \varepsilon_{\text{eff}} [\{ C_1^+ r_G(M) + C_1 r_G(X) \}]_{\text{`ball'}} + (4a_H/3)_{\text{`stick'}}], \quad (3)$$

where ε_{ff} (≥ 1) is an effective dielectric constant[3] (≈ 1.05 in most cases) and $CR_0^\pm = \varepsilon_{\text{eff}} C_1^\pm$ with C_1^+ ($\sim 2.15 \sim \pi^{2/3}$) and C_1^- ($\sim 2.37 \sim \pi^{4/3}/2$) are semi-empirical parameters[4] (for $\varepsilon_{\text{eff}} = 1$). The ideal 1,3 non-bonded distance, d_{XX}^{00}, is expected to be a function of a characteristic size, $CR(X)$, for a given type of bonding interaction. In order to be consistent with the charge-transfer[3,4] sizes of eq. (1) we take[2]

$$d_{XX}^{00} = 2CR(X) \equiv 2CR_0^-(X) = 2[2.49 r_G(X) + 111]. \quad (4)$$

The observed 1,3-X---X distance, d_{XX}(obs), of terminal X–M–X linkages may be expressed[3] by a term F_S, such that

$$d_{XX} = 2CR(X)/F_S. \quad (5)$$

The term F_S has been introduced earlier[3] to express changes in interatomic (1,2- as well as 1,3-) distances due to the presence of n_v 'extrabonding' valence electrons on an atom with spin $S_v = n_v/2$. In general the size $CR_0^\pm$ of an atom is changed to $CR_0^\pm/F_S$ where $F_S \approx [1 + (2/\pi)^2 \{S_v(S_v + 1)\}^{1/3}] \approx 1$, 1.18, 1.26. 1.32, 1.38 an 1.46 for $n_v = 0$, 1, 2, 3, 4 and 5 respectively. The 1,3-X---X distance is given as $2CR_0^-(X)/\langle F_S(X) \rangle$, where $\langle F_S(X) \rangle =)\{1/F_S(X) + 1/F_S(X')\}$ with X and X' allowed to have different values, n_v and n_v'. The ligand close-packed radius, r_{LCP}, of Gilles-

pie and coworkers[5] is well expressed by $CR_{n,n'}{}^-(X) = [CR_0^-(X)/\langle F_S(X)\rangle$. We have compared as an illustration, the various r_{LCP} with $CR_{n,n'}(X)$ (in pm) by the notation $r_{LCP}[CR_{n,n'}(X)$ $(n_v,\ n_v')]$. For oxygen we have (ionic radii, 140 pm) 140[140(0, 0)], 134[129(0, 1)], 120[118(1,1)], 114[114.5 (1,2)]; for chlorine, we find 181[180(0,0)], 168[166(0,1)], 151[152(1,1)], 144[147(1,2)], and so on.

We require obtaining F_S as a function of atomic sizes from a mechanical model that expresses the dependence of the X---X distance on the M atoms. For this, we define an ideal charge-transfer 'tensegrity' factor, $t_{00}^{\pm}$ (similar to the tolerace factor[6] in perovskites), that is a measure of the matching between ideal distances d_{MX}^{00} (eq. (1)) and d_{XX}^{00} (eq. (4)), the idealized distance between X atoms. Thus

$$t_{00}^{\pm} = d_{MX}^{00}/d_{XX}^{00} = 0.5\{CR_0^+(M)/CR_0^-(X) + 1\}. \tag{6}$$

The superscript, $\pm$, refers to charge-transfer states CR_0^+ and CR_0^- in eq. (1). Equation (6) is an *ab initio* quantity based on simple geometry and dependent only on the core atomic size of M and X atoms (eqs (1) and (4)) without requiring separate estimates of ionic character, for example. It is this tensegrity factor that defines bounds on distances between pairs of atoms in a molecule and to identify the struts.

