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Van der Waals radii and their application in chemistry

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ABSTRACT. Published systems of van der Waals radii (VR) have been examined and compared. The many ways of using VR in various branches of chemistry, in particular in crystal chemistry, stereochemistry, and X-ray diffraction (primarily to describe and interpret molecular conformations and crystal structures and to determine new structures) have been analysed. Particular attention has been paid to the detection of specific non-valence interactions (both inter- and intramolecular). Various structural-biological problems, in particular the production of 'incorrect' pairs of bases in DNA and the use of VR to explain the physicochemical properties of substances, have been examined. The properties of crystals determined by the effective volume, dimensions, and shape of the molecules, and the characteristic features of the structures of inclusion compounds, clathrates, and organic conductors, have been discussed. The use of VR to investigate the mechanism and predict the possibility of various chemical reactions has been described. The bibliography contains 173 references.

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I. Introduction

Quantum-mechanical ideas play an exceptionally important role in present-day chemistry, yet the classical theory of the structure of molecules and classical stereochemistry, whose foundations were laid by Butlerov, Kekulé, Van't Hoff, Le Bel, and Werner, today still remain the basis of organic and coordination chemistry. In recent years they have been supplemented significantly by the quantitative geometric characteristics of molecular systems, based mainly on empirical generalisations of the results of studies by X-ray diffraction and other physical methods.

One such generalisation is the system of covalent radii, which makes it possible to estimate the lengths of valence bonds. However, as a consequence of the variety of valence states and the significant deviations from additivity, the use of covalent radii has been extremely limited. For practical purposes, tables of 'standard' bond lengths,[1] which together with 'standard' values of the valence angles make it possible to construct in a first approximation a rod-and-sphere model of a molecule, are more useful. Even these concepts are inadequate, however, since they do not make it possible to take account of non-valence intramolecular interactions and cannot be used to analyse the packing of molecules.

The need for a comprehensive discussion of the geometry of molecules and their packing made it necessary to develop the concept of van der Waals radii (VR), which is now widely used in various branches of chemistry. It might seem that with the present availability of such effective means of taking account of non-valence interactions as atom–atom potentials,[2,3] it would be possible to carry out a more rigorous and accurate quantitative analysis of the geometry of molecular systems. The universal nature, simplicity, and clarity of the VR concept, however, make it appropriate for use in preliminary qualitative estimates, and often for the final solution of many problems of practical importance.

II. Systems of van der Waals radii and the dispersion of intermolecular contacts

The first attempts to relate the distances between the atoms of neighbouring molecules in crystals to the corresponding radii of the atoms (or atomic groups)[4–6] included the first representations of large molecules as overlapping van der Waals spheres and of crystal structures as close-packed molecules in contact. Pauling[7] gave the first table of VR, consisting of the rounded values of the ionic radii. It was Kitaigorodskii,[8] however, who fully recognised the value of this approach for chemistry and molecular physics and who laid the foundations of the theory of the close-packing of molecules.

Table 1. Van der Waals atomic radii (Å) of the elements of organic compounds.

Element	Pauling, 1939 (Ref.7)	Kitaigorodskii, 1955 (Ref.8)	Kitaigorodskii, 1971 (Ref.9)	Bondi, 1964 (Ref.16)***	Zefirov and Zorkii, 1974 (Ref.11)
C	1.85*	1.72**	1.80	1.70	1.71
H	1.2	1.17	1.17	1.20	1.16
O	1.40	1.36	1.52	1.52	1.29
N	1.5	1.57	1.58	1.55	1.50
Cl	1.80	1.78	—	1.75	1.90
S	1.85	2.02	—	1.80	1.84 [15]

* Half the thickness of an aromatic molecule (in the third edition of his book,[7] Pauling changed this quantity to 1.70 Å, leaving the other quantities unchanged).

** The radius of the carbon atom in aromatic molecules; the radius of aliphatic carbon is given as 1.80 Å (in his next publication,[9] Kitaigorodskii adopted the universal value 1.80 Å).

*** Radii for atoms forming only single bonds (for aliphatic compounds in the case of hydrogen).

The VR values proposed by Kitaigorodskii[8] were extremely close to those of Pauling[7] (Table 1). Later Kitaigorodskii[9] modified his table slightly (in the present authors' opinion making it less satisfactory). A common disadvantage of these VR systems was that they were constructed from extremely limited structural data (sometimes the value of a VR was established from only one structure). Although the proposed VR values in many cases were close to the best values, the VR are in principle essentially statistical quantities, and should be determined by averaging over a large number of structures.

