The Sum of van der Waals Radii – A Pitfall in the Search for Bonding

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The most widely used criterion for the evaluation of chemical bonding, especially of weak bonding, are interatomic distances shorter than the sum of the van der Waals radii, $d(X \cdots Y) < \Sigma r(\text{vdW})[X, Y]$. The shortcomings of these radii are, however, so serious, that illicit conclusions are easily arrived at. It is proposed to discard the 'shorter than $\Sigma r(\text{vdW})$' criterion altogether and to rely on alternative criteria.

Key words: Polarized Covalent Bonds, Supramolecular Aggregates, Weak Attractive Interactions, van der Waals Radii, Limits of Precision

Introduction

Chemistry is concerned with interatomic attractive forces, called bonds. Various types of attractive forces exist, including the ionic bond (Coulomb attraction between ions of opposite charge) and the hydrogen bond (an attractive interaction mediated by a hydrogen atom). The strongest interatomic attractive force is the covalent bond which is effected by two electrons residing between the two bonded atoms. Atomic aggregates held together by covalent bonds are termed molecules; the formation and scission of such bonds makes up the realm of molecular chemistry. Between molecules, other attractive forces may be operative, giving rise to larger atomic aggregates. The formation and properties of such species constitute the realm of supramolecular chemistry.

Molecular and supramolecular chemistry are not clearly separated, because hybrids of covalent bonds and other types of attraction exist. It is the rule rather than the exception that covalently bonded atoms have different electronegativities (which is true even for atoms of the same element, *e. g.* C(sp^3) and C(sp^2)). The bonding electrons are unevenly distributed, so that such covalent bonds are polarized and the involved atoms carry partial charges. Such bonds, then, are intermediate between covalent and ionic bonds. They tend to undergo heterolytic cleavage; if so, they are termed dative bonds [1] and are designated by the special symbol →. Because they depend on the number of valence electrons, covalent bonds are restricted in number per atom; they have distinct bond angles and bond lengths and are very resistant against stretching so that, within the simplistic model of atoms as spheres, covalent bond radii, $r(\text{cov})$, can be assigned. Two-electron bonds of low polarity exhibit the same features. Current interest tends to focus on highly polarized bonds which are more akin to ionic bonds. Monoatomic ions can reasonably well be treated as spheres whose sizes determine the solid state structure and hence the coordination numbers, interionic distances $d(X^+ \cdots Y^-)$ and angles $X^+ \cdots Y^- \cdots X^+$ and $Y^- \cdots X^+ \cdots Y^-$. From $d(X^+ \cdots Y^-)$, ionic radii, $r(\text{ion})[X^+]$ and $r(\text{ion})[Y^-]$, can be deduced. The anionic radii $r(\text{ion})[Y^-]$ exceed $r(\text{cov})[Y]$ considerably (*e. g.*, $r(\text{cov})[Cl] = 99$ pm, $r(\text{ion})[Cl^-] = 181$ pm [2, 3]). For cationic radii $r(\text{ion})[X^+]$ no such comparison is easily at hand, because due to the scarcity of nonpolar covalent bonds for most metals reliable values of $r(\text{cov})[X]$ are not available. An exception is, *e. g.*, mercury: $d(\text{Hg–Hg}) = 254$ pm in Hg_2Cl_2 [4] suggests $r(\text{cov})[Hg] = 127$ pm. In this case, however, $r(\text{ion})[Hg^+]$ is not available. Textbooks equal covalent radii with atomic radii, $r(\text{atom})$ [2, 3]; $r(\text{atom})[X]$ exceeds $r(\text{ion})[X^+]$ considerably (*e. g.*, $r(\text{atom})[X]/r(\text{ion})[X^+]$ for $X^+ = Li^+$ 135/60, Mg^{2+} 130/65 pm [2]). Thus, $\Sigma r(\text{cov})[X, Y]$ and $\Sigma r(\text{ion})[X^+, Y^-]$ may accidentally be similar (*e. g.* for LiCl, 234 and 241 pm, respectively), but neither constant bond lengths nor particular bond angles are characteristic properties of the ionic bond. The repercussions of these features on highly polarized cova-

lent bonds have so far not been satisfactorily explored, and yet many interatomic distances much longer than $\Sigma r(\text{cov})[X, Y]$ and $\Sigma r(\text{ion})[X^+, Y^-]$ have been claimed to be evidence for attractive interactions between X and Y, such as secondary bonding, dative bonding, weak donor-acceptor interactions *etc*.