One requires an interpretation of $CR_0^+(M)/CR_0^-(X)$ to exploit eq. (6) and obtain X---X (strut) distances for given M and X in a manner that is independent of the actual (cable) M–X dynamics or without really requiring an understanding of the complex dance (equations of motion) of the charged particles. In real physical space, the cumulative effect of these tension elements is represented by the way the M atom is positioned, which is then expressed in terms of omni-symmetrical aspects of the basic tensegrity structure. We adopt Fuller's assertion that both 'macrocosmic and microcosmic structures interact in the same way' as far as the balance of forces are concerned and ensure 'most economic equilibrious packings'. The packing could be expressed by the ratio $R^{\pm} = CR_0^+(M)/CR_0^-(X)$, which is characteristic for different coordination numbers, e.g. $R^{\pm} = 0.414$ – equivalent to $t_{00}^{\pm} = 0.707$ – is the upper limit for tetrahedral coordination or lower limit for octahedral coordination. We may write

$$F_S(\text{cal}) = 2 - 1.414 t_{00}^{\pm}, \tag{7}$$

such that $d_{XX} = 2CR(X)$ (eq. (5)), when $CR_0^+(M)/CR_0^-(X) \to 0.414$ $(F_S = 1)$. We find (surprisingly) that for all gas-phase MX_n $(n \leq 4)$ compounds, eq. (7) reproduces well the observed X---X distances with $CR(X) = CR_0^-(X)$, when M is an atom of an insulating elements (at NTP) and $CR(X) \approx 1.1 CR_0^-(X)$, when M is an atom of a metallic element. We discuss this aspect in another communication, noting for the present that $CR_0^-(X)$ could represent an ionic size and $1.1 CR_0^-(X)$, a van der Waals size.

Figure 1 shows a comparison of the observed and calculated values (using eqs (5) and (7)) of the 1,3- X---X

distance, d_{X---X} for all gas-phase MX_2 compounds listed in Weast[7]. The fit (R factor > 0.98) is surprisingly good considering that the data have been obtained at a wide range of temperature and pressure. For all gas-phase MX_n $(n \leq 4)$ compounds, we find that eqs (5) and (7) give an equally good fit (using similar methods as above) that

$$d_{XX}(\text{obs}) = 1.04(0.004)d_{XX}(\text{calcd})$$
$$(R = 0.99,\ \text{SD} = 9\ \text{pm}). \tag{8}$$

The 1,3 O–O distance in compounds such as NO_2, SO_2, SeO_2, SO_3 and SO_2Cl_2 are given surprisingly well by eqs (5) and (7). The main exceptions are the linear compounds KrF_2 and XeF_2 (not shown). The 'expansion' of X---X distances in dihalides, when M is a metallic element is an additional new result, as expanding (or repulsive) non-bonded interaction is not anticipated in dispersion forces nor in Deb's mechanical model[2]. Repulsive Casimir forces could be expected for metallic spheres under certain boundary conditions[8].

We emphasize that the universal function of core size that yields the tensegrity factor, $t_{00}^{\pm}$, does not have any experimental input or adjustable parameter, given the 'core' atomic sizes, r_G. Our procedure also does not use circular arguments in the sense that we do not use as inputs the very parameters we wish to calculate. Not only is $d_{X---X}(\text{obsvd})$ different from the ideal value of $2CR(X)$ (eq. (5)), the observed M–X distance is also different from the ideal 'single'-bond distance (eq. (1)). This is shown in Figure 2. For MO_2 compounds such as NO_2, SO_2, SeO_2, ClO_2 and CO_2, the M–O distance is given by $d_{M-X} \sim d_{MX}^{00}/1.18$, which is consistent with a 'double bond' character[3]. The calculated X---X distance, however, does not
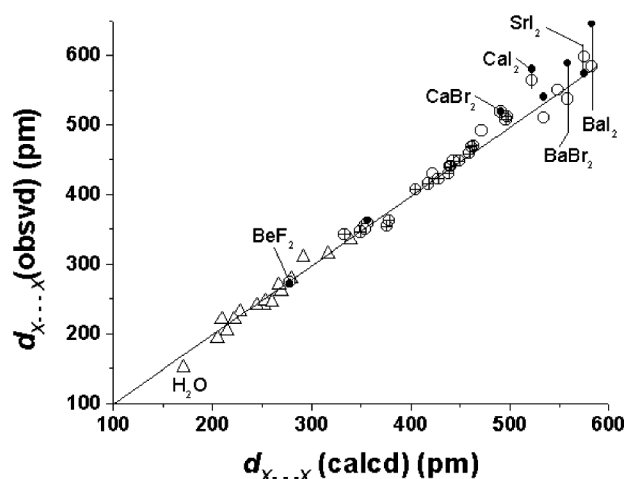
Figure 1. Plot of observed non-bonded 1,3-X---X distance, d_{X---X} (obs) in MX_2 compounds vs calculated distance, d_{X---X}(calcd) (eqs (5) and (7)) when X is an insulator atom. Triangles: M is an insulator atom $\{CR(X) = CR_0^-(X)\}$; circles M = metal, $CR(X) = 1.1CR_0^-(X)$; circles with cross: M is the transition metal atom; Filled circles: Calculated in the literature (ref. 9).
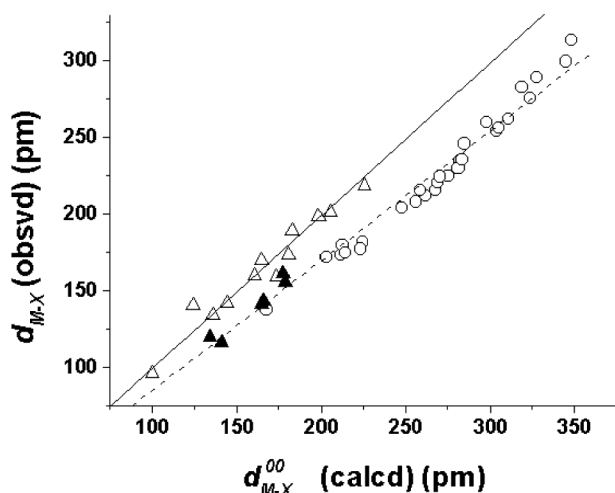
Figure 2. Plots of observed *M–X* distance for various *MX*$_2$ compounds (*X* = insulator). Triangles: *M* = insulator; Filled triangles *M–X* double bond; Circles: *M* = metal.