The starting point for the construction of a system of VR is essentially the basic postulate of the theory of the close-packing of molecules, according to which the molecules, bounded by the outer surface of intersecting van der Waals atomic spheres, touch one another in the crystal, that is they do not penetrate one another and are not suspended in a cavity. The problem is to select suitable VR values. Kitaigorodskii[8] showed that a satisfactory solution to this problem exists.

The quantities $\Delta r_{ij} = r_{ij} - (R_i + R_j)$, where R_i and R_j are the van der Waals radii, and i and j are the indices of atoms belonging to neighbouring molecules, will be used. If the VR are known, it is possible, for each pair of molecules, to find the smallest value of Δr_{ij}, that is $(\Delta r_{ij})_{\min}$. This postulate implies that the quantity $(\Delta r_{ij})_{\min}$ is never negative and is equal to zero for a certain number of molecule–molecule contacts, whose existence is sufficient to ensure a three-dimensional system of contacts (significant contacts) in the crystal.

In fact, the accuracy of this postulate is extremely low (the deviations exceed the uncertainty of the X-ray diffraction data by factors of 10–100). To make it more realistic, it is better to take for the significant contacts not the equality $\Delta r_{\min} = 0$ but the inequality $|\Delta r_{\min}| < \delta$, assuming that $\Delta r_{\min}$ may also be negative (that is that overlap of the van der Waals spheres is possible), but that the quantity δ is fairly small. Kitaigorodskii[8] assumed that the postulate applies if it is assumed that $\delta = 0.05 r_{ij}$. However, firstly some deviations are still observed even in this case, and, secondly, the objectively justified selection of a specific value of δ guaranteeing a correct description of a wide range of molecular packing is apparently in general impossible. A more fundamental analysis makes it necessary to adopt a statistical approach to VR with allowance for the dispersion of intermolecular contacts.

The dependence of the energy of interaction φ of two free atoms A and B on the distance r between them is given by a potential curve (Fig. 1*a*) with a minimum at the equilibrium distance r_0. If however the atoms A and B are in molecules, the 'contact' distance r_{AB} between them is less than r_0. This can be demonstrated by the hypothetical example shown in Fig. 1*b*. For simplicity, it is assumed that the atoms in the triatomic molecules being considered are identical; it will be assumed that the molecules can approach one another only by translation along a certain axis. If the energy of interaction of the molecules is regarded as the sum of the atom–atom potentials $\sum_{ij}\varphi_{ij}$, it follows that in the equilibrium position of the molecules, $r_{AB} < r_0$, since in the interaction of atoms which are not in direct contact, attraction predominates over repulsion, and with increase in the size of the molecules (Fig. 1*c*), the difference $r_0 - r_{AB}$ should increase. This difference naturally also depends on the orientation of the molecules.

Thus strictly speaking, the VR of an atom is in general not a physical constant. As a result of the rapid increase in the energy φ with decrease in r_{AB}, however, this distance rapidly reaches a quasi-limiting value. This in fact justifies the existence of tabulated values of R. It may be assumed, however, that shorter intermolecular contacts should be observed for large molecules.

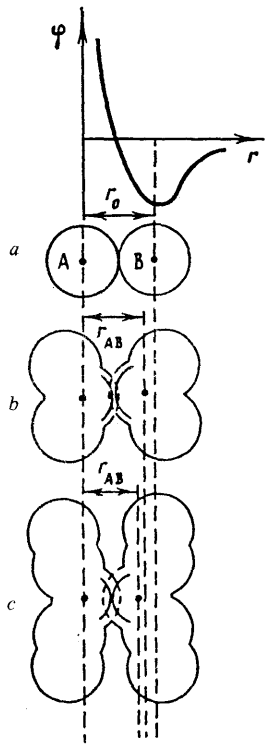


Figure 1. Dependence of the length of an atom–atom van der Waals contact on the composition and geometry of the molecule: *a*, interaction of free atoms A and B; *b*, interaction of atoms A and B in triatomic molecules; *c*, the same for penta-atomic molecules.