Discussion

The criterion for the frequently proposed non-covalent or partially covalent attractive forces are interatomic distances intermediate between the sums of covalent and van der Waals radii, $\Sigma r(\text{cov})[X, Y]$ and $\Sigma r(\text{vdW})[X, Y]$, respectively, called short contacts. By definition, $\Sigma r(\text{vdW})[X, Y]$ is the equilibrium distance at which interatomic repulsion forces and the notoriously weak (and isotropic) van der Waals attractive forces between the atoms X and Y are equal, the atoms again being assumed to be spheres [5]. Any attractive force ('bond') stronger than the van der Waals forces must therefore lead to shorter interatomic distances. The axiomatic assumption of spherical atoms at $\Sigma r(\text{vdW})$ distance is reasonably well met only for the noble gases. The spherical shape of the atoms is still a good approximation in, *e. g.*, metallic lithium, but $d(\text{Li}\cdots\text{Li})$ must be shorter than $2r(\text{vdW})[\text{Li}]$, because the metallic bond is stronger than van der Waals attraction. Therefore, even for elemental metals, the evaluation of $r(\text{vdW})$ is not straightforward, and published values, consequently, are at best approximate. Pauling had restricted himself to propose van der Waals radii for hydrogen and the elements of groups 15 to 17, with an estimated accuracy of *ca.* 3 to 5 % [6], hence *ca.* 6 to 10 % for the sum of two van der Waals radii. The most popular set of van der Waals radii continues to be the list compiled in 1964 by Bondi [7]. Bondi assembled a list of "recommended" intermolecular van der Waals radii of nonmetallic elements (essentially Pauling's list extended by C, Si and the noble gases) for the purpose of volume calculations and warned expressly that these radii "*may not always be suitable for the calculation of contact distances in crystals*". He added that "*the van der Waals radii of metals in metal organic compounds are very difficult to obtain… It is not certain, therefore, how best to estimate the van der Waals radii of metals in metal organic compounds.*" From critical volumes he evaluated "radii of metal atoms in nonbonded state" which have not expressly been equated with van der Waals radii of "metals (in nonmetallic compounds)". The textbook of Dicker-

son, Gray, Darensbourg and Darensbourg refrains altogether from assigning van der Waals radii to metals [3]. Elsewhere, van der Waals radii of metals have been proposed [8], but their precision may be even lower than that of the nonmetals. Even for the latter, various tables of van der Waals radii exhibit substantial differences [3, 7 – 10]. Shortenings based, *e. g.*, on Bondi's figures should not be accepted as evidence for bonding unless in compliance with alternative scales, and, in view of the low precision, small shortenings not at all. Since all attractive interactions between atoms X and Y will cause $d(X\cdots Y) < \Sigma r(\text{vdW})[X, Y]$, it is trivial (though frequently ignored) that from 'short contacts' no conclusions can be drawn that a particular type of bond (such as dative bonding $Y \rightarrow X$) is operative.

The assignment of radii becomes increasingly problematic, the more the assumed spherical shape of the atoms is disturbed by stronger interatomic forces, *e. g.* covalent bonds [11]. The value of van der Waals radii for an assessment of intermolecular interactions of covalently bound atoms is, hence, at least questionable. For interactions $Y\cdots X$ of atoms X attached by covalent bonds to atoms Z of different electronegativity ($Y\cdots XZ_n$) another difficulty arises: Assume that in a molecule XZ_n the bonds X-Z are covalent and strictly nonpolar. Then, according to a wide-spread custom, for a non-covalent interaction between X and Y, $r(\text{vdW})[X]$ would be applied. If, on the other hand, XZ_n is entirely ionic ($X^{n+}n\,Z^-$), for an additional interaction $X\cdots Y$ the ionic radius $r(\text{ion})[X^{n+}]$ would be applicable. Similarly, the interacting atom Y may be attached to other atoms Z' by unpolarized covalent bonds $Z'-Y$ so that $r(\text{vdW})[Y]$ would be applicable, or, alternatively, the $Y\cdots Z'$ interaction may be entirely ionic ($Y^-\cdots Z'^+$) so that the ionic radius $r(\text{ion})[Y^-]$ becomes pertinent. As a rule, van der Waals and anionic radii do not or hardly differ within the limits of precision [12] (*e. g.*, F/F$^-$ 130/135 pm, Cl/Cl$^-$ 180/181 pm, Br/Br$^-$ 190/195 pm, I/I$^-$ 210/216 pm [13]) so that polarization of the $Z'-Y$ bonds leaves $r[Y]$ unaffected. For cations, however, $r(\text{ion})[X^+]$ is much smaller than $r(\text{vdW})[X]$ (*e. g.*, $r(\text{ion})[\text{Li}^+] = 60$ pm, $r(\text{vdW})[\text{Li}] = 260$ pm, $\Delta r = -200$ pm!). Therefore, *e. g.*, for an interaction $Y\cdots\text{Li-R}$ of an organolithium molecule, a formal shortening $d(Y\cdots\text{Li}) < \Sigma r(\text{vdW})[Y, \text{Li}]$ would be grossly misleading because of the highly polar two-electron bond Li-C which imposes a substantial positive charge on the Li atom. Even if the degree of polarization

could be precisely evaluated, it cannot be assumed that the relationship existing between [r(vdW)[Li] – r(ion)[Li$^+$]] and the charge on Li is, *e. g.*, linear, so that an adequate correction of r[Li] is impossible. Conclusions in favour of, *e. g.*, R$'_2$O → Li-R, R$'_3$N → Li-R, R$'_2$O/R$'_3$N → Mg(R)Hal coordination based on d(O/N···Li/Mg) < Σr(vdW)[O/N, Li/Mg] are abundant, but may be unwarranted because r[Li/Mg] has been overestimated.

Though to a lesser extent, the same objection applies to many alleged R$'_3$N → SiR$_4$ coordinations, *etc.*, especially when the atoms covalently bound to Si are strongly electronegative and therefore impose a high polarization on the Si-R bonds. In phosphorus chemistry, research on hypercoordination based on the 'shorter than Σr(vdW)' criterion led to the conclusion that phosphines, R$_3$P, are rarely inclined to engage in hypercoordinative bonding for which P-bound electronegative atoms like F, O, N are essential. According to Pauling's scale, phosphorus is only slightly less electronegative than carbon (2.1 and 2.5, respectively) [14]. The P–C bonds in R$_3$P are, therefore, only slightly polarized. The electronegativities of F, O, N (4.0, 3.5, 3.0, repectively [14]) render P–F/O/N bonds much more polar and thereby create a substantial positive charge on the P atom. Again, r(vdW)[P] ought to be substantially reduced, but to what extent, cannot be assessed with any precision. Many alleged cases of hypercoordination may, therefore, be artefacts due to an inadequate choice of reference values.

For intramolecular non-covalent and related interactions, it has frequently been ignored that d(X···Y) < Σr(vdW)[X, Y] is a necessary, but not a sufficient criterion for bonding. In polyatomic molecules, bond lengths and natural bond angles create a multitude of interatomic distances much smaller than Σr(vdW) which are a matter of course rather than evidence for bonding [15]. The argument is not restricted to rigid structures (as, *e. g.*, to the *ortho*-positions of 1,2-disubstituted benzenes and the *peri*-positions of 1,8-disubstituted naphthalenes [16, 17]). For example, in 2-substituted benzyl compounds 2-X-C$_6$H$_4$-CH$_2$-Y, rotation around the single bonds is usually not restricted. Simple trigonometric calculations based on typical bond lengths and angles reveal that in the process of free rotation conformations with d(X···Y) < Σr(vdW)[X, Y] are passed by. In these conformations, d(X···Y) is at a minimum, but the minimum is not indicative of particularly efficient bonding, but on the contrary of a maximum of repulsive steric interac-

tion. If steric repulsion is overcompensated by attractive forces (*e. g.* Coulomb attraction, when X and Y are atoms of different electronegativity), such *cisoid* conformations may become more favourable than, *e. g.*, the *transoid* conformation with d(X···Y) > Σr(vdW)[X, Y]. In such cases, an interatomic distance shorter than Σr(vdW) would indeed indicate attractive forces, but it would still not permit to infer a particular kind of bonding interaction such as hypercoordinative dative bonding N → Si for X = R$_3$Si and Y = NR$'_2$ [18]. Furthermore, such non-covalent attractive forces (*e. g.*, a hydrogen bond O-H···N for X = OH, Y = NMe$_2$) may force neighbouring atoms into sub-Σr(vdW) distance; in such cases the short contacts would enhance steric congestion and thereby energetically destabilize the system rather than contribute to its bonding energies by additional attractive interaction.

Intermolecular interactions comply better with the concept of van der Waals radii as outlined by Bondi [7], but suffer from the same limitations. Molecules may associate to supramolecular aggregates by attractive forces of significant strength (*e. g.* by strong hydrogen bonds; ions to ion pairs by Coulomb attraction [19]) which place non-bonded atoms at the peripheries of the associating faces at short distances. For example, many short contacts C-H···X purported to be weak hydrogen bonds may in fact be conditioned by stronger forces which determine the supramolecular aggregation [20].

A number of far-reaching conclusions have been drawn from d(X···Y) < Σr(vdW)[X, Y] as a measure of bonding. Dative bonds Y → X are frequently believed to be able to assume any bond lengths between Σr(vdW)[X, Y] and Σr(cov)[X, Y] *ad libitum* [21]. Depending on the degree of shortening, the alleged donor-acceptor interactions are termed weak or strong. In the realm of hypercoordination, it has frequently been observed that such 'weak interactions' do not affect the bond angles; *e. g.* in potential R$'_3$N → SiR$_4$ interactions, the six R-Si-R angles retain the sum of 6 · 109.47° instead of conforming with the angles of a trigonal bipyramid (TBP). The phenomenon triggered the concept of the (mono-, bi-, tri-, tetra-) capped tetrahedron and of [4+n] coordination (n = 1, 2, 3, 4) instead of penta-, hexa-coordination *etc.* [17]. As a consequence, dative bonds seemed to be fundamentally different from "normal" covalent bonds. Claims are frequent that short contacts are the cause of certain properties though the latter may in fact be conditioned by quite different parameters and the pertinent distances a
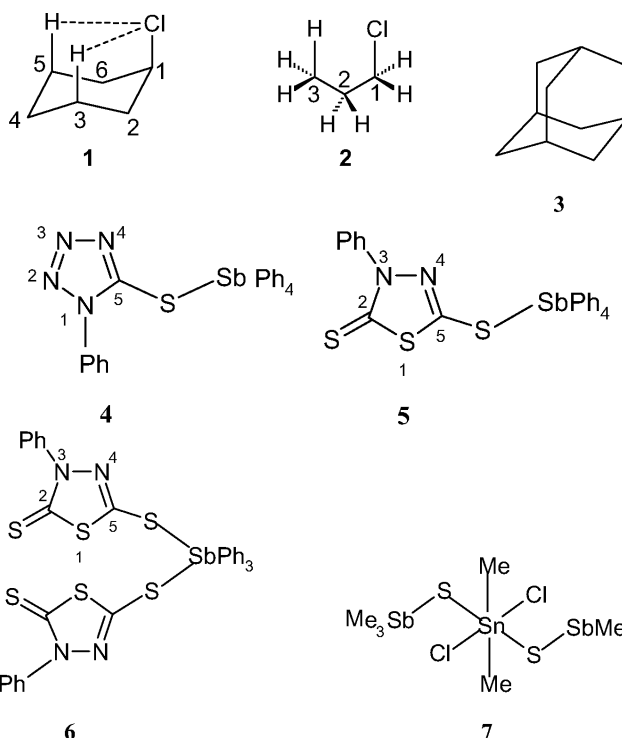
consequence of the molecular geometry, crystal packing effects, *etc.* Rationalizations of 'short contacts' are sometimes supported by quantum chemical calculations, but satisfactory simulation of the experimental distances means only that a particular orbital interaction is compatible with the data; only a countercheck with deliberate neglect of the proposed interaction giving significantly inferior agreement could suggest that it plays indeed a decisive role.

Some striking cases selected from recent literature underscore the fragility of the 'shorter than Σr(vdW)' criterion. At least for intramolecular interactions, even the van der Waals radii of nonmetals may lead astray.

The discovery of a novel 1,3 diaxial H···Cl weak (attractive) interaction in chlorocyclohexane (**1**) has been claimed [22]. The authors isolated an inclusion complex of **1** and 9,9'-bianthryl which contains **1** as the chair conformer with axial Cl. The X-ray structure determination revealed H···Cl distances of 290 and 288 pm between the Cl atom at C(1) and the axial H atoms at C(3) and C(5) of the cyclohexane chair, only 5–7 pm (*ca.* 2 %) shorter than the sum of the van der Waals radii of H and Cl, Σr(vdW)[H, Cl] (120 and 175 pm, respectively, according to Bondi [7]). The

slight deviation is still within Pauling's limits of precision and thus in no need of a rationalization [23]. Nevertheless, it was concluded that "these data suggest the presence of a weak interaction between the axial Cl and H" [22].

The Cl–C(1)H–C(2/6)H_2–C(3/5)H_2 segment of **1** can be regarded as a substituted 1-chloropropane (**2**) in which free rotation around the C–C bonds is precluded. In **2**, the conformation with the dihedral angle zero for Cl-C(1)···C(3)-H is the equivalent of the 1,3 diaxial arrangement in **1**. Because of the ecliptic arrangement of one H atom at C(3) and the Cl atom at C(1), it represents a maximum of steric repulsion within the process of rotation around the C–C bonds. In an idealized molecule, all angles (H–C–C, C–C–C, Cl–C–C) are tetrahedral (109.47°). With typical bond lengths (C–C: 154 pm [24], Cl–C: 175 pm in 2-Cl-C_3H_7 [24], H–C: 107 pm [25]), standard trigonometric calculations lead to a distance d(H···Cl) = 187 pm, 108 pm (37 %) shorter than Σr(vdW)[H, Cl] as a measure of substantial steric repulsion rather than attractive interaction. In **1**, d(C(1)–Cl) = 180.4 pm [22] is longer, d(C(3)–H_{axial}) = 97.0 pm [22] and the average of the pertinent C–C bonds, d(C(1)–C(2), C(2)–C(3)) = 151.7 pm [22], shorter, and the averages of the

angles Cl–C–C, C–C–C and C–C–H equal to 109.6°, 112.1° and 109.4°, respectively. The trigonometric calculation yields $d(H \cdots Cl) = 199$ pm, 12 pm longer, but still 33 % shorter than $\Sigma r(vdW)[H, Cl]$ [26].

We conclude *i)* that in **1** $d(H \cdots Cl)$ is not significantly shorter than $\Sigma r(vdW)[H, Cl]$ and *ii)* that any shorter distance would indicate an interaction of the same type as the well-known repulsion between substituents at $C(sp^3)$ atoms in the ecliptic conformations in processes of rotation around $C(sp^3)$–$C(sp^3)$ bonds. In a related reasoning, the Cl atom at C(1) and the H atoms at C(3,5) are the geometric equivalents of geminal methylene C atoms in adamantane (**3**). The distance $d(H_2C \cdots CH_2) = 249.5$ pm [27] is shorter than $\Sigma r(vdW)[C, C] = 340$ pm [8] by 27 %. The short contact is evidence of steric crowding rather than of an attractive interaction between the C atoms of the methylene groups.

According to the 'shorter than $\Sigma r(vdW)$' criterion, the higher main group elements such as Sn, Sb and Bi seem to engage more readily in hypercoordinate dative interactions than their lighter analogs (Si, P). This is surprising, because the increasing difference in the size of the interacting atoms (*e. g.* N < Si, P, but N ≪ Sn, Sb) should make the required overlap of the donor and the acceptor orbitals less efficient. However, the shortening with respect to $\Sigma r(vdW)[donor, acceptor]$ may be deceiving. Because of the reduced electronegativities (P 2.1, Sb 1.8 [14]), Sb–X bonds will be more polarized than P–X bonds; hence, $r(vdW)[Sb]$ requires a greater reduction than $r(vdW)[P]$. In addition, the uncertainty of $r(vdW)$ may be misleading. For example, crystalline 2-chloro-1,3-dimethyl-2-stiba-4-imidazoline "consists of molecules that are connected by intermolecular Sb $\cdots$ Cl contacts (3.86 Å) slightly shorter than the sum of van der Waals radii (4.00 Å)" [28]. The assessment rests on the van der Waals radii of Cotton *et al.*, $\Sigma r(vdW)[Sb, Cl] = 220 + 180 = 400$ pm [10]; the formal shortening of 3.5 % is within the limits of precision and may even be excessive, because the polarization of the Sb–Cl bond has not been taken into account. If instead, Batsanov's values ($r(vdW)[Sb] = 175$ pm, $r(vdW)[Cl] = 180$ pm [8]) are used, $d(Sb \cdots Cl)$ exceeds $\Sigma r(vdW)[Sb, Cl] = 355$ pm by 31 pm.

For tetraphenyl-(1-phenyl-tetrazol-5-ylthio)antimony (**4**), tetraphenyl-(3-phenyl-2-thioxo-2,3-dihydro-1,3,4-thiadiazol-5-ylthio)antimony (**5**), and triphenyl-bis(3-phenyl-2-thioxo-2,3-dihydro-1,3,4-thiadiazol-5-ylthio)antimony (**6**), the geometry around

the hypercoordinate Sb atom has been described as distorted trigonal-bipyramidal (TBP) with the S atom(s) in apical position(s) [29]. In **4**, the distance $d(N(4) \cdots Sb) = 371.1$ pm was found to agree well with $\Sigma r(vdW)[Sb, N] = 220 + 150 = 370$ pm according to Cotton *et al.* [10] so that no bonding interaction was apparent. In **5**, $d(N(4) \cdots Sb)$ is 8 % shorter than 370 pm, but as independent methods (*viz.* IR spectroscopy) did not indicate N(4) $\cdots$ Sb interaction, it was concluded that this 'shortening' did not either. In **6**, both N(4) $\cdots$ Sb distances are even slightly shorter, *viz.* $11 - 12$ % less than $\Sigma r(vdW)[Sb, N] = 370$ pm; in this case, the authors deduced an (albeit very weak) bonding interaction and described the geometry around Sb as a distorted capped trigonal prism. In fact, the phenomenon is again an artefact depending on the choice of $r(vdW)$: According to Batsanov's scale [8], $\Sigma r(vdW)[Sb, N] = 175 + 155 = 330$ pm exceeds neither $d(N(4) \cdots Sb) = 338.8/340.7$ pm (in two independent molecules of **5**) nor – within the limits of precision – $d(N(4) \cdots Sb) = 329.1/324.5$ pm (in **6**). The IR spectrum of **6** has been believed to provide independent proof of the alleged N(4) $\cdots$ Sb interaction: A weak band at *ca.* 430 cm^{-1} has been attributed to N $\cdots$ Sb vibration, and a high frequency shift of the C=N band by *ca.* 20 cm^{-1} has also been ascribed to the N $\cdots$ Sb coordination [29]. To be sure, these assignments are only tentative, and the features call for alternative explanations once the proposed rationalization is no longer supported by the 'shorter than $\Sigma r(vdW)$' criterion.

Intermolecular short contacts have been claimed to create supramolecular structures [29]: In **4**, $d(H \cdots N(2)) = 261.6$ pm between N(2) of the tetrazole ring and a *meta*-bound H atom of one of the phenyl rings at Sb of a second molecule is shorter than $\Sigma r(vdW)[H, N] = 275$ pm by 5 %, hence not significantly within the limits of precision. Nevertheless, $d(C \cdots N(2)) = 341.2$ pm (exceeding $\Sigma r(vdW)[C, N] = 325$ pm by 5 %), $d(H \cdots N(2)) = 261.6$ pm and the angle C–H $\cdots$ N(2), 143.8°, have been interpreted as a weak C–H $\cdots$ N(2) hydrogen bond which links the molecules to an intermolecular chain. In **5**, a pair of intermolecular C–H $\cdots$ S=C hydrogen bonds between a *meta*-H of Sb-bound phenyl and the thioxo sulfur atom at the thiadiazoline ring has been held responsible for the formation of "an interesting macrocyclic dimer" [29]. Again, the data do not support this conclusion: $d(H \cdots S) = 291.7/293.6$ pm is only 4 % (hence insignificantly) shorter than $\Sigma r(vdW)[H,$

S] = 305 pm, and $d(C \cdots S)$ = 375.5/385.3 pm exceeds $\Sigma r(vdW)[C, S]$ = 355 pm by 6 – 9 %. (The angle $C–H \cdots S$, 150.6/168.3°, deviates less from linearity than the $C–H \cdots N(2)$ angle in **4**.) **6** exhibits almost identical features: $d(H \cdots S)$ 297.2 pm = $\Sigma r(vdW)[H, S]$ – 3 %, $d(C \cdots S)$ = 379.9 pm = $\Sigma r(vdW)[C, S]$ + 7 %, angle $C–H \cdots S$ 148.8°, again not indicating the alleged weak hydrogen bonds. It should be kept in mind that the C–H bond is a poor hydrogen bond donor and sulfur not a good hydrogen bond acceptor [30] and that the proximity of C–H and S has not been proven to be associated with any gain in energy and thus to qualify for a bond.

Trimethylantimony dichloride and dimethyltin sulfide were found to give an adduct, $(Me_3SbS)_2SnMe_2Cl_2$ (**7**), in which both Sn and Sb were claimed to be hypercoordinate [31]. While the Sn atom is unequivocally hexacoordinate with two Cl atoms, two S atoms and two C atoms at the corners of an only slightly distorted octahedron, the claim for Sb rests solely on the distance $d(Sb \cdots Cl)$ = 357.7 pm, 98 pm longer than $d(Sn \cdots Cl)$, but 43 pm shorter than Bondi's $\Sigma r(vdW)[Sb, Cl]$. If, however, Batsanov's van der Waals radii are used, $\Sigma r(vdW)[Sb, Cl]$ = 175 + 180 = 355 pm and $d(Sb \cdots Cl)$ = 357.7 pm are identical within the precision of van der Waals radii. The average of the C–Sb–C and C–Sb–S bond angles is 109.37°, hence perfectly tetrahedral and thus not indicative of hypercoordination. Sb is significantly less electronegative than C and S (1.8 *vs.* 2.5 for both C and S according to Pauling's scale) so that the three C–Sb bonds should give rise to a partial positive charge at the Sb centre. Hence, $r(vdW)[Sb]$ should be somewhat reduced. On the other hand, the polarity of the Sn–Cl bond would put some negative charge on the Cl atom; this, however, would remain without consequences (*vide supra*). Hence $\Sigma r[Sb, Cl]$ should be even shorter than 355 pm so that $d(Sb \cdots Cl)$ = 357.7 pm actually exceeds the estimated non-bonding distance. The claim of twofold hypercoordination in **7** is thus not corroborated.

In the Schiff bases of the (2-formyl-phenyl) tri(phenyl)(group 15) onium cations with 4-methoxy-aniline, **8a** – **c**, $N \cdots P/As/Sb$ distances intermediate between the sums of the covalent and van der Waals radii of the respective elements were found and the P/As/Sb atoms rated as pentacoordinate [32]. While the phosphonium and arsonium salts **8a,b** exhibited only modest and similar 'shortenings' with respect to $\Sigma r(vdW)[N, P/As]$, the phenomenon is more pro-

8 (cisoid)   **8** (transoid)

E = P^+ (**8a**), As^+ (**8b**), Sb^+ (**8c**)
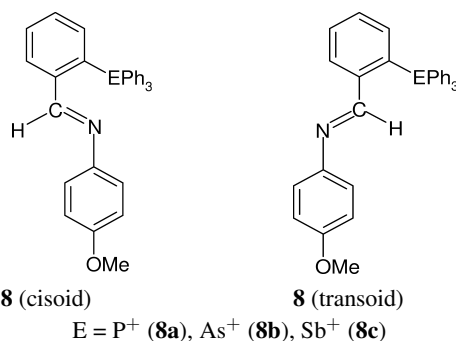
nounced in the stibonium salt **8c**. Dative interaction $N \rightarrow P/As/Sb$ would be unexpected in view of the comparatively weak donor capacity of azomethine nitrogen, much stronger nucleophiles such as phenyl lithium being required to induce tetraorgano-onium phosphorus, arsenic and antimony to hypercoordination [33]; tertiary amine nitrogen does not enter into $N \rightarrow P^+$ interaction even when a hypercoordinate N-P bond would strongly reduce intramolecular distortion [34].

In fact, $d(N \cdots P)$ = 275.7 and 281.0 pm in two independent molecules of **8a** is *ca.* 16 – 18 % shorter than $\Sigma r(vdW)[N, P]$ = 335 pm according to Bondi [7, 35]. The 'shortening' is slightly smaller with respect to Batsanov's scale [8] (−13.5 to −15 %) and shrinks further if an incertitude of *ca.* 5 % for each $r(vdW)$ and the impact of the positive charge upon $r(vdW)[P]$ are taken into account [36]. Not unexpectedly, the figures for **8b** are similar ($d(N \cdots As)$ = 277.2 pm = $\Sigma r(vdW)[N, As]$ −18.5 % (Bondi [7]), −14.7 % (Batsanov [8])).

Though $(d(N \cdots P/As))$, then, is clearly shorter than $\Sigma r(vdW)[N, P/As]$, it still provides no proof for $N \rightarrow P/As$ bonding. In solution, no restriction of the rotation around the C(2)–CH bond is indicated by the NMR spectra. Rotation can therefore be assumed to pass through the two coplanar conformations. In the *transoid* conformation, $d(N \cdots P/As)$ is much larger than $\Sigma r(vdW)[N, P/As]$. However, for the *cisoid* conformation, trigonometric calculations with model parameters ($d(C(1)–P/As)$ from $Ph_4P^+ ClO_4^-$ [37] and $Ph_4As^+ BPh_4^-$ [38], $d(C(2)–CH)$ and $d(HC=N)$ from Ph-CH=N-Ph [39], $d(C(1)–C(2))$ = 139 pm as in benzene; all angles 120°) yield $d(N \cdots P/As)$ = 255 and 257 pm, respectively, even *ca.* 24 % shorter than Bondi's $\Sigma r(vdW)[N, P/As]$. In the process of rotation, $\Sigma r(vdW)[N, P/As]$ is, hence, no obstacle to an approach of the N and P/As atoms to distances even shorter than those found in the solid state and thus

(according to common tenets) to establish an even stronger N→P/As dative bond. Cases in which a rigid geometry favours a distance $d(N \cdots P)$ of *ca.* 250 pm suggest that the approach of N and P/As in the *cisoid* conformation would suffice to enable the hetero atoms to establish a full hypercoordinate N–P bond of *ca.* 215 pm length [21a] in spite of increased steric resistance, if there were an incentive to do so. The fact that, instead, **8a,b** prefer N $\cdots$ P/As distances substantially longer than necessary, indicates that no driving force for the formation of a N→P/As bond is operative. The moderate increase of $d(N \cdots P/As)$ with respect to the *cisoid* conformation may reflect a tendency to adopt a coplanar arrangement of the C_6H_4–CH=N–C_6H_4 segment which is disturbed by the bulky *ortho*-Ph_3P^+/As^+ substituent. Such coplanarity would benefit from the through-conjugation between the C_6H_4 groups across the HC=N bond. The preponderance of the *cisoid* over the *transoid* conformation may tentatively be ascribed to Coulomb attraction between N and P^+/As^+ (Pauling electronegativities: N 3.0, P^+: *ca.* 2.4, As^+: *ca.* 2.3 [36]). The importance of Coulomb attraction and its capability to establish sub-Σr(vdW) distances are borne out by the trihydrobromide of tris(2-dimethylaminomethyl-phenyl) stibine, (2-$Me_2HN^+CH_2$-C_6H_4)$_3$Sb 3 Br^-, in which ion pair formation between N^+ and Br^- establishes $N^+ \cdots Br^-$ distances of 320.9 and 324.2 pm, 7 and 6 % shorter than Batsanov's Σr(vdW)[N, Br] = 345 pm, at the expense of a close approach of N and Sb: The N $\cdots$ Sb distances remain well above Σr(vdW)[N, Sb] [40].

It emerges that a rationalization without recourse to Σr(vdW)[N, P/As] and N→P^+/As^+ dative bonding is possible. The C-P^+/As^+-C bond angles are not indicative of hypercoordinate interaction either: Though some of the individual angles deviate from tetrahedrality by several degrees, their sums add well to $6 \cdot 109.47° = 656.8°$ (**8a**: 655.7 and 656.3°; **8b**: 655.9°). The geometry around P^+/As^+ can therefore adequately be described as slightly distorted tetrahedral, whereas most of the N $\cdots$ P^+/As^+–C angles amount to only *ca.* 75° and do, therefore, not look like bond angles. To be sure, inclusion of N as a coordinating atom would permit to formally describe the arrangement as a N-monocapped C_4P^+/As^+ tetrahedron (or even as a severely distorted TBP), but this is

a matter of course due to the intramolecular geometry from which no conclusions concerning the nature of the N $\cdots$ P^+/As^+ interactions can be drawn.

In **8c**, $d(N \cdots Sb)$ = 257.7 pm is 30 % shorter than Σr(vdW)[N, Sb] = 370 pm (according to Cotton and Wilkinson [10]) and 22 % longer than Σr(cov)[N, Sb] = 211 pm (according to Pauling [25]). A serious discrepancy of r(vdW)[Sb] in Cotton's and Wilkinson's and in Batsanov's scale (220 and 175 pm, respectively) reduces the 'shortening' to 22 % if Batsanov's scale is used. Further reductions are called for by the polarity of the Sb^+–C(Ph) bonds (Pauling electronegativities C 2.5, Sb^+ *ca.* 2.0 [14, 36]) which will further enhance the charge at Sb^+. The latter effect will be anticipated to play a much greater role than in **8a,b** so that with reference to a realistic value of r(vdW)[Sb^+] the 'shortening' may not greatly exceed that of $d(N \cdots P^+/As^+)$ in **8a,b**. A trigonometric model calculation with d(C–Sb) = 208 pm (as in Ph_4Sb^+ BPh_4^- [38], all other parameters as for **8a,b**) yields $d(N \cdots Sb)$ = 262 pm for the *cisoid*, coplanar conformation of **8c**, identical with the experimental distance within the limits of precision of the calculation.

In Batsanov's scale, the van der Waals radii of P (170 pm), As (170 pm) and Sb (175 pm) are equal within the limits of precision. However, because of d(C-Sb) > d(C-As) > d(C-P) steric opposition of the *ortho* substituent against coplanarization would be smaller in **8c** than in **8a,b**. Adoption of either the *transoid* or the *cisoid* conformation should therefore be facilitated. If there is already a predilection for the *cisoid* arrangement in **8a,b**, this should be more pronounced in **8c**, because Coulomb attraction between N and Sb is stronger. Again, the experimental features are amenable to a rationalization in which Σr(vdW)[N, Sb] and N→Sb interaction play no role. As is not unusual for 5th period elements, the C–Sb–C angles conform with tetrahedrality with decreased precision (sum of 6 angles $656.8 - 5.4°$), but still permit to describe the C_4Sb^+ segment as a slightly distorted tetrahedron.

Conclusion

Clearly, the value of van der Waals radii as source of information about bonding, and in particular about weak bonding, seems so limited that it may be best to discard the 'shorter than Σr(vdW)' criterion altogether and to turn to safer criteria [21b, 41].

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