depend on the *M–X* bond order. More significantly, the *M–X* distance in *MX*$_2$ compounds in which *M* is a metal atom is also given by $d_{MX}^{00}/1.18$, even if they are nominally 'single' bonds. The simultaneous 'contraction' of *M–X* distance and 'expansion' of 1,3-*X---X* is contrary to that anticipated from eqs (5) and (7). This aspect will be treated in more detail in another communication in the context of atomic size and metallization of elements.

We further find that:

(1) The 1,3-*X---X* non-bonded distance is the more important structure-defining parameter (varying by ~ 1%) than the 1,2-*M–X* bonded distance (varying by ~ 4%) in an *X–M–X* linkage.

(2) Once the 1,2- and 1,3-distances are known, the geometry (linear or bent, say, in *MX*$_2$ halides) follows quite simply without requiring complex theoretical modelling[8] (such as participation of *d* electrons).

(3) Our methodology is (understandably) applicable to terminal linkages in any gas-phase molecules, but not always to the distance in ring systems, including, for example, bridged linkages[9] in *M*$_2$*X*$_6$ dimers.

(4) Changes in core size due to changes in valence or spin state are required to obtain 1,3- non-bonded *X---X* distance for transition metal elements in *MX*$_n$ compounds (*n* = 3, 4).

In conclusion, we have shown that the 1,3-non-bonded distance in an *X–M–X* linkage is a fundamental and environment-independent property of the 'core' sizes of *M* and *X* atoms, without requiring inputs from quantum chemical (valence bond or molecular orbital) procedures. This follows from a simple mechanical model of molecular tensegrity, when various forces are balanced for a μ = 0 condition for the chemical potential. Molecular geometry seems to be available *ab initio* from purely classical considerations, given a 'core' atomic size.

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Molecular differentiation in *Murraya Koenig ex L.* species in India inferred through ITS, RAPD and DAMD analysis

S. A. Ranade[1,*], T. S. Rana[2], A. P. Srivastava[1] and K. N. Nair[2]

[1]Plant Molecular Biology – Genomics, and
[2]Conservation Biology and Molecular Taxonomy,
National Botanical Research Institute, Rana Pratap Marg, Lucknow 226 001, India

Two species of *Murraya*, viz. *M. koenigii* (L.) Spreng. (2*n* = 18) and *M. paniculata* (L.) Jack. (2*n* = 18), occurring in India and used in indigenous system of medicine, have a long-standing problem on systematic disposition of the wild and cultivated forms (*M. exotica/*

*For correspondence. (e-mail: shirishranade@yahoo.com)