In fact, this tendency is masked by the individual characteristic features of the composition, shape, and packing of the molecules. The picture is much more complicated when the arrangement of not two but several molecules is considered. The tendency to adopt a packing ensuring the lowest energy of the crystal structure as a whole may lead to the appearance of local more closely packed and less closely packed regions, whose arrangement in space is specific for each specific crystal. The interatomic distances corresponding to the significant contacts of a given type A...B may differ considerably in different molecular crystals, but should be distributed within a certain range. For a specific structure, the VR give only the most probable (*a priori*) values of the intermolecular contacts.

Another important feature complicating the analysis of intermolecular contacts using VR is that the postulate formulated above assumes that the VR are additive, that is it is based on a combination rule according to which $\bar{r}_{AB} = (\bar{r}_{AB} + \bar{r}_{BB})/2 = R_A + R_B$, where $\bar{r}$ is the average length of the significant contact. Although at first sight this rule appears obvious, in fact it does not follow from any more general considerations. Moreover, the presence of effective charges on the atoms indicates that there will be deviations from additivity.

Good and Hope[10] examined possible combination rules for equilibrium distances, and gave preference to the equation $r_0(AB) = \sqrt{r_0(AA) \cdot r_0(BB)}$. When applied to intermolecular contacts, this corresponds to the expression $\bar{r}_{AB} = 2\sqrt{R_A R_B}$, which shows better agreement with experiment than the additivity usually assumed, but this is revealed only by a statistical analysis.[11]

Mean-statistical values of the VR of the elements of organic compounds were found[11] by treatment of X-ray diffraction data for 75 organic crystal structures without intermolecular hydrogen bonds. For each of these structures, significant contacts ensuring the existence of a three-dimensional framework of contacts were selected. The minimum number of such contacts is 4 when the molecules are in general positions, and 6 when they are at a centre of inversion. Even in the selection of the significant contacts it is necessary to specify some VR system. In a first approximation, the radii of Kitaigorodskii[8] were taken (except for the Cl atom, for which the value 1.86 Å [12] was used). Since the final (refined) VR values given in Table 1 were found to be fairly close to the original values, the significant contacts on the whole were apparently selected correctly.

Table 2, taken from the paper by Zefirov and Zorkii,[11] gives the values of $\bar{r}_{ij}$ for significant contacts of different types. The mean-statistical VR were selected to give best agreement between $\bar{r}_{ij}$ and $2\sqrt{R_i R_j}$; as already noted and as can be seen from Table 2, this is more effective than using the $R_i + R_j$ values. This last feature can apparently be interpreted as follows. If the atoms i and j are atoms of the same kind, then $R_i = R_j$ and $R_i + R_j = 2\sqrt{R_i R_j}$; if however they are atoms of different kinds, then $R_i + R_j > 2\sqrt{R_i R_j}$, that is according to statistical data when these atoms are in contact there is a tendency for the van der Waals spheres to overlap slightly. Since atoms of different kinds often have effective charges of opposite sign, their approach may be due to electrostatic attraction.

Table 2. Interatomic distances in the 'significant' intermolecular contacts, and comparison with the van der Waals radii.

Contact	$R_i + R_j$			$2\sqrt{R_i R_j}$ (Ref.11)	$\bar{r}_{ij}$	r_{ij} (min)	r_{ij} (max)	n *
	(Ref.8)	(Ref.9)	(Ref.11)					
C...C	3.44	3.60	3.42	3.42	3.41	3.32	3.53	31
H...H	2.34	2.34	2.31	2.31	2.31	2.04	2.58	58
C...H	2.89	2.97	2.87	2.81	2.81	2.57	3.12	160
O...C	3.08	3.32	3.00	2.97	2.97	2.85	3.11	12
O...H	2.53	2.61	2.45	2.44	2.44	2.25	2.59	44
N...C	3.29	3.38	3.21	3.20	3.17	3.03	3.27	24
N...H	2.74	2.75	2.66	2.63	2.64	2.53	2.84	51
Cl...H	2.95	—	3.06	2.96	2.96	2.88	3.03	26

* n is the number of contacts over which the averaging was carried out.

The similarity in the values of $\bar{r}_{ij}$ and $2\sqrt{R_i R_j}$ makes it possible to base the determination and application of VR on the condition $|(r_{ij} - 2\sqrt{R_i R_j})_{min}| \leqslant \delta$, where δ is sufficiently small. Bound by tradition, however, research workers more frequently use the classical and more obvious relationship $|r_{ij} - (R_i + R_j)| \leqslant \delta$, even when the radii proposed by Zefirov and Zorkii[11] are used. Strictly speaking, this is incorrect, but since the difference between $2\sqrt{R_i R_j}$ and $R_i + R_j$ is usually small, its does not lead to significant errors, and in the present review, in some cases, the authors of the works cited will be followed, and the intermolecular (or non-valence intramolecular) contacts will be compared with the sum of the VR, without this being specially pointed out.

For a correct understanding of the physical significance of the comparison of r_{ij} with $2\sqrt{R_i R_j}$ or with $R_i + R_j$, it is important to characterise the distribution of the values of r_{ij} corresponding to significant contacts of a definite type (that is to contacts between atoms of a definite type). For this purpose it is convenient to use the observed limiting values of r_{ij}(min) and r_{ij}(max), given in Table 2, and also the values of $\Delta_1 = \bar{r}_{ij} - r_{ij}$(min) and $\Delta_2 = r_{ij}$(max) $- \bar{r}_{ij}$. The values of Δ usually do not exceed 0.3 Å, or 0.15 Å for contacts not including H atoms. The values of $2\sqrt{R_i R_j}$ 'centre' fairly satisfactorily the range between r_{ij}(min) and r_{ij}(max), that is the distribution is close to normal. The values of $R_i + R_j$ for atoms of different kinds, however, are usually displaced considerably towards the upper limit.

The most familiar and most frequently used systems of VR are compared in Table 1.† As noted above, the most important VR obtained by Zefirov and Zorkii[11] are extremely close to those given by Kitaigorodskii,[8] except for the VR of the S and Cl atoms (in the last case the discrepancy is due to the fact that Kitaigorodskii[8] did not take account of the specific nature of the Cl...Cl contacts; see section III below). Subsequently, however, a much larger value was adopted[9] for the O atom, coinciding with that recommended by Bondi.[16] Bondi[16] used a statistical approach, but with extremely few data, and the final results were distorted by a number of significant errors.

Thus according to the original postulate of the theory of close-packing, significant contacts should be used to determine VR. This obvious feature was overlooked by Kitaigorodskii[9] and Bondi,[16] so that the VR of the O atom was too high. Thus when using Bolton's data[17] to examine the shortest interatomic distances between two neighbouring molecules of chloranil $C_6O_2Cl_4$, Bondi[16] used the 'contacts' O...O 3.26 Å and O...C 3.06 Å, without noticing that there is also an O...C distance of 2.85 Å (corresponding to a significant contact), which cannot be reconciled with the adopted value $R_0 = 1.52$ Å. A similar error was made by Kitaigorodskii[9] in the examination of the structure of alloxan $C_6H_2O_4$: he took as 'contacts' the O...O distances 2.94, 3.05, and 3.07 Å, which gave the average value $R_0 = 1.51$ Å, but the diagram given shows that this structure contains the significant contacts O...C 2.79 Å and O...H 2.38 Å and 2.47 Å, indicating that this VR value leads to unacceptable overlap of the van der Waals spheres.

A completely unreasonable statistical procedure, called 'revision of van der Waals atomic radii', was recently used by Nyburg and Faerman,[18] who determined VR using the Cambridge Structural Data Bank and determined all the shortest distances between atoms of the same kind in neighbouring molecules. The fact that many of them did not correspond to atom 'contacts' was completely ignored. A rational approach to the problem being discussed requires a correct analysis of the packing of the molecules in each of the structures being considered.

It is also important to emphasise the following significant feature. Contacts between atoms of the same kind are most convenient for determining VR. It is these contacts, however, which often show specific properties, making it impossible to obtain at this level a system of universal VR showing additivity (or satisfying the rule

† The mean-statistical VR of the F, Br, and I atoms[13,14] can be added to the data in Table 1.

$\bar{r}_{ij}$ (significant) $\simeq 2\sqrt{R_iR_j}$). Thus oxygen atoms, which (together with fluorine) have the highest electronegativity, usually carry an appreciable effective negative charge. It is for this reason, and also because of their relatively small size, that O atoms rarely form significant contacts with one another. An exception is provided by compounds rich in oxygen (for example containing a large number of nitro-groups). Even if a significant contact O...O is formed, however, it will generally be longer than twice the universal VR, because of the strong electrostatic repulsion. Special account can and must be taken of features of this kind (in particular, a special oxygen VR can be introduced just for O...O contacts), but the tabulated value of R_0, suitable for analysing ordinary contacts such as O...C, O...N, etc., obviously should not be derived from O...O distances.

For F...F contacts, in certain cases, another situation arises. Zefirov and Porai-Koshits[13] obtained the VR of fluorine by examining the significant contacts F...F in the crystals of compounds with the general formulae $(MF_5)_4$ and EF_6. This was possible, because in the molecules of these compounds the high negative charge on the F atoms is compensated by the 5 or 6 times larger positive charge on the M or E atoms, but in organofluorine compounds, the average F...F distances should be longer (greater than $2R_F$).

The contacts between other halogen atoms of the same kind (Γ...Γ) show another characteristic feature: here, a stronger exchange interaction is often superimposed on the purely van der Waals interaction. Contacts involving these interactions, described as specific interactions (see section III), are naturally unsuitable for determining VR. If this feature is not taken into account the VR obtained for the halogens are too low (as for example in data given by Kiraigorodskii[8] and Bondi[16]). Γ...Γ contacts can still be used to find the VR of halogens, however, if contacts with specific interactions are excluded. Zefirov and Porai-Koshits[14] determined the angular geometric characteristics corresponding to these contacts. This made it possible to exclude them from the set of distances examined and to obtain for the VR of the Cl, Br, and I atoms the values 1.90, 1.97, and 2.14 Å respectively. The value of R_{Cl} obtained by Zefirov and Porai-Koshits[14] coincided with that previously obtained by Zefirov and Zorkii[11] from an examination of the significant contacts between chlorine and other atoms.

III. The application of van der Waals radii in crystal chemistry, stereochemistry, and X-ray diffraction

Since they are based on X-ray diffraction data on the structure of crystals, VR are naturally used primarily to describe and interpret crystal structures, and also to determine new structures. When intermolecular interactions are considered, contacts of two types are examined: normal contacts corresponding to ordinary van der Waals interactions, and shortened contacts, where specific intermolecular interactions are revealed. A remarkable feature is that although they represent a geometric approach to the structure of a substance, VR can also be used to examine its energy, since they are used to obtain atom–atom potential functions, which now represent the most universal and effective means of calculating the energy of interaction of comparatively complex molecules. Although intermolecular contacts represent the source of data for compiling tables of van der Waals radii, one of their most important uses is in the analysis of the non-valence interactions within molecules and in the related discussion and prediction of molecular conformations.

1. Normal intermolecular contacts

Since a system of VR together with data on the dispersion of the lengths of the significant contacts reflects the usual picture of the packing of molecules in crystals, in the study of each new substance a comparison of the shortest intermolecular (atom–atom) distances with the sums of the VR or the quantities $2\sqrt{R_iR_j}$ usually makes it possible to establish the 'normal' character of the intermolecular interactions and confirms that the crystal does in fact consist of discrete molecules. Data on the shortest intermolecular distances (selected using VR) are often given as standard tables (see for example Ryabova and co-workers[19] and Romanenko and co-workers[20]).‡

For coordination compounds, the determination of the molecular character of a crystalline substance is often difficult, and the result is difficult to predict. An example is provided by the study[21] of a structure which was found to contain dimeric anions $[Cu_2(OCH_3)_2.\{2,6\text{-}(NO_2)_2C_6H_3O\}_4]^{2-}$, each joined by hydrogen bonds to two piperidinium cations $C_5H_{12}N^+$ forming the second coordination sphere of the complex. There are no contracted intermolecular contacts between these associates, so that the structure could be described as molecular.

The use of VR makes it possible to introduce the concept of molecular coordination number (MCN), which provides an extremely useful means of describing the structure of molecular crystals.[8,22] The distribution of the values of Δr_{min} (see section II) on a numerical axis usually appears approximately as shown in Fig. 2*a*, which gives the distribution of the Δr_{min} values for 3,3,'-bithienyl. Figures indicating the multiplicity of the given molecule–molecule contact are given above the vertical lines corresponding to the Δr_{min} values. A characteristic feature is the gap between the two values of Δr_{min} denoted μ and ν, where μ corresponds to the molecule with the largest Δr_{min} still in the coordination sphere, and ν corresponds to the molecule with the smallest Δr_{min} not included in the coordination sphere. The larger the gap between μ and ν, the more clearly defined the coordination sphere.§ Later,[23] this qualitative approach to the determination of the MCN was supplemented by the quantitative conditions: 1) $\nu - \mu \geqslant 0.6$ Å, and 2) -0.3 Å (or -0.15 Å) $\leqslant \mu \leqslant 1.0$ Å; this value in brackets corresponds to contacts not involving hydrogen atoms. In all 155 examples of the coordination environment of molecules examined,[23] it was possible, in the distribution of the Δr_{min} values, to select values of μ and ν satisfying the above conditions. At the same time, in 25% of cases, a picture similar to that shown in Fig. 2*b* was observed. Here, two appreciable gaps are observed in the sequence of Δr_{min} values, making it possible to distinguish a coordination sphere between the first and second spheres (a 'sesqui-sphere'). The MCN in these cases is written as a sum (for example 12 + 2). The quantitative criteria for the coordination 'sesqui-sphere' are: 1) $\nu_1 - \mu_1 \geqslant 0.3$ Å; 2) $\nu_2 - \mu_2 \geqslant 0.6$ Å; 3) $\mu_1 \geqslant -0.3$ (-0.15) Å; and 4) $\mu_2 \leqslant 1.0$ Å. Here it is assumed that $\nu_2 > \mu_2 \geqslant \nu_1 > \mu_1$.

‡ The advantages of a table of this kind over a table of distances shorter than some single value for contacts of all types are obvious; intermolecular distances selected without comparison with VR usually by themselves do not carry any valuable information.

§ The definition of MCN, previously introduced by Kitaigorodskii,[8] as the number of molecules having at least one contact with the molecule being considered does not make it possible to determine this quantity objectively.[22]

In homomolecular crystals, a continuous series of MCN from 9 to 18 has been observed. The most common values are 14 (about half of the structures) and 12 (about one third of the structures). An expanded form of notation for the MCN (in layers and in chains) has been proposed and analysed[24,25] for a more detailed characterisation of the coordination environment of molecules.

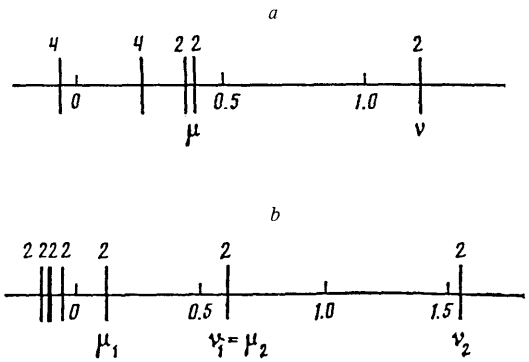


Figure 2. Diagrams illustrating the determination of the molecular coordination number (the values of Δr_{min} are shown on the numerical axis): *a*, structure of 3,3′-bithienyl; *b*, hypothetical structure with a coordination 'sesqui-sphere'.

In X-ray diffraction studies it is often pointed out that the intermolecular distances are greater than the ordinary values, and that this might indicate loosening of the packing. These conclusions are not sufficiently reliable, however, and are usually reached without taking account of the natural dispersion of the significant contacts.¶

On the other hand, the existence of anomalously short contacts indicates either that the X-ray diffraction data are unreliable or (when there is crystal-chemical justification) the existence of specific intermolecular interactions (see next section).

In some X-ray diffraction studies, VR are used to identify atoms. For example, in the determination of the structure of methylammonium hexachloroferrate(II) hydrate,[26] difficulties were encountered in identifying the nitrogen and carbon atoms, which give electron density maxima of similar height. The formation of a short intermolecular contact (2.76 Å) between an oxygen atom and one of the atoms difficult to identify indicated that this was a nitrogen atom, since this distance for the nitrogen and oxygen atoms, with allowance for their van der Waals radii, is normal, whereas it is too short for carbon and oxygen atoms.

The detection of unrealistic intermolecular contacts using VR plays an important part in the analysis of crystal structures with incomplete ordering. These structures are often described as a statistical sequence of molecules in which one of a number of possible positions of some atomic group is realised. For example, in an X-ray diffraction study[27] of the selenium derivative of biepoxycyclopentyl $C_{16}H_{16}O_4Se$ it was suggested that randomly distributed molecules with different angles of rotation of the phenyl groups coexist in the structure (the angle between two positions of the ring is close to 90°). It was shown,[28] however, that this model unavoidably leads to extremely short intermolecular contacts. A detailed analysis made it possible to construct a model of the structure consisting of enantiomorphic domains in which the molecules are packed in accordance with the usual VR values (the ways in which these domains are connected were also studied).

A domain structure was also proposed[29] for the crystals of 3-bromobicyclo[3.3.1]non-2-en-4-one, where random arrangement of the oxygen atoms leads to shortened O...O contacts with a length of 2.31 Å. Unrealistically short intermolecular Cl...Cl contacts (2.33 Å) were also noted[30] in the random structure of $Ni(p\text{-}H_2NC_6H_4OCH_3)_4(Cl_3CCOO)_2$. In the last two studies, however, the problem was not fully analysed, and a model which does not contradict the observed diffraction pattern and at the same time is consistent with crystal-chemical considerations has not yet been constructed.

The modelling of non-valence interactions by means of VR was an essential part of such outstanding and familiar studies as the determination of the structure of the α-helix of polypeptides[31] and the double helix of DNA.[32] At the present time also, the initial models of proteins and other biological materials are constructed using VR (these models are subsequently verified and refined by X-ray diffraction and NMR spectroscopy).

VR have recently been used[33] to solve structural-biological problems associated with the formation of 'incorrect' pairs of bases in DNA. In the transfer of inherited information, an exceptionally important role is played by the so-called 'Watson–Crick pairs' adenine–thymine (uracil) or guanine–cytosine. The use of mean-statistical VR values and allowance for the dispersion of van der Waals contacts showed that the nucleic acids of the incorrect pairs of bases in the usual tautomeric forms can be arranged in a double helix without producing shortened interatomic contacts or significant distortion of the sugar–phosphate core. It was found that the sugar–phosphate core is sufficiently flexible to allow the arrangement in a double helix of nucleotide pairs having dimensions approximately 2 Å larger (the inosine–adenine pair) and 2 Å smaller (the uracil–cytosine pair) than the canonical Watson–Crick pairs, and also pairs in which one base is displaced relative to the other by ~2 Å along a two-fold axis (the guanine–uracil pair).

The systems examined above contain only normal intermolecular contacts. This last feature is an experimental fact or is postulated on the basis of empirical generalisations, so that the requirement that the contacts be normal can be used to construct or correct structural models. At the same time, as already noted, shortened intermolecular contacts also arise regularly in certain systems; these systems are examined in the next section.

2. Shortened intermolecular contacts (SInterC)

The detection of anomalously short (shortened) contacts in crystal structures is of particular importance, since these contacts usually indicate the existence of specific intermolecular interactions which are appreciably stronger than ordinary van der Waals interactions and which have a significant influence on the structure and properties of molecular crystals. The most common example of specific interactions (SI) is the hydrogen bond. Metal–metal, halogen–halogen, sulphur–sulphur, and various other intermolecular SI are less well known. The detailed study of SInterC will undoubtedly lead to the detection of new types of SI which have not yet been studied.

¶ An exception is provided by crystals made up of very small molecules (containing a small number of atoms), studied at relatively high temperatures.

The term shortened intermolecular contacts is used to describe the distances r_{ij} between the atoms of different molecules if $r_{ij} < R_i + R_j - \delta$ or $r_{ij} < 2\sqrt{R_iR_j} - \delta$,[34] where δ is the overlap of the van der Waals spheres acceptable for a normal contact. Many workers discussing SInterC assume that $\delta \simeq 0$, which has no physical significance. As noted above, statistical analysis shows that it is appropriate to take $\delta = 0.15$ Å for contacts not involving hydrogen atoms, and $\delta = 0.30$ Å for contacts involving hydrogen atoms.

Contacts for which $2\sqrt{R_iR_j} - \delta < r_{ij} < 2\sqrt{R_iR_j}$ can be described as contacted. More or less contracted contacts are sