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New applications of van der Waals radii in chemistry

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Abstract. This review is part of a continuing study of the many applications of van der Waals radii (WR) in various fields of chemistry, and especially in crystal chemistry and stereochemistry. An analysis of relevant publications has shown that WR systems are used most often and most successfully in studies of the conformation of molecules, though their original source is usually an analysis of intermolecular contacts. This review will deal with traditional applications of WR and with some new aspects, including the geometrical modelling of chemical reactions and new types of specific intermolecular interactions. The bibliography includes 149 references.

I. Introduction

Our previous review of the application of van der Waals radii in chemistry, published[1] in 1989, dealt with information published between the mid-1930s and 1988. However, for a number of reasons several interesting publications (especially those published in the second half of 1987, when our review had been completed) failed to be included. In recent years the flow of information on the application of WR has grown steadily, and the areas of application have also increased. Because of its universality, simplicity, and objectiveness the WR method is convenient for rapid qualitative estimates, and it is often used in the final solution of many problems of practical importance, though (as we have already pointed out) the detailed features of crystal structures are more satisfactorily identified and explained by using concepts such as molecular orbitals, energy calculations, and atom–atom potentials.

These omissions compelled us to extend our critical analysis of the use of WR radii in chemistry, and resulted in the publication of the present review. But even now we cannot be certain that our review is exhaustive, in spite of the very large volume of information which we have assembled and presented. The theme of this review differs substantially from that of our earlier review.[1] Firstly, the section entitled 'Conformations of molecules' has been enlarged significantly, in keeping with the increasing amount of space devoted to the structure of the molecules (as opposed to the description of the molecular packing in the crystals) and to the effect of the molecular structure on the reactivity of compounds. Secondly, the present review introduces new methods of using the WR, and identifies situations not previously discussed which show, in particular, that steric effects can not only stretch the valence bonds but also initiate bond shortening, and that in some parts of the molecule these effects produce an enforced approach of atoms not joined by a valence bond in other parts of the same molecule, leading (under favourable conditions) to the formation of a valence bond. Thirdly, some already traditional methods of using the WR and the results of their application, which had not been adequately dealt with in Ref. 1, are discussed more fully: these include the geometric modelling of chemical reactions, new types of specific interaction, some new types of hydrogen bond, etc. Because of the very large (and continuously growing) number of studies in which WR are used we cannot claim that the whole of this information has been assimilated into this review. To some extent our choice has been arbitrary, but we have at all times endeavoured to make the choice balanced and representative of the methodological aspects of the problem (by the correct use of the optimum WR values). This task could be adequately satisfied by examining in the first instance the work of Russian workers. It should be noted that successful applications of the WR are more often found in studies carried out in this country than in reports from foreign workers. This is not fortuitous: the science of organic crystal chemistry (and its associated field, the concept of WR) were created largely by the work of Kitaigorodskii in this country).

The WR are most often used to detect contracted (or shortened) contacts between atoms which are not covalently bound. These contacts can be intermolecular or intramolecular. A correct choice of the reference point is important in the determination of the shortening. If the length of the contact (whether taken as the sum of the WR or as twice the geometric mean, $2\sqrt{R_i R_j}$) is close to this point the choice of the value from which the difference is calculated assumes an even greater importance. In our work the most probable length of the reference contacts between different atoms (by using the statistically averaged WR values, see below) was determined by giving priority to the doubled geometric mean. Nevertheless in our presentation of published material we quote (following the appropriate authors) a comparison of the length of the atom–atom contacts with the sum of the WR. On the whole no serious discrepancies were found, because the quantities $2\sqrt{R_i R_j}$ and

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Table 1. Length of ordinary and of contracted atom – atom intermolecular contacts, in ångströms.

Contact	$2\sqrt{R_iR_j}$	d_{ij}
C···C	3.42	3.27
C···H	2.82	2.52
C···N	3.20	3.05
C···O	2.97	2.82
C···S	3.55	3.40
C···F	3.09	2.94
C···Cl	3.60	3.45
C···Br	3.67	3.52
C···I	3.82	3.67
N···N	3.00	2.85
N···H	2.64	2.34
N···O	2.78	2.63
N···S	3.22	3.17
N···F	2.90	2.75
N···Cl	3.38	3.23
N···Br	3.44	3.29
N···I	3.58	3.43
O···O[a]	2.58	2.43
Br···H	3.02	2.72
O···H	2.45	2.15
O···S	3.08	2.93
O···F	2.69	2.54
O···Cl	3.13	2.98
O···Br	3.19	3.04
O···I	3.32	3.17
S···S	3.68	3.53
S···H	2.92	2.62
S···F	3.21	3.06
S···Cl	3.74	3.59
S···Br	3.81	3.66
S···I	3.97	3.82
F···F	2.80	2.65
F···H	2.54	2.24
F···Cl	3.26	3.11
F···Br	3.32	3.17
F···I	3.46	3.31
Cl···Cl	3.80	3.65
Cl···H	2.97	2.67
Cl···Br	3.87	3.72
Cl···I	4.03	3.88
Br···Br	3.94	3.79
Br···I	4.11	3.96
I···I	4.29	4.14
I···H	3.14	2.84
H···H	2.31	2.01

Note. $2\sqrt{R_iR_j}$ is the mean length of the normal van der Waals contact; d_{ij} is the boundary between the shortened (by van der Waals interaction) and the contracted contacts, or in other words between the ordinary van der Waals interactions and the specific interactions.
[a] See Section II.

$R_i + R_j$ do not usually differ very markedly. We should note that the term bearing contact refers to interatomic molecule–molecule contacts whose existence is a necessary and sufficient condition for the creation of a three-dimensional system of contacting molecules in the crystal.

There is a group of WR systems for which the difference between the members is determined both by the chosen set of structural data and by the procedure used to define the WR. They were analysed in Refs 1 and 2. However, we should stress once again that in many cases the procedures used by some authors were not followed strictly, or they were approximated to an unacceptable degree, and that occasionally a single standard structure was used to determine the radius, thus invalidating the statistical nature of the WR. An important constituent of each system should be not only the averaged WR values but also a clear statement of the 'normal' van der Waals contact limits. This is because the length of the intermolecular contacts formed by the van der Waals interaction depends on many factors: the size of the molecules, their mutual orientation, the distribution of effective atomic charges, etc. These limits were first stated for contacts involving the H, C, N, O, and Cl atoms (see Ref. 3). The statistically averaged values for these atoms [H (1.16 Å), C (1.71 Å), N (1.50 Å), O (1.29 Å), and Cl (1.90 Å), see Ref. 3], were later supplemented with statistically averaged WR values for the sulfur (1.84 Å),[4] fluorine (1.40 Å),[5] bromine (1.97 Å), and iodine atoms (2.14 Å) (see Ref. 6). In the same study[6] the value for chlorine was redetermined by a different method, and was again found to be 1.90 Å. This is the only system of statistically averaged WR values which quotes the maximum deviations (δ) of the length of van der Waals reference contacts from their average values. For the contacts not involving hydrogen atoms $\delta \leqslant 0.15$ Å, whereas for the contacts involving hydrogen atoms $\delta \leqslant 0.30$ Å.

In this review (as in the previous one[1]) we shall use the terms 'contracted' and 'shortened' contacts. A shortened contact is shorter than the statistically average value for the van der Waals interaction, but does not go beyond the limit

$$d = 2\sqrt{R_iR_j} - \delta, \qquad \text{or} \qquad d = R_i + R_j - \delta,$$

or in other words, it can be defined as a contact of length r_{ij} for which

$$d < r_{ij} < d + \delta.$$

If $r_{ij} < d$ the intermolecular contacts are referred to as contracted.

In our analysis of the length of atom – atom contacts we shall use the parameters listed in Table 1.

In some of the studies examined in this review the noncovalent contacts between silicon and other atoms are discussed. Because of the lack of statistically averaged WR values for silicon in these Si···X contacts we compare them in our discussion with tentative values of the sum of the WR for the corresponding atoms. We take the van der Waals radius of silicon atom to be $\sim 2.1 \pm 0.1$ Å, because the WR of nonmetal atoms of the third period is $\sim 0.4 - 0.5$ Å greater than the WR of the corresponding atoms in the second period, and the WR of the carbon atom is 1.71 Å.

The WR system closest to the system of statistically averaged WR values[3–6] is the Pauling system,[7] except for the radii of oxygen and chlorine. The Pauling system is a system of rounded-off ionic radii (except for the Group V elements), which could be identified (according to Pauling) with the van der Waals radii. Pauling lowered the rounded-off values of the ionic radii of the Group V elements by 0.2 Å. We believe that when statistically averaged values of the WR are not available the best procedure is to adopt the values proposed by Pauling.

Descriptions of structures which are pierced by weak or very weak 'hydrogen bonds' of the X–H···Y type are often met in recent publications. In many of these 'H-bonds' the H···Y distance is equal to or even greater than (by a large amount in some cases) the average length of the normal van der Waals contact. Wherever hydrogen atoms exist these 'contacts' can be found with great ease. In the present review we shall be concerned only with H-bonds which form real associations of molecules, as indicated (when appropriate measurements are carried out) by the physical properties of the crystals.

II. Normal intermolecular contacts

In studies of a new substance, if a comparison of the shortest intermolecular (atom–atom) distances with the sum of the WR or with the parameters $2\sqrt{R_iR_j}$ in conjunction with data on the dispersion of the length of the reference contacts gives the expected molecular packing in the crystals we may call the intermolecular interactions 'normal'. This concept can be formulated in different ways: (1) the intermolecular contacts are similar to the normal contacts; (2) the structure consists of a packing of discrete molecules connected by van der Waals contacts; (3) in the structure the intermolecular contacts correspond to van der Waals interactions, etc. (see, for example, Refs 8–15).

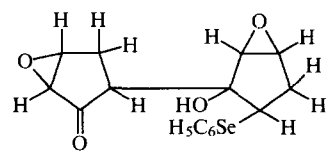
Among the normal intermolecular contacts recognised in the past few years special attention should be paid to the O···O contacts without a hydrogen bond, 2.58, 2.62, 2.68, and 2.72 Å long in different organic crystals.[16] These contacts are among the shortest intermolecular contacts of this type, and are close to twice the statistically averaged value of the oxygen WR (2.58 Å). The latter observation is also of interest, because the 1.29 Å value[3] for the oxygen atom, which 'works' well in intermolecular contacts between oxygen and other atoms, usually involving interactions between atoms with large residual charges of the same sign, appears too low in O···O contacts. This problem has been examined in depth in previous reviews.[1,2]

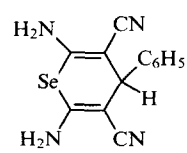
A broader concept of the structure of a van der Waals crystal in terms of the WR is obtained by determining the molecular coordination number (MCN), which is often a useful characteristic of the packing of the molecules in the crystal. In homomolecular crystals a continuous series of MCN between 9 and 18 was reported,[17] the number 9 being found only once (in the pyrene structure), and 18 also only once [in the structure of dichlorobis(vinylbenzotriazole)cobalt(II)].[18] The most widely found MCN are 14 and 12 (in ~50% and ~30% of cases respectively).[17,19] An analysis of the intermolecular contacts in the structure of molybdenum(IV) dioxobispropiohydroxamate, based on the rules laid out in Ref. 17, showed that the MCN for this complex is 8 (see Ref. 20). Thus the MCN series in homomolecular crystals has now been extended slightly and covers the range from 8 to 18.

In order to obtain a more complex picture of the structure of a van der Waals crystal, and to identify the molecules which are most strongly bound and form various types of association (dimers, chains, layers), the geometrical analysis must be supplemented by energy calculations, since the energies of the van der Waals interactions even in the first coordination sphere can be markedly different (in some cases by a large factor).[21] According to a calculation of the intermolecular interaction energies the molecules in a crystal of nickel(II) bis-[4-(n-heptyloxy-*N*-(4′-methoxyphenyl)benzaldimino-2-olate] form layers parallel to the (100) plane; the energy within the layer (54.3 kcal mol^{-1}) exceeds the interlayer energy (11.2 kcal mol^{-1}) about 5-fold.[22] In spite of the well known difficulties associated with the calculation of effective charges on atoms (resulting from the need to reconcile the methods of calculating the different components of the overall energy of the molecular crystal †) the intermolecular interaction energies should be calculated allowing for the electrostatic component, which can have a substantial influence on the total (overall) interaction energy of the molecules.[21]

The role of the steric factor is most clearly seen in the packing of molecules of the fluorine derivatives of *p*-methoxybenzylidene-*p*′-butylaniline in crystals. Combining the WR with an energy calculation showed that the replacement of hydrogen atoms (WR 1.16 Å) by fluorine atoms (WR 1.40 Å) in the $F_3C-C_6H_4-CH=N-C_6H_4-C_4F_9$ molecule increases the volume of the two end substituents, making the packing arrangements which are standard in liquid-crystalline phases seriously unfavourable.[23]

The identification by WR of the unreal (extremely contracted) intermolecular contacts was used in an unexpected way to establish the real structure of partially disordered crystals. The first studies of this type were reported in our previous review.[1] Their further development (for example, in Refs 24 and 25) will be considered here. The fundamental idea of these studies is that by using the WR we can reveal the unreality of the statistical structure given by X-ray structural analysis, in which the benzene rings are located (with assumed equal probabilities) in two mutually perpendicular positions, and in which the true structure of the crystral (domains or layer block) is thus established almost unequivocally.[24] Thus, crystals of the selenium compounds $C_{16}H_{16}O_4Se$ and $C_{13}H_{10}N_4Se$ consist of fully ordered layers each of which displays one of the two possible methods (*a* or *b*) of accommodating the benzene rings which form the core of the layer and are packed (in both cases) in a parquet floor pattern, so that rings having both a primary and a secondary orientation are matched in a well defined way. The surface of the layer, and therefore also the method of superposing the layers, remain unchanged. This creates the possibility of obtaining a special kind of polytype: (1) the crystal consists of *a* layers: (2) the crystal consists of *b* layers; (3) the crystal consists of a random (or a regular) alternation of *a* and *b* layers. The latter situation is seen in these compounds, in which blocks of *a* layers alternate with blocks of *b* layers.





A similar result was obtained for the crystal structure of 3-bromobicyclo{3.3.1}non-2-en-4-one. According to X-ray structural analysis data[25] the oxygen atoms in these crystals are accommodated randomly in two positions (with populations of 2/3 and 1/3 respectively). This means that the substance contains L and D enantiomers, but (as was pointed out[25]) these cannot have a random distribution because it would lead to unrealistic intermolecular contacts. By using the WR and calculating the intermolecular interaction energy it was shown[26] that the crystal most probably consists of an assembly of domains of two types: (1) racemic [L, D] domains, containing equal amounts of the L and D enantiomers, and (2) [L] (or [D]) domains, consisting of L (or D) enantiomers. A domain structure of the [L], [D] type, in which each domain contains only enantiomers of one type, must of course be excluded.

In addition to the above comments many examples of the use of WR to identify the normal intermolecular contacts in problems of structural biology and to interpret the physicochemical properties of substances are discussed in our previous review[1] and in Section V of the present review.

III. Contracted intermolecular contacts

Contracted intermolecular contacts usually denote the presence of specific interactions (SI), which are much stronger than ordinary van der Waals interactions. Specific interactions are of the attractive type, and they have a marked effect on the structure and properties of molecular crystals. Unlike contracted intermolecular contacts, contracted intramolecular contacts are only seldom associated with attractive interactions, and they are much more frequently the result of steric stress. In the present review we shall examine, in addition to the types of SI previously discussed, other types of SI not considered in Ref. 1.

† See the review by T V Timofeeva et al. in *Uspekhi Khimii* **49** 966 (1980) [*Russ Chem. Rev.* **49** 509 (1980)]

The validity of the conclusions on the contraction of intermolecular contacts and on SI of the O···X type can be tested by using 1.29 Å as the WR of oxygen (i.e. the value recommended by the present writers[3]): this value is substantially lower than the values proposed by other workers. Its use has allowed the SI to be identified in the packing of 2-bromo-1,4,8-trinitro-6(5H)-phenanthridinone molecules.[27] In this case we have the Br···O contact 2.967 Å long (for an average length of the normal contact of 3.19 Å and a lower limit d of the normal van der Waals interaction for these atoms of 3.04 Å). The C–Br···O angle (171.1°) probably denotes the direction of the SI.[27]

The contracted intermolecular contacts, which indicate the presence of SI, justify the conclusion that molecular associations of various types are present in the various structures. Thus, in the crystal structure of 4-methylbenz-2,1,3-thiadiazolecopper(I) iodide a strongly contracted N···S intermolecular contact (3.01 Å) has been detected,[28] whereas the length of the normal contact between these atoms is 3.32 Å, and $d = 3.17$ Å.[29] In this structure we have chains of molecules connected by pairs of antiparallel contracted intermolecular contacts of this type.

Among the crystal structures studied in recent years we again find structures with strongly contracted Cl···Cl intermolecular contacts. They include the 1,3-dichloro-2,2,4,4-tetrachlorodiphosphethane structure,[30] with contracted (3.311 Å) Cl···Cl intermolecular contacts, and the *O*-carbamoylacetohydroximoyl chloride structure with contracted Cl···Cl intermolecular contacts 3.333 Å long, which is much less than double the WR of chlorine (3.800 Å). These contacts lie at the very beginning of an almost continuous series of contracted Cl···Cl intermolecular contacts, beginning with 3.26 Å. In a crystal of the dichloroneopentylglycollic ester of 3,4-dichloro-1,3-butadiene-2-chloro-2-butene-2-phosphonic acid we can distinguish chains of molecules which contain contracted (3.386 Å) Cl···Cl contacts,[32] and in the structure of the dichloroneopentylglycollic ester of 1,3,4-trichloro-2-butene-2-phosphonic acid the contracted Cl···Cl intermolecular bonds (3.408, 3.540, and 3.550 Å) are said[32] to be retained in the structure of the corresponding polymer, thus creating bonds between the units of one polymer chain or of neighbouring polymer chains.

A recent paper from our laboratory[33] describes an extension of an earlier study[34–36] of the geometric aspects of halogen···halogen intermolecular contacts in organic crystals. A statistical analysis of the geometric characteristics of 330 Cl···Cl intermolecular contacts in organic crystals without hydrogen bonds was carried out. The contacts were divided into four groups: strongly contracted in comparison with double the WR of chlorine, weakly contracted, normal, and stretched.

Occasionally contracted Cl···Cl intermolecular contacts can coexist with hydrogen bonds. In this case the Cl···Cl contacts and the hydrogen bonds jointly give rise to complex associations of molecules. In crystals of the Graw salt $[Pt(NH_3)_4Cl_2]Cl_2$ the $Pt(NH_3)_4Cl_2$ complexes are combined into infinite columns arranged on the tetrad symmetry axis[37] through the axial chlorine atoms, which form contracted Cl···Cl intermolecular contacts 3.54 Å long. the N–H···Cl hydrogen bonds (N···Cl 3.44, N–H 0.9, H···Cl 2.47 Å, NHCl angle 172.6°) connect the columns into a framework through the bridging chlorine atoms. We have discussed[38] the topology of the chlorine derivatives of phenol containing cooperative hydrogen bond systems (CHBS). Three examples of the association of molecules of this type with contracted intermolecular contacts shorter than 3.5 Å were given. In the pentachlorophenol structure the chains containing helical CHBS are connected into a framework by Cl···Cl contacts 3.43, 3.46, 3.48, and 3.54 Å long. The shortest contracted Cl···Cl intermolecular contacts in these structures (3.27 Å) are observed in the 3,4-dichlorophenol structure. There are also clusters containing four chlorine atoms each which are connected by Cl···Cl contacts 3.48 Å long. Paired and fourfold Cl···Cl contacts connect the chains of the CHBS into a framework. In the tetrachlorohydroquinone structure contracted Cl···Cl contacts (3.37 and 3.43 Å) connect the layers containing CHBS into a framework.

In the *p*-bromo-[*N'*-(5-nitrofurfurylidene)benzhydrazide] structure contracted Br···Br intermolecular contacts (3.381 Å)[39] are formed between the molecules of neighbouring chains (double the WR of bromine is 3.94 Å).[6] This contact denotes an intermolecular SI between the bromine atoms in the crystal, which hinders the packing of the ketohydrazone molecules into stacks by the 'head-to-tail' principle, as in crystals where the Br atom is replaced by H or by the SO_2CHF_2 group.

More than 150 symmetrically independent contracted S···S intermolecular contacts have been identified in crystals of cation-radical salts.[40–45] The cations of these salts are usually packed into stacks, often with formation of contracted S···S contacts, and the stacks into layers, often with formation of S···S contacts between the stacks. These contacts are now observed as commonly as the contracted halogen–halogen intermolecular contacts (except the F···F contacts, in which no SI exists).[5] Thus the most recent work has filled all the gaps in the series of S···S contacts from double the WR of sulfur (3.68 Å) to 3.27 Å (a contraction of 0.4 Å).[4]

In the crystals of organometallic compounds contracted intermolecular contacts involving metal atoms can be found. This problem is often very difficult to discuss, because no reliable WR for these atoms are available. For example, the WR values for the mercury atom quoted in the literature vary from 1.5 to 1.9 Å or more.[1] Nevertheless in some cases the presence of SI and of contracted intermolecular contacts in these crystals can be established unequivocally. In the structure of *Z*-1-methyl-2-chloromercury-2-phenylethenyl acetate Hg(B)···Cl(A) contacts (3.110 Å) are observed between the A and B molecules: these can undoubtedly be classified as contracted if the WR of mercury is taken as 1.50 Å and that of chlorine as 1.90 Å.[46] The presence of intermolecular SI in this contact is confirmed by the deviation from 180° of the bond angle C–Hg–Cl (171.2°) in the B molecule. In the A molecule the deviation of the bond angle C–Hg–Cl is smaller (177.4°), and the Hg(A)···Cl(B) contact is longer (3.326 Å), denoting a weaker attractive interaction in this contact. An Hg···Cl intermolecular contact shorter (3.082 Å) than those previously observed[46] was found in the dimethyl ester of *cis-exo*-3-chloromercuro-4-azidotricyclo-[4,2,2,$0^{2,5}$]dec-7-en-*cis-endo*-9,10-dicarboxylic acid.[47] In this molecule the Cl–Hg–C bond angle has fallen to 173.2°. In the structure of the monohydrate of the *N*-phthaloylglycinate of trimethyltin the SI between the tin atom and the oxygen atom of a water molecule (contracted Sn···O contacts of 2.385 Å and 2.520 Å for a tin WR of 2.122 Å[49] and an oxygen WR of 1.29 Å)[3] replaces the tetrahedral coordination of the Sn atoms by a distorted trigonal bipyramid.[48] The contract Sn···O intermolecular contact (2.385 Å) is the shortest of the contacts of this type known when the paper by Ovsetsina et al. was published.[48]

In the research on intermolecular SI a special place must be given to studies of hydrogen bonds, because their presence (or absence) in the structure is often postulated to account for the different methods of packing molecules in crystals, for some conformational properties of the molecules, and even some physicochemical properties of substances. We have previously discussed[1] the geometrical criteria of the H-bond, and in particular we have pointed out that conclusions based on geometrical criteria obtained from structural data and from IR spectral data are often inconsistent. Therefore the criteria for the existence of hydrogen bonds are still an active topic of discussions (see, for example, Refs 50 and 51).

In this context we shall discuss only the relatively short hydrogen bonds which have a marked effect on the methods of packing molecules in crystals or on their physicochemical properties. From the very large number of new methods of using WR to describe H-associations of molecules we shall choose only examples which unambiguously characterise the different types of associations.

Crystals of 1-(2-methylphenyl)-3-methyl-5-(benzothiazol-2-yl)formazane contain A and B conformers (the contact conformation phenomenon).[52] In this structure two intermolecular H-bonds of the N–H···N type have been detected: N···N 2.910, N–H 0.89, H···N 2.08 Å, NHN 155°, and N···N 2.991, N–H 0.85, H···N 2.16 Å, NHN 165° (for d=2.34 Å), which combine the A and B molecules into dimers.‡ As a result of the presence of N–H···O bonds (N···O 3.00, N–H 1.05, H···O 2.01 Å, NHO 155° for d=2.15 Å) the molecules in the $C_{39}H_{56}N_2OBP$ crystal (see Litvinov and Naumov[53]) form centrosymmetrical dimers. In the α-diphenylphosphoryl-*o*-cresol crystal the molecules are connected into 16-member dimeric associations by pairs of P=O···H–O bonds in which the O···H distances are 1.81 Å,[54] and in the β-diphenylphosphorylethyl alcohol crystal three independent molecules are connected into an overall chain by P=O···H–O bonds (H···O distances 1.80, 1.84, and 1.86 Å).[54] Because of the presence of N–H···N bonds (N···N 2.828, N–H 0.94, H···N 1.96 Å for d=2.34 Å, NHN 165°) the molecules of 3,5-dichloro-1*H*-1,2,4-triazole form strong rings of three molecules arranged round the six-fold inversion axis of the crystal. Contracted N···Cl intermolecular contacts (3.149 Å for a sum of the WR of nitrogen and chlorine of 3.40 Å)[3] connect these rings into layers.[55] The existence of these layers, i.e. the fact that the most strongly bound molecules are combined, is confirmed by the anisotropy of the thermal deformation of these crystals (see Section V).

In the structure of *N*-(3-nitrocinnamoyl)-*N*-(2-chlorophenyl)-hydroxylamine a system of H-bonds often seen in hydroxamic acids has been detected: it includes two crystallographically independent O–H···O bonds (O···O 2.617, O–H 0.99, H···O 1.63 Å, OHO 176°, and O···O 2.634, O–H 0.81, H···O 1.82 Å, OHO 179°).[56] These hydrogen bonds connect the molecules into chains. O–H···Cl hydrogen bonds (O···Cl 3.00, O–H 1.04, H···Cl 2.02 Å for d=2.67 Å, OHCl 155°, and O···Cl 3.00, O–H 1.16, H···Cl 1.88 Å, OHCl 158°) were found in the complex anion $[2Cl^- + H_5O_2^+]^-$ of the $(BT)_2 \cdot 2Cl \cdot H_5O_2$ structure, where BT is bis-(butylenedithio)tetrathiafulvalene.[57] In the hydroxonium ion $H_5O_2^+$ a symmetrical O–H···O bond is formed (O···O 2.475, H···O 1.24 Å, OHO 168.1°). The hydroxonium ions are arranged on the diad symmetry axis and are interconnected through bridging Cl^- ions into an infinite chain by O–H···Cl hydrogen bonds.

A slightly different behaviour is observed in the cation···anion contacts of complex ions consisting of twenty or more atoms over which an excess of charge is distributed. In these contacts the distance between the X and Y atoms is not necessarily shorter than the average normal van der Waals contact. In the 1,2-dimethylacenaphthylene-1,2-*S*-phenylepisulfonium tetrachloroaluminate structure the $C_{20}H_{17}S^+$ cations and the $AlCl_4^-$ anions are grouped into stacks arranged in a checkerboard pattern, and the S···Cl contacts are found to be longer than the sum of the WR for sulfur and chlorine (3.74 Å).[58] The cation···anion contacts are occasionally shortened within limits acceptable for van der Waals interactions: for example, the S–Cl contacts of 3.602 and 3.691 Å,[40] 3.635 Å (see Ref. 59), and 3.65 Å[60] (for a sum of WR of 3.74 Å). However, in cation-radical salts we also find contracted cation···anion contacts, including strongly contracted contacts. Thus, a group of strongly contracted S···Cl cation···anion contacts forming in almost continuous series from 3.25 to 3.49 Å has been observed[40,42,59,60,61] in cation–radical salts (d=3.59 Å). In the $(ET)_3(ZnCl_4)_2$ structure, where ET is bis(ethylenedithio)tetrathiafulvalene, the strongly contracted S···Cl contacts of 3.253, 3.261, 3.295, 3.367, 3.371, and 3.424 Å have been observed,[60] in $(ET)_3Cl_2 \cdot 2H_2O$ the 3.328, 3.434, and 3.485 Å contacts,[61] in $(ET)_4ZnCl_4 \cdot C_6H_5CN$ the 3.356 and 3.488 Å contacts,[40] in $(ET)_4PtCl_6 \cdot C_6H_5CN$ the 3.410, 3.433, and 3.474 Å contacts[59] at T=293 K and 3.404 and 3.413 Å at T=218 K, and in the $(ET)_3CuCl_4 \cdot H_2O$ structure the 3.372 Å contact.[42]

Contracted S···Br cation···anion contacts of 3.536 and 3.614 Å,[45] and also of 3.625 and 3.638 Å (d=3.66 Å)[62] were found in the $(ET)_4PtBr_6$ and $BT \cdot IBr_2$ structures respectively.

As reported,[60] in $(ET)_3(ZnCl_4)_2$ the presence of a series of strongly contracted S···Cl contacts (see above) and also of a strongly contracted C···Cl contact (3.34 Å, d=3.45 Å)[60] can account for the nonequivalence in the $(ZnCl_4)_2^{4-}$ dianion of both the bond angles (from 105.9° and 115.6°) and the Zn–Cl distances (from 2.258 to 2.305 Å). We should stress the fact that these anomalies are produced not by internal steric stresses, which will be discussed in the next section, but by strong attractive external interactions. Similar phenomena were discovered in crystals of chlorine trifluoride at −100 °C (see Antipin et al.[63]) and of bromine trifluoride at −120 °C.[64] In the ClF_3 structure Cl···F contacts were found at 2.706 and 2.740 Å, shortened as compared with the normal Cl···F van der Waals contact (3.26 Å) by 0.52–0.55 Å but causing an extension of the Cl–F bridging bonds of 0.03–0.05 Å with respect to the axial bonds and of 0.16 Å with respect to the equatorial. In the BrF_3 structure we find Br···F contacts (2.45 Å) shortened by 0.87 Å with respect to a normal contact (3.32 Å) and extending the Br–F bridging bonds by 0.11 Å with respect to the axial and by 0.18 Å with respect to the equatorial Br–F bonds. Judging by the size of the contacts the stronger intermolecular SI in BrF_3 as compared with ClF_3 is responsible for the more substantial extension of the bridging bond in the former. By means of the SI mentioned above the molecules in crystals of ClF_3 form centrosymmetric cyclic tetramers, and in BrF_3 crystals they form chains. The strongly contracted B···F intermolecular contacts (2.663–2.705 Å) previously observed[65] in the BF_3 structure at 145 °C interconnect the molecules into infinite layers.

The above examples show that fluorine atoms tend to undergo strong attractive interactions with many other atoms (B, Cl, Br, and others). An example of the F···S intramolecular specific interaction is given below. However, as has already been pointed out, fluorine does not produce contracted F···F intermolecular contacts, and therefore specific F···F interactions are atypical.[5]

These effects of intermolecular SI on covalent bonds are well known in the case of intermolecular hydrogen bonds, and in particular of O–H···O symmetrical H-bonds.

A complex system of three types of SI has been observed[66] in 1,2-dimethyl-4-amino-5-ethoxymethylpyrimidinium iodide. In these crystals the cations are connected into dimers by pairs of antiparallel N–H···N hydrogen bonds (N···N 3.10, H···N 2.32 Å for d=2.34 Å, NHN 155.8°) The bridging $I^-(2)$ anions, which occupy individual positions at the inversion centres, form strong N–H···I H-bonds (N···I 3.66, H···I 2.58 Å for d=2.84 Å, NHN 156.6°) which connect the dimers in the direction of the *a* axis. The bridging $I^-(1)$ anions, which occupy individual positions on the 2 axes, interconnect the dimers in the direction of the *b* axis as a result of I···C specific interactions (3.573 Å for d=3.67 Å and a sum of WR of the iodine and carbon atoms of 3.85 Å). The resulting corrugated layers create the crystal structure by superimposing in the direction of the *c* axis in response to the van der Waals interaction.

IV. Conformations of molecules

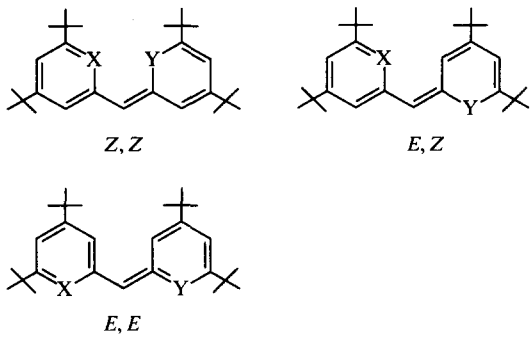
The classical conformational analysis[67–69] has recently undergone some far-reaching developments, and is now usually called 'molecular mechanics'.[70] It is based on the postulate that the conformation of a molecule is a compromise between the tendency for covalent bonds and bond angles to optimise their value (in the additive approximation corresponding to a minimum energy) and the tendency to minimise the resulting

‡ Here and elsewhere we shall use the term H-bond to denote the d value of the H···Y contact.

steric stresses, which create a repulsion between excessively close atoms which are not covalently bound and make a positive contribution to the energy of the molecule; at the same time the fragments of the molecule can rotate round ordinary bonds and thus lower the energy of the non-covalent interactions.

This model relies on the use of isotropic atom–atom potentials and, for approximate calculations based on the same idealogy, it can call upon the WR system. However, in practice isotropic atom–atom potentials are often inadequate. This situation is very well seen, for example, in the presence of both intermolecular and intramolecular SI. Intermolecular SI have been discussed in the previous section. Here we shall be concerned with intramolecular SI, and we shall examine some examples of their effect on the conformation of molecules.

The cation of 4,6,4′,6′,tetra-*tert*-butyl-substituted thiopyrylo-2-monomethenecyanine perchlorate adopts a *Z,Z* conformation.[71,72]



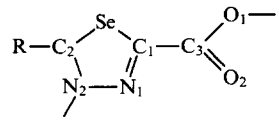
Under these conditions we find a strongly contracted S···S intramolecular contact (CIC) of 3.1 Å (taking 3.68 Å as double the WR of the sulfur atom). Obviously, this close approach of the sulfur atoms is due to their attractive interaction, which exceeds the repulsion between the residual charges of the same sign (+0.053 electronic units).[72] A closer approach is also favoured by the tendency towards conjugation in the carbon skeleton of the cations and symmetrical localisation of the ClO_4^- anions in the cavities between the heterocyclic rings. The stress in the cation is revealed by the increase (to 133.8° as compared with the ideal value of 120°) of the bond angle at the carbon atom which connects the heterocycles, and also by the increase to 122.1° in the exocyclic SCC and S′C′C angles (see Tolmachev et al.[71]).

An even shorter intramolecular S···S contact of 2.960 Å (i.e. a shortening of 0.72 Å) has been found in *Z*-4-methyltetrafluoroethyl-2-(tetrafluorothioacetylmethylene)-2*H*-thiopyran.[73] The sulfur atom lies in the plane of the thiopyran ring on the extension of the C–S bond of this ring; the CS···S angle is 174.7°. As reported,[73] this geometry of the –S···S= fragment is the most favourable to the formation of a CIC. As was pointed out above, SI of the S···S type are often met in intermolecular contacts: as we have seen, they are quite common also within molecules.

Replacing one of the sulfur atoms by oxygen in the cation studied by Tolmachev et al.[71] also produces a *Z,Z* configuration.[72] This creates a contracted intramolecular S···O contact of 2.74 Å ($2\sqrt{R_S R_O} = 3.08$ Å, $\Delta r = r - 2\sqrt{R_S R_O} = -0.34$ Å). The spatially unfavourable *Z,Z* conformation of this dye can be stabilised by the electrostatic attraction between the oppositely charged oxygen (−0.147) and sulfur atoms (+0.063). Furthermore, according to Sereda et al.[72] the length of the S···O contact (2.74 Å) allows specific interaction due to electronic factors which also stabilises the *Z,Z* conformation. A similar effect has been observed in the cyclohexane fragment 2,8-disulfonate-5,7-bis(dimethylsulfonium)bicyclo-[4,2,0]-oct-3-ene,[74] in which we find a *cis* configuration of the substituents stabilised by the CIC of the S′ atom with the oxygen of the sulfonate group; the S′···O distance is 2.854 Å.

Attractive interaction of nitrogen and oxygen atoms has been detected in one of the *O*-tosylhydroxylamines.[75] This interaction produces a strongly contracted intramolecular contact of 2.526 Å (as compared with the sum of WR of nitrogen and oxygen atoms of 2.79 Å). The attractive nature of the interaction of the nitrogen and oxygen atoms in this contact was confirmed by an analysis of the bond angles in the molecule. In 3,4-difluoro-8-*exo*-fluoro-12-*syn*-(2′-nitrophenylthio)-tetracyclo-[4.4.0.$1^{2,5}$.$1^{7,10}$]-dodec-3-ene the S···F distance (2.942 Å) was shorter[76] by 0.27 Å than the normal noncovalent S···F contact[5] of 3.21 Å. This shows that specific attractive interaction can exist between sulfur and fluorine atoms.[76]

Various examples in which the CIC denote conjugation of the bonds in various fragments of the molecule were quoted in our previous review.[1] Similar observations were made in more recent X-ray structural studies. Thus, in the 2-(*p*-ethoxybenzylidene)-3-phenyl-5-ethoxycarbonyl-1,3,4-selenadiazoline molecule[77]



in spite of the short Se···O distance (2.87 Å) as compared with the sum of the WR, the $C_1C_3O_1O_2$ plane makes an angle of 5° with the $SeC_1N_1C_2$ plane (the $N_1C_1C_3O_2$ torsion angle is −6°). This suggests[77] the presence of conjugation in the $N_1=C_1-C_3=O_2$ system. Similar examples are given in papers[71,72] on the structure of monomethinecyanines.

By analogy with the halogen···halogen contacts, in which the SI increase from chlorine to iodine, it may be assumed that similar effects take place in a contact between Group VI atoms and that the shortened Se···Se contacts denote the presence of SI in these materials. An analysis[78] of the complex bis-(1-isopropyl-3-methyl-4-cyclohexylaldimino-5-selenopyrazolato)nickel(II) supports this assumption. For steric reasons the *cis* compression of the NiN_2Se_2 observed in this complex is less favourable than the *trans* compression. The evidence for this conclusion is the intramolecular Se···Se′ distance (3.667 Å), which is less than double the WR of selenium (4.00 Å).[7] Nevertheless a *cis*-compressed NiN_2Se_2 tetrahedron is observed: as suggested,[78] this effect may be attributed to a Se···Se′ attractive interaction between not covalently bound atoms.

Specific interactions identified by using WR in crystals containing the cluster groups $M_3X_7^{4+}$ and $M_3X_4^{4+}$ (M = Mo, W; X = O, S, Se) are discussed in a recent paper.[79] It was noted that the $M_3X_7^{4+}$ derivatives form interionic contacts substantially shorter than the sum of the van der Waals or ionic radii of the X atoms, which occupy axial positions with respect to the M_3 plane, and the nitrogen, chalcogen, or halogen atoms of the counter ion or of the ion of the same sign. In some derivatives of $M_3X_4^{4+}$ these workers observed the formation of centrosymmetric dimers with the participation of (μ_2-X_2) ligands, in which the X···X distances were also markedly lower than the sum of the WR. These SI are often realised in spite of the coulombic repulsion between particles carrying charges of the same sign. These workers[79] consider that the criterion of the sum of WR[3,4,6] is also applicable to ionic radii in calculations of the degree of 'shortening' of a noncovalent contact.

In the crystal structure of 3-methyl-2-azoniafluorene tetrachloroaurate(III) a short Au···Cl distance (3.510 Å) was detected (for a sum of WR of 4.1 Å), corresponding to a noncovalent contact.[80] Allowing for this contact we can consider the coordination of the gold atom to be tetragonal–pyramidal.

The conformation of the molecules can also be strongly influenced by hydrogen bonds. We shall choose some examples from recently published work in which the presence of contracted intramolecular contacts is confirmed by the presence of an intramolecular H-bond. In the structure of diaqua-bis(nitroaminoguanidine)nickel(II) perchlorate stable N–H···O hydrogen bonds have been observed within the cations between the oxygen atoms of the nitro groups and the coordinated amino

groups; these bonds have N···O distances of 2.56–2.68 Å.[81] In the central fragment of the *N,N'*-di-(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl)-*N*-diethylphosphorylurea molecule[82] we find a six-membered ring (···HNCNPO···) formed by an intramolecular H···O hydrogen bond 1.96 Å long (the Zefirov criterion[83] is $d_{O\cdots H} < 2.1$ Å). This hydrogen bond is retained in solution at moderately high temperatures, as shown by the IR spectrum of the substance.[82] A geometrical modelling of the reaction of ammonia with perfluoro-2-methyl-2-pentene-3-thiocyanate showed that in one of the intermediate products of this reaction (the carbanion A^1) an N–H···F intramolecular hydrogen bond is formed (H···F 1.71 Å for $d_{H\cdots F} = 2.2$ Å,[5] N···F 2.59 Å, NHF 141°).[84]

There can be no doubt (according to the geometrical criteria established for intermolecular hydrogen bonds) that an unusual intramolecular O–H···P H-bond is present in the ···PC=CBOH··· six-membered ring of the $C_{39}H_{56}N_2OBP$ structure (see Ref. 53). In this molecule the OH group has a short contact with the phosphorus atom (O···P 3.103, O–H 0.93, H···P 2.30 Å, OHP 145°). As reported,[53] this contact can be taken as a proof of the formation of an intramolecular O–H···P hydrogen bond, since the quoted distances correspond to the H-bond criterion (sum of the WR of the phosphorus and oxygen atoms 3.3, of the phosphorus and hydrogen atoms 3.0 Å),[7] and furthermore the OH group is positioned in the direction of the phosphorus atom. However, in the IR spectrum of this compound the stretching vibrations band of the OH group (3560 cm^{-1}) is not significantly shifted and is not broadened.[53] Therefore the existence of an O–H···P hydrogen bond in this compound remains an open problem.[53] Doubts have also been expressed concerning the presence of an N–H···N H-bond in the thiosemicarbazone of methylglyoxal.[85] In the five-membered $\cdots N_2N_1CN_3H_2\cdots$ ring of this molecule the presence of an $N_3\cdots N_2$ CIC of 2.637 Å suggests an intramolecular hydrogen bond. However, the $N_3H_2N_2$ angle of 104.9° is said by these workers to be 'unfavourable to bonding'.

Unusual C–H···F–C intramolecular hydrogen bonds have been reported[86] in *exo-cis*-2,3-dichloro-5,5-dicyano-6,6-bis(trifluoromethyl)-norbornane. This structure contains two intramolecular H···F contacts (2.16 and 2.30 Å) which are markedly shorter than the sum of the WR of the hydrogen and fluorine atoms (2.56 Å). One of these contacts is less than 2.2 Å long (the parameter corresponding to the criterion of 'guaranteed' existence of an F···H hydrogen bond).[5] These workers have suggested[86] that the short C–H···F–C contacts in this substance "should probably be interpreted as intramolecular H-bonds". A similar state of affairs was encountered[87] in 2-methyl-5α,6β-7,8-tetrakis(trifluoromethyl)-5,6-dihydro-Δ^2-1,3,4-oxadiazolino-[2,3-*a*]-azepine. This structure contains four short intramolecular H···F contacts, of length much smaller than the sum of the WR of the H and F atoms, and one as short as 2.13 Å. It is again suggested[87] that these contacts should be interpreted as intramolecular C–H···F–C H-bonds. Some doubt arises from the fact that in the five-membered HCCCF 'rings' of these compounds the free motion of the atoms within the molecule is limited, and the C–H···F angles are small; 114° in the first structure and 111° in the second. In relation to this work[86,87] it should be noted that according to the criteria formulated by Zefirov and Porai-Koshits[5,83] a hydrogen bond can be confidently identified only in intermolecular contacts, or for intramolecular interactions in which the contacts are not imposed by the rigid conformation of the molecule.

Thus doubts concerning the presence of SI (and in particular of H-bonds) in the system usually arise because a contracted intramolecular contact can denote either an attractive interaction or an imposed steric stress. For example, in 10-bromo-2,4,8-trinitro-6(5H)-phenanthridinone a Br···H intramolecular contact of 2.43 Å has been discovered; it is strongly contracted as compared with the value $2\sqrt{R_H R_{Br}} = 3.02$ Å as a result of substantial steric hindrances.[88] These effects increase the out-of-plane angles of the carbon atoms in the six-membered ···BrCCCCH··· ring. By relying on the geometrical characteristics of the C–H···Br contact (C···Br 3.161, C–H 0.90, H···Br 2.43 Å, CHBr 138°) it could be thought that a bond of the C–H···Br type is present. However, the shortening of the distance may also be induced by the resulting decrease in the steric stress. Often correct conclusions on the shortening of a contact can be reached by allowing for 'subsidiary' factors. However, if even additional information fails to produce a fully definite conclusion we can only assume that the existence of SI is a possibility.

A comparison of the interatomic distances with the sums of the WR is often used to prove the absence of a hydrogen bond. For example, in the 4,4',6,6'-tetranitro-2,2'-dicarboxybiphenyl and 6,6'-dinitro-2,2'-dicarboxybiphenyl molecules the intramolecular distances 3.434 and 3.933 Å (between the oxygen atoms of the carboxylic acid and of the nitro groups respectively) are so much greater than double the WR of oxygen that the presence of any significant hydrogen bond can be excluded.[89]

It was pointed out above that the use of the statistically averaged value (1.29 Å)[3] for the WR of oxygen offers reliable conclusions on the presence of shortened and contracted O···X contacts in the structure, from which reliable deductions can be made. However, the large positive charges on the oxygen atoms usually prevent the formation not only of short intermolecular bonds but also of short intramolecular O···O contacts, even when the conformational conditions appear to be satisfied. The cation of 4,6,4',6'-tetra-*tert*-butyl-substituted pyrylo-2-monomethinecyanine (I) exists in the *Z,E* form,[72] and not in the *Z,Z* form (see above), though the latter is sterically advantageous, since the WR of oxygen is much smaller than the WR of the carbon atom. One possible reason for the existence of the cation (I) in the *Z,E* form is the repulsion between the similarly charged oxygen atoms.[72] According to quantum-mechanical calculations (CNDO/2 method) negative charges are collected on the oxygen heteroatoms (O −0.083, O' −0.137 electronic units), the charge on the O' atom being 0.035 electronic units greater in absolute value than the charge on the C'_1 atom (−0.102 electronic units). In the *Z,E* form of the cation (I) we find the shortened contacts C'···O (2.94) and H'···O (2.29 Å) for WR sums of 3.00 and 2.45 Å respectively. Since the molecule is flat, and the H···O contact closes a six-membered ring, one could conclude that this ring contains a weak intramolecular C–H···O hydrogen bond. However, Sereda et al.[72] reach a different conclusion. In this case the C–H···O contact is constrained, and is created not by an H-bond but by its accommodation in the carbon skeleton of the molecule between the heterocyclic rings. The steric stress within this contact is made evident by the large increase in the exocyclic bond angles at the C_2 and C'_2 atoms (attached to the C_7 atom, which connects the heterocyclic rings) to 129.0°, and the bond angle of the C_7 atom to 128.2°. Nevertheless the shortenings detected in the C···O and H···O contacts do not reach the lower limits expected from the van der Waals interaction (2.82 and 2.15 Å respectively).

To establish the cause of the appearance of a *Z,E* conformation in the above example of 4,6,4',6'-tetra-*tert*-butyl-substituted pyrylo-2-monomethinecyanine a calculation of the effective charges on the atoms of the cation was required.[72] In many other cases of nonrigid molecules the existence of a particular conformation can be explained simply by a geometrical analysis. In the bis-(5,5-dimethyl-1,3-dioxan-2-yl) molecule ($C_{12}O_4H_{22}$) the H···H and O···H contacts (which determine the degree of steric stress) are 2.335 and 2.646 Å long, and exceed the normal van der Waals contacts (2.31 and 2.45 Å), i.e. we observe[90] an unstressed $E(\perp)$ conformation § with $\varphi = 90°$.

§ φ is the angle between the plane of symmetry of one dioxan ring and the orientation (averaged atomic plane) of the other. For a parallel orientation of the two rings $\varphi = 90°$.

A geometrical analysis was carried out in order to identify the steric stress in other conformations of the $C_{12}O_4H_{22}$ molecule, i.e. the shortest noncovalent contacts were calculated on the assumption that the conformation of the rings remains unchanged. It was found that the intramolecular contacts are always shortened except in bisequatorial conformers with φ between 90° and 45°.[90] It was suggested that the advantage of the parallel orientation of the dioxan molecules ($\varphi = 90°$) over the crossed orientation ($\varphi = 45°$) is due mainly to the effect of the crystal field (the tendency for the molecule to retain its centre of symmetry in the crystal). In *P*-methoxy-*C*,*C*-bis(trimethylsilyl)methylen-*N*-(2,4,6-tri-*tert*-butylphenyl)-imino-σ^3,λ^5-phosphorane we find a *cis* orientation (torsion angle 5.1°),[91] whereas the characteristic orientation for the original iminophosphines is the *trans* (torsion angle 180°). This orientation is due to steric causes: the difficulty of bringing the methyl group bound to the oxygen atom close to the bulky $SiMe_3$ substituent. The geometrical analysis showed that the rotation of this group round the P–O bond by 180° relative to the position found in the molecule leads to impossibly short C···C contacts (2.152 and 2.614 Å).

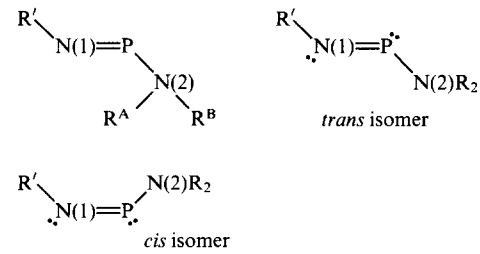
In four biphenylcarboxylic acids (4,4′-dinitro-2-carboxybiphenyl, 2′,4-dinitro-2-carboxybiphenyl, 2′-nitro-2-carboxybiphenyl, and 2′,4,4′-trinitro-2-carboxybiphenyl) the dihedral angle between the aromatic rings takes the values[92] −57.9°, −67.3°, +78.6°, and +89.4° because of the repulsion between the substituents. As a result of internal rotation round a single bond the intramolecular distances between not covalently bonded atoms and atomic groupings in all these molecules exceed the distances corresponding to normal van der Waals contacts.

Furthermore, steric hindrances often produce a distortion of the bond angles and an extension of the valence bonds. The distortion increases the probability of bond breaking, and therefore many workers place special emphasis on these sources of instability. Shortened contacts resulting from the distortion of the bond angles have been observed recently[93–98] in various structures by using statistically averaged values of the WR. In some cases inflections in the heterocycles of the molecule are accompanied by repulsion of the atoms which are not covalently bonded, as shown by the WR values,[99] and in other cases the CIC is accompanied by the loss of coplanarity of various fragments of the heterocycle.[100] In the [*N*,*N*,*N*′-tris-(trimethylsilyl)-diamido-*N*″-trimethylsilyl-*P*-phenyl-phosphon-imidato]phenylzinc molecule the presence of bulky trimethylsilyl substituents produces marked steric overloading with CIC (Si···C 3.274, P···C 3.352, C···C 3.166 Å), which leads to substantial nonequivalence of some covalent bonds of the same type on the nitrogen atoms and to a strong distortion of the tetrahedral coordination of the silicon atoms.[101] In the 2-methylphenyl ester of *N*-[2,4,6-tri(*tert*-butyl)phenyl]imidophosphenous acid we find a whole group of contracted intramolecular C···C contacts (2.801–2.882 Å) and N···C contacts (2.942–3.035 Å), which lead to an increase of the CCC bond angles in the 2,4,6-$(Bu^t)_3C_6H_2N$ fragments by ~3° with respect to the ideal values.[102]

The stress generated by steric hindrances in any part of the molecule becomes distributed (if possible) more or less uniformly over the whole of the molecule. A clear example of this behaviour is seen in 3,4′-difluoro-8-*exo*-fluoro-12-*syn*-(2′-nitrophenylthio)-tetracyclo[4.4.0.$1^{2,5}$.$1^{7,10}$]dodec-3-ene, in which the stress due to C···C intramolecular contacts (3.118 Å) and magnified by the H···H contacts (1.88 Å) leads to a fairly uniform distribution of the distortion of the six bond angles in the polycyclic framework of the molecule.[76]

As we know, the deformation of the bond angles is associated with much smaller energy losses than the extension of bonds in the molecule. Therefore bond stretching effects produced by steric hindrance in overloaded molecules are met more rarely than the distortion of bond angles produced by the same effects. Recent X-ray structural studies produced new examples of this behaviour. In 2-amino-5-methyl-3-(1-methylisopropoxyallyl)-1-formyl-3,4,4-tricyanocyclopentene[103] we observe a whole group of CIC with C···C values 3.022, 3.037, 3.048, and 3.057 Å and C···H values of 2.66 Å. The C_2-C_3 and C_3-C_{11} bonds, 1.542 and 1.571 Å long, are elongated by 0.03 Å with respect to the corresponding standard values of the $C(sp^3)-C(sp^2)$ and $C(sp^3)-C(sp^3)$ distances. According to the authors[103] this is probably due to steric overloading. In bicyclic iminoester molecules we find a group of intramolecular contacts shorter by 0.6 (C···C) and 0.4 Å (C···H) than the sum of the corresponding WR. These steric effects lengthen some of the covalent C–C bonds to 1.56–1.59 Å,[104] which increases the reactivity of these compounds (see also Section VI).

An analysis of the influence of steric and electronic factors on the conformation of three sterically overloaded λ^3-aminoiminophosphines [2,4,6-$(Bu^t)_3C_6H_2N{=}P-NR_2$, where R = Me (I), (Pr^i) (II),[105] and $SiMe_3$ (III) [106]] showed that the realisation of *cis* and *trans* forms in these materials is determined by a fine balance between these factors, and that the steric factors revealed by WR calculations have a strong effect on the length of the covalent bonds.



The predominant influence of the R···R′ repulsion following an increase in the volume of the R substituent favours the *trans* isomers. In the *trans* isomers of II and III the N(1)···C(19) (2.934 Å) and N(1)···Si(2) distances (3.227 Å) are greatly shortened with respect to the sums of WR (3.20 and ~3.60 Å); the stronger repulsion between the N(1) atom and the closely accommodated substituent R produced by replacing isopropyl by the bulkier substituent $SiMe_3$ is accompanied by an increase in the N(1)PN(2) bond angle from 105.6° to 109.3° and by an elongation of the P=N(1) bonds from 1.555 to 1.566 Å and of the P–N(2) bonds from 1.656 to 1.668 Å [though the lengthening of the P–N(2) bond may be due at least partially to the effect of the $SiMe_3$ acceptor groups], and also by an increase in the distortion of the configuration of bonds at the N(2) atom.

Steric effects in overloaded molecules can produce not only an elongation but also a shortening of the covalent bonds. The *cis* isomers of λ^3-aminoiminophosphine is energetically more favoured when the volume of the R substituent is small (i.e. for R = Me), when the electronic factors become predominant.[105,106] Nevertheless in the *cis* isomer I the N(1)PN(2) bond angle increases (for steric reasons) to 115.9° as compared with 105.6° in II and 109.3° in III, and the PN(1)C(1) angle increases to 140.7° as compared with 117.6° in III and 129.6° in II. This increase in the bond angles ultimately leads to a shortening of the P=N bond to 1.539 Å as compared with 1.555 Å in II and 1.566 Å in III. The shortening of the P=N bond is due to electronic factors: an increase in the *s*-character of the hybrid atomic orbitals which form this bond and an increase in the *p*-character of the unshared electron pairs in the nitrogen and phosphorus atoms, which favours the $n-\sigma^*$ interactions.

An even stronger shortening of the P=N covalent bond (by 0.04–0.08 Å, i.e. to 1.500 Å) is stimulated (for steric reasons) by the marked increase in the CNP angle in molecules of derivatives of two-coordinated phosphorus in which the –N=P–N< group is replaced by –N=P–O–. This is observed in molecules of 2,4,6-$(Bu^t)_3-C_6H_2N{=}P-OR$, where R = 2-MeC_6H_4 (IV)[102] and 2,6$(Bu^t)_2$-4-MeC_6H_2 (V).[107] A geometric analysis has shown that the main cause of the increase in the CNP bond angle to 164.1° in IV and to 170.9° in V is the repulsion between the aryl

substituents on the nitrogen and the oxygen atoms; the decrease in the angle at the nitrogen atom to 140° reveals the formation of a strongly contracted C···C intramolecular contact (3.048 Å).[102] The CPN bond angles are increased by steric hindrances to 164.1° in IV and 173.7° in V, i.e. they go beyond the limits of 107.7° – 140.7° previously established for these iminophosphines. The increased bond angles also induce a shortening of the P=N bond to 1.497 Å in IV and to 1.500 Å in V (the P – N distance in the previously studied iminophosphines lay in the 1.539 – 1.575 Å range).

The influence of the steric factor on the electronic factor has been demonstrated[108] for the so-called aroylotropy of 2-substituted carboxylic acids. Here the steric effect of the F, Cl, Br substituents produces a rotation of the carboxy group round the C – C single bond and destroys its conjugation with the benzene ring: this group experiences only the inductive electronic effect of the substituent.

The contracted intramolecular contacts in overloaded molecules are often the cause, and sometimes also the consequence, of the stress in the intramolecular contacts in other parts of the molecule, and are also used to explain some anomalies in the geometric characteristics of these parts. These anomalies, in their turn, account for some of the physicochemical or chemical properties of the substance (see Section VI). Therefore the CIC in nonrigid molecules, offering the possibility of rotation round single bonds, have claimed the widest interest of research workers.

In the *N*-trimethylsilyl-2,4,6-tri-*tert*-butylphenylamidochlorophosphite molecule $[Me_3Si(Ar)N-PClOR$, where Ar = 2,4,6-$(Bu^t)_3C_6H_2$ and R = 2,6-$(Bu^t)_2$-4-MeC_6H_2] the Si and Cl atoms in the planar SiNPCl group are drawn together to within 3.330 Å by steric effects.[109] This is much shorter than the normal distance, since the normal van der Waals Si···Cl contact should be substantially longer (3.60 Å is observed in the normal C···Cl contact, and the WR of the atoms of the third-period elements, P, S, and Cl are 0.4 – 0.5 Å longer than the WR of the corresponding second-period element atoms N, O, F). The formation of the strongly contracted Si···Cl contact in this molecule is due to the presence (near the oxygen atom) of the bulky 2,6-$(Bu^t)_2$-4-MeC_6H_2 substituent, which prevents the perturbation of the planarity of the SiNPCl group. Indeed, as was shown by a geometric analysis,[109] the rotation of this substituent round the P – N bond by +30° relative to the position found in the molecule produces the unacceptably short C···Cl 2.711 and C···C 3.044 Å contacts, and the rotation through −30° produces the short C···C 2.841, 3.294, and 3.299 Å contacts. In two other phosphites of this type, where the 2,6-$(Bu^t)_2$-4-MeC_6H_2 radical is replaced by the phenyl (Ph) and by the adamantyl (Ad) radical, there are no spatial effects opposing the mutual repulsion of the Si and Cl atoms, and therefore the SiNPCl torsion angle in these materials is 68.6° and 67.7° respectively, and the Si and Cl atoms are 3.932 and 3.916 Å apart.[109] A similar case has also been described.[110] In the *N*-(2,4,6-trinitrophenyl)-*N,N'*-di-*p*-anisylbenzamidine structure the intramolecular N···C distance (2.66 Å) between the amidine nitrogen atom and the carbon atom of the picryl group is strongly shortened as compared with the normal van der Waals distance, which could be taken as evidence of both SI and of a strong steric stress. However, as was shown by a detailed analysis of noncovalent contacts carried out during an X-ray structural investigation, this shortening is due to the steric overloading of the molecule, produced by the presence of four benzene rings in the molecule. In both the structures described above the CIC directly affect the chemical properties (reactivity) of the molecules which contain them: this important problem is examined in Section VI.

V. Physicochemical properties of substances

The interpretation of the physicochemical properties of crystalline substances is often treated as the ultimate goal of crystal chemistry. Therefore the possibility of using WR to solve these problems undoubtedly confirms their effectiveness. The WR are most often used in discussions of the structural properties of crystals and molecules, but sometimes these features are directly related to the properties being discussed. In these cases we can directly attempt the interpretation, and even the predictive calculation, of the physical and physicochemical properties. Examples of this kind are discussed below.

Statistically averaged values of the WR were used as Onsager radii of the hydrogen atoms (1.16 Å) and of the CH_3 radicals (2.0 Å) in calculations of the band structure on the surface and in the bulk of polyethylene.[111] The band structure of the polyethylene molecule was calculated by semiempirical CNDO method on the surface of and within a polyethylene mass, treated as a uniform dielectric medium. The energy of the interaction of the polymeric molecule with the medium is expressed through the Onsager radii of the atoms, their average charges, valences, and bond indices. It was established that the immersion into a polyethylene mass lowers the ionisation potential of the polyethylene molecule by 0.87 eV, narrows the band gap by up to 1.9 eV, and raises the bottom of the valence band by 1.2 eV (see Semenov[111]).

As was pointed out above, the use of WR allows the detection in molecular crystals of associations of the molecules which are most tightly interconnected as a result of SI effects. The presence of these true associations must, of course, affect the physicochemical properties of the crystals. Thus, in the 3,5-dichloro-1*H*-1,2,4-triazole structure contracted intermolecular N···Cl contacts (3.149 Å for $d = 3.23$ Å) unite the cyclic trimers formed by hydrogen bonds into layers parallel to the XY plane.[55] The distance between these layers is 3.33 Å. The layer character of this crystal structure accounts for the sharp anisotropy of its thermal deformations,[55] the thermal expansion coefficient being greater in the direction perpendicular to the layers $[\alpha_3 = (161 + 0.29t) \times 10^{-6}\ K^{-1}]$ than it is within the layer $[\alpha_1 = (34 + 0.19t) \times 10^{-6}\ K^{-1}]$.

An analysis[112] of the intra- and intermolecular interactions in $(CCl_3)_2PCl_3$ and $Cl_3P{=}N-C(CF_3)_3$ crystals led to an interpretation of the differences in the character of the thermal motion of the PCl_3, CCl_3, and CF_3 groups. The rotation of the CCl_3 group in the $(CCl_3)_2PCl_3$ crystal is obstructed by strong intramolecular $CCl_3\cdots Cl_3P$ interactions which limit the mobility of these groups to small librations about the long axis of the molecule; the lengths of the intramolecular Cl···Cl contacts between the CCl_3 and the PCl_3 groups are 3.21 and 3.22 Å (for $d_{Cl\cdots Cl} = 3.65$ Å and $2R_{Cl} = 3.80$ Å). Furthermore the intermolecular contacts formed by the two groups $C(1)Cl_3$ and $C(2)Cl_3$ in the molecule are substantially different, the chlorine atoms of the $C(2)Cl_3$ group [unlike those of the $C(1)Cl_3$ group] having no contracted contacts. As a result of 300 K the mean square amplitude of the libration $\langle\varphi^2\rangle$ is 32 deg^2 for the $C(2)Cl_3$ group and only 3 deg^2 for the $C(1)Cl_2$ group. A decrease in temperature freezes out the enhanced libration of the $C(2)Cl_3$ group, and at 153 K the parameter $\langle\varphi^2\rangle$ for both groups is 0.5 deg^2, i.e. the molecule behaves effectively as a rigid body. A similar state of affairs exists in a $Cl_3P{=}N-C(CF_3)_3$ crystal, where we find an intermolecular Cl···F contact (3.07 Å) and three shortened Cl···F contacts (two intermolecular and one intramolecular). The $\langle\varphi^2\rangle$ values are 41 deg^2 at 208 K and 0.4 deg^2 at 153 K, i.e. the libration of the PCl_3 group is frozen by the decrease in temperature.

Great interest has been stimulated by shortened and by contracted contacts in organic conductor structures, as was pointed out in several reviews.[113 – 115] A large group of workers[40 – 45, 57, 59 – 62, 116, 117] attempted to interpret these contacts as factors determining the conductivity.

The organic metal $(ET)_4Cl_2 \cdot 4H_2O$ contains cation–radical layers alternating along the Z axis with layers of the complex anions $Cl_2 \cdot 4H_2O$ (see Shibaeva et al.[117]). The cation–radical layer is formed from ET stacks stretched along the Y axis, and the intermolecular S···S contacts contracted between stacks (3.451, 3.475, 3.489, and 3.541 Å) are aligned with the X axis: the maximum conduction is observed along this axis. A calculation of the conduction anisotropy (from the band structure) gives the ratio $\sigma_a/\sigma_b \approx 7$ (the anisotropy could not be determined experimentally because of the small size of the crystals). The conductivity of $(ET)_4Cl_2 \cdot 4H_2O$ crystals at room temperature is $10-50\ \Omega^{-1}\ cm^{-1}$; at ~ 20 K the material passes into the dielectric state. In the $(ET)_3Cl_2 \cdot 2H_2O$ structure the cation–radical layers along the Z axis alternate with layers of $Cl_2 \cdot 2H_2O$ complex anions, and the cation–radical layer is formed of ET stacks stretched along the X axis.[61] The anisotropy of the conductivity in these crystals is characterised by the ratio of the specific conductances $R_b : R_a : R_c = 1 : 7 : 1000$. The authors[61] suggest that the crystals should have a maximum conductivity along the Y axis; strongly contracted S···S contacts between the stacks (3.343–3.431 Å long) are stretched in this direction, and are complemented by less strongly contracted contacts (less than 3.53 Å). The average conductivity ($\sim 40\ \Omega^{-1}\ cm^{-1}$) should correspond to the X axis, i.e. to the direction of the cation–radical stacks, and the minimum conductivity to the Z axis. The anisotropy of the conductivity in crystals of $(ET)_3CuCl_4 \cdot H_2O$ (see Shibaeva et al.[42]) and of $(BEDOTTF)_2ReO_4 \cdot H_2O$, where BEDOTTF is the symmetrical bis(ethylenedioxy)tetrathiafulvalene,[44] can also be explained in terms of the length of the S···S contacts.

However, as could have been expected, the electric conductivity of these cation–radical salts does not show a direct relationship to the length of the S···S contacts. Thus, in crystals of the cation–radical salt $(ET)_4ZnCl_4 \cdot C_6H_5CN$ we find a whole series of short S···S lengths, including contracted ones,[40] but the complex internal structure of the conducting cation–radical layer gives a conductivity of only $\sim 0.9\ \Omega^{-1}\ cm^{-1}$ at room temperature; the substance is a semiconductor. But in $(BT)_2 \cdot 2Cl \cdot H_5O_2$ crystals the S···S contacts were found to be not contracted but merely shortened (lying between limits of 3.68 and 3.53 Å). Nevertheless the substance has a conductivity of $\sigma \approx 100\ \Omega^{-1}\ cm^{-1}$ and is a quasiunidimensional organic conductor.[57]

Some features of the IR spectra of chemical compounds are sometimes attributed to specific interactions. Thus, Br···Br contacts 3.55 and 3.75 Å long ($2R_{Br} = 3.94$ Å) are found in the $[(Me_2S)AuBr_3]$ structure. The authors suggest[118] that these interactions are responsible for the broadening of some bands in the IR spectrum of the complex.

By using the WR we can study the size and form of the cavities and channels in crystal structures, and in particular in zeolites. The volume and shape of the free space in zeolites strongly affect the diffusion processes in these materials and their adsorption and catalytic properties. The geometry of the free space in the pentasil ZSM-5 has been determined[119] by using the WR: the composition of this material (not allowing for the water) is described by the formula $M_xAl_{1.1}Si_{94.9}O_{192}$, where M_x is a mixture of sodium and tetraalkylammonium cations. The van der Waals radii were taken to be 1.80 Å for the Al and Si atoms and 1.29 Å for oxygen. A calculation showed[119] that all the free space in the pentasil forms an interconnected region with channels and connecting bridges of various sizes. The most favourable sites for the adsorption and diffusion of molecules are the infinite channels with a radius of 2.70–3.30 Å separated by bridges having radii of 2.64 and 2.68 Å.

Very different physicochemical properties directly related to the effective volume, size, and shape of the molecule are often found in substances.[1] Special attention is devoted to the volume of the molecules in this context. In particular, by inserting into the formulae the volumes of the self-repeating units of the polymer a large number of physical characteristics were calculated: density, coefficient of volume expansion, melting point, and many others.[120] By using the volume of the molecules of compounds to be separated a model was made of the chromatographic separation of cyclopentadienylcarbonyl complexes of the transition metals.[121] It has been reported[122] that in the similar structures $Cu(C_9H_{13}N_2O_2CH_3)_2$ and $Cu(C_9H_{13}N_2O_2CF_3)_2$ which differ only by the replacement of the CH_3 by the CF_3 radicals, the difference in the volume ascribed to one formula unit is completely explained by the difference in WR of the F (1.40 Å) and the H atom (1.16 Å).

By combining previous X-ray structural studies[124] with an allowance for the WR of the atoms the shape of several mesogenic molecules containing metal atoms with a square coordination has been described:[123] it can be adequately approximated by an anisometric prism $30 \times 10 \times 6$ Å in size. WR have been used[125] to study the structure of aqueous solutions of electrolytes, and in the analysis of structural solvation effects.

Sets of volume increments for the atoms and atomic groups present in molecules had been proposed to facilitate the calculation of molecular volumes.[120,126] The common foundation of all these calculations were the WR. More recently new methods of calculating the volumes and surface areas of molecules from the WR (as well as the density of substances) have been published.[127–131] A paper by Gavezzotti[128] (like the earlier publications of the same author) discusses the correlation between the volumes and surfaces of molecules and the energy of sublimation of the crystal. The method of calculating the atomic volume increments described by Shil'nikov et al.[129] is carried out in three steps: an analysis of the intersection of interpenetrating spheres whose size is determined (fixed) by the WR, a calculation of the increments for atoms with surroundings compatible with the use of analytical expressions, and a Monte Carlo calculation of the increments for the other atoms. Kuz'min and Katser[130] obtained the statistically averaged volume increments of individual atoms and molecular fragments by least squares. Koch and Fischer[131] used the method of constructing Dirichlet regions for the same purpose.

An empirical model which allows the density of a substance to be predicted from approximate data on the geometric structure of the molecule has been proposed.[132,133] The model is based on the concept of the WR, but in this model a special modelling function allows for the effect of the immediate surroundings of an atom on its WR. Furthermore in the calculation of the molecular volume the WR of the end atoms are artifically increased; in liquid substances this produces a more correct allowance for the vibrational motions of the molecules.

It should be noted that the dependence of the effective WR of an atom on the individual properties of the molecule which includes that atom has been discussed previously. Kitaigorodskii suggested[126] distinguishing between the WR of carbon atoms in aliphatic and in aromatic compounds (1.80 and 1.72 Å), but in subsequent publications he did not adopt this differentiation. It was postulated[134] that sterically overloaded molecules are more loosely packed in a crystal, i.e. that the atoms in these molecules have effectively larger WR (the authors called this effect the 'saturability of van der Waals bonds'). This concept was tested[135] by calculating the energies of noncovalent interactions and the packing density coefficients (K) for 159 substances. The van der Waals volumes of the molecules were calculated by using the Pauling WR.[7] This study revealed a tendency for K to decrease with increasing 'density of the molecule' (which is generally consistent with the model proposed by Atovmyan et al.[134]). However, it was concluded[135] that the straight line giving the average dependence of K on ρ_{mol} (the mass of the molecule related to its volume) cannot be used directly to determine the density of the crystal.

It should be noted that conclusions on the looseness of packing are sometimes reached too hastily. The fact that some intermolecular bearing contacts in the crystal exceed the conventional values is not sufficient to justify such a conclusion.

Thus, in a crystal of 2-methylthio-3-phenyl-5-methylthiocarbonyl-1,3-thiazolium-4-olate the molecules are located at a distance generally exceeding the sum of the statistically averaged WR of the atoms in contact, and this (as suggested[136]) accounts for the loose packing. However, these conclusions need to be reconsidered if they were made without allowance for the natural dispersion of the bearing contacts.

VI. Chemical reactions

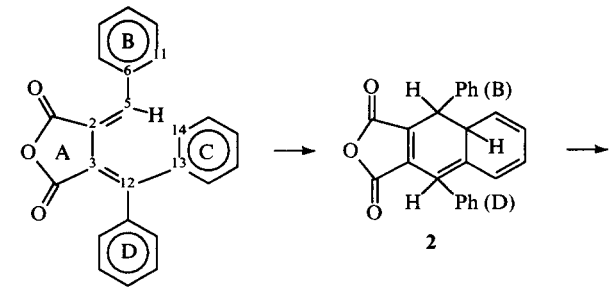
We have previously discussed[1] the steric effects of various types (discovered by using WR) which influence the reactivity of a substance: (1) steric hindrances, leading to the extension of covalent bonds or to the distortion of bond angles; (2) the shielding or complete blocking of the active centre of the molecule; (3) steric factors, which determine the angle of nucleophilic or electrophilic attack, and some other variants of the effect of steric factors on chemical processes. In the present review we shall examine, in addition to recently reported new studies in some of the directions mentioned above, examples of the use of WR in one direction not discussed in Ref. 1.

In some cases the steric effects in overloaded molecules force closer together the not covalently bound atoms: as a result the activation energy of the chemical reaction leading to the establishment of covalent bonds between these atoms is substantially lowered. Thus, in the amidochlorophosphite molecule $Me_3Si(Ar)N-P(Cl)OR$, where $Ar = 2,4,6\text{-}(Bu^t)_3C_6H_2$ and $R = 2,6\text{-}(Bu^t)_2\text{-}4\text{-}MeC_6H_2$ (I), the Si and Cl atoms are drawn together to a distance of 3.330 Å, whereas in other phosphites, where R = Ph (II) or R = Ad (III), there are no obstacles such as those found in (I), and the silicon and chlorine atoms lie at distances of 3.932 and 3.916 Å from each other respectively.[109] The covalent Si–Cl bond is 2.03 (±0.03) Å long.[137] In order to reach this value in the case of the molecule I we must contract the distance between the atoms by ~1.3 Å, and in the case of molecules II and III by ~1.9 Å, i.e. by a much greater amount. Not surprisingly the amidochlorophosphite I easily splits off trimethylchlorosilane (even at 20 °C) in a solution of tetrahydrofuran: this converts it into the λ^3-iminophosphine

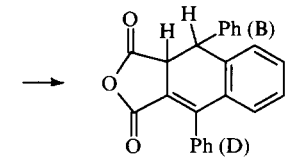
$$Ar-N(Me_3Si)-P(Cl)-OR \longrightarrow Ar-N=P-OR + Me_3SiCl.$$

Conversely, the compounds II and III are stable up to 180 °C, and they cannot be converted into iminophosphines even by lengthy heating.[109] Similarly, in the *N*-(2,4,6-trinitrophenyl)-*N*,*N*′-di-*p*-anisylbenzamidine molecule[110] the distance between the amidine nitrogen atom and the ipso carbon atom of the picryl group (N···C 2.66 Å) is shortened by 0.54 Å in comparison with the normal van der Waals contact. This close approach of the atoms assists the migration of the picryl group towards the amidine nitrogen atom in solution.

An X-ray structural study has shown[138] that the direction of the photo- and thermochromic cyclisation reactions of *E*-benzylidene-(diphenylmethylene)succinic anhydride **1** is controlled by steric factors. The molecule of this compound is sterically overloaded (especially its diphenylmethylene fragment). In this fragment the C(3)=C(12) double bond (1.37 Å) is 0.02 Å longer, as a result of steric hindrances, than the C(2)=C(5) double bond (1.35 Å) in the benzylidene fragment. For the same reason the C(12)–C(13) bond (1.48 Å) is 0.02 Å longer than the corresponding C(5)–C(6) bond in the benzylidene fragment (1.46 Å). Furthermore the C(3)=C(12) double bond is twisted by 9.4° more strongly than the C(2)=C(5) bond (the torsion angles are 24.4° and 15.0° respectively). As a result the noncovalent distance between the C(5) and C(14) atoms, which are potential reaction centres, is 3.30 Å, which is 0.12 Å less than double the WR of carbon and 0.16 Å shorter than the distance between the atoms C(11) and C(12), (3.46 Å). Thus in the



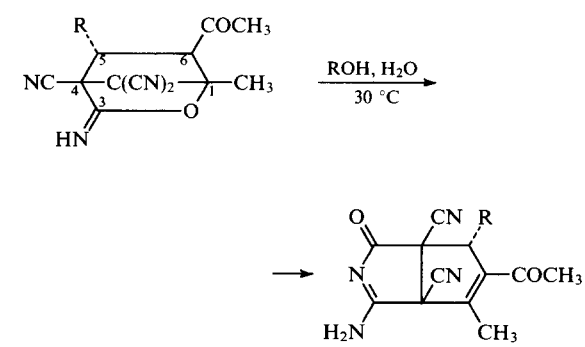
1 2



3

sterically more overloaded diphenyldimethylene fragment the benzene ring C is more closely connected to the methylene centre C(5), and because of the lower barriers to rotation round the extended C(3)=C(12) and C(12)–C(13) bonds it should be more mobile than the benzene ring B in the benzylidene fragment. It was pointed out[138] that in the molecule I the noncovalent distance between the atoms H(14) and C(2) (2.76 Å) is much shorter than the H(11)···C(12) distance (3.00 Å), which can account for the fast migration of the H(14) atom (in the intermediate **2** formed by cyclisation) towards the C(2) atom, and to the formation of the stable product **3**.

In the 3-imino-4,7,7-tricyano-2-oxabicyclo[2,2,1]-heptanes,[104] which belong to the series of bicyclic iminoesters, we find several CIC between the substituent in position 5, the *gem*-dicyano group, and the C(3) atom. These CIC are 0.6 Å (C···C) and 0.4 Å (C···H) shorter than the sum of the statistically average WR of the corresponding atoms. Steric strain lengthens the C(4)–C(5) bonds to 1.58–1.59 Å and the C–C(CN)$_2$ bonds to 1.56–1.57 Å, which increases the reactivity. When kept in aqueous ethanol (or in ethanol) this compound is converted into a mixture of 3-azabicyclo-[3,3,0]octadienes even at slightly elevated temperatures:[104]



The site of the initial nucleophilic attack on one of the carbon atoms of the cyano group in the 3-(*N*′,*N*′-dimethyl-*N*-acetylhydrazino)-1,1,2,2-tetracyano-5-methylcyclopentane was investigated by a calculation[139] of the role of the steric factor based on a geometrical modelling relying on published values[3] of the WR. It was established that only the *trans* C≡N group (in the β position with respect to methyl) is accessible to nucleophilic attack: large steric hindrances are met in other positions. This conclusion was confirmed experimentally: nucleophiles are added selectively to this cyano group.

A geometrical modelling of one of the Ugi reactions for an N···C=S angle of attack of 90° in the initial stage of the nucleophilic addition for $R' = CH_3$ and $R' = CH_2R$ to 1-methyl-2-thio-4-benzylimino-5-spirocyclohexanehydantoin was carried out[140] by using statistically averaged values[3] of the WR. It was found that for $R' = CH_3$ contacts much shorter than the sum of the corresponding WR are not formed in the initial stage of the nucleophilic addition, whereas for $R' = CH_2R$ the system is highly stressed and a closer approach of the atoms is unlikely. The stereochemical features of the reaction of ammonia with perfluoro-2-methyl-2-pentene-3-thiocyanate have been analysed by the same procedure.[84] The parameter δ, defined as $R_A+R_B-d_{AB}$, where R_A and R_B are the WR of the A and B atoms and d_{AB} is the distance between them (in this case, contracted), was used as a criterion of the possible existence of various stages in the reaction. The geometrical modelling demonstrated the dominant role of the lower steric factor and led to the prediction of the following conformational consequences: for $\delta > 0.35$ Å the stresses are removed by the distortion of valence and torsional angles and of bond lengths, for $0.55 < \delta < 0.65$ Å the stresses are partially relieved by the same factor, but the system remains stressed and the probability of encountering this conformation is small, and for $\delta < 0.85$ Å the system cannot exist in this conformation. Thus the stereospecificity of the reaction indicated by the formation of only one *E*-stereoisomer (2-aminoperfluoro-4,4-dimethyl-4,5-dihydro-5-ethylidene-1,3-thiazole) is due to the lower steric stress in the anion leading to the *E*-isomer than in the anion leading to the *Z*-isomer. Strong steric stresses prevent the cyclisation on heating of *E*-3,4-diaminoperfluoro-4-methyl-2-pentene-3-thiocyanate (through the amino group of the double bond) with formation of a thiazole ring.

In a special program assembled[141] for calculating the steric shielding of the metal atom in complexonates the complex is modelled as a coordination centre with its surrounding ligands (consisting of atoms with known WR). Another program[142] for calculating the shielding of the metal atom in compounds of the MR_n type in terms of WR has been discussed.[1]

The WR method is often used to account for the spatial conditions consistent with various solid-state reactions. Let us examine a new example of this application. An X-ray structural analysis of 4,4'-methylene-bis(phenyl isocyanate) has shown[143] that N···C intermolecular contacts (3.146 Å) are formed in the packing of molecules in a crystal between pairs of isocyanate groups connected by the centre of symmetry. Though this distance is only 0.05 Å shorter than the sum of the WR of the nitrogen and carbon atoms the optimum orientation of the NCO group in the structure is compatible (as suggested[143]) with dimerisation reactions between these groups in the solid phase. This assumption agrees with the conclusion by Shklover et al.[144] that solid-phase polymerisation which produces a bond between the A and B atoms of neighbouring molecules is possible if the r_{AB} distance is not greater than $R_A + R_B + 0.5$ Å, where R_A and R_B are the van der Waals radii of the A and B atoms.

An updated method[146] of calculating the rate constants and the heats of some gas-phase reactions over a wide temperature range by using internuclear distances, WR, and the vibrational energies of molecules has been proposed in a development of a previous method.[145]

The van der Waals radii have been used also for mapping chemical reactions from X-ray diffraction data. We have already discussed[1] in depth the mapping of the tautomeric transition[147] of tropolone derivatives in terms of four aryl-substituted tropolones. A more recent study[148] of five other compounds of this series allowed the geometrical changes in the molecules to be monitored more thoroughly.

* * *

The data discussed in the present review show that the van der Waals atomic radii are still finding extensive and varied applications in chemistry. We note that the WR are much more generally used than the covalent radii, since in order to discuss the geometrical aspects of chemical bonds we need a more exact estimate of the interatomic distances, and tabulations of averaged bond lengths are most frequently used. The pathways available for these transformations were the object of both our previous review[1] and of the present work.

However, we must stress that van der Waals radii will 'work' reliably and give useful results only if used correctly.

In conclusion we should remind the reader that the concept of van der Waals radii was formulated in the 1930s and 1940s, and is the central attribute of the classical organic crystal chemistry, based on the postulate of molecular close packing. However, in recent years there has been a rapid production of data indicating the limitations of this postulate. Our increasing understanding of specific (strongly nonisotropic) atom–atom interactions has led to new views on the structure of organic crystals.[149] The results of nonempirical quantum-chemical calculations are playing an increasingly important role in discussions of molecular structures: they are now carried out systematically not only for the simplest but also for relatively complex polyatomic organic molecules. Strictly speaking these concepts leave no room for the van der Waals radii. However, van der Waals radii are a very convenient and correct means of calculating the possible lengths of noncovalent interatomic contacts: they have become an integral part of modern chemistry, and we believe that they will so remain for a long time.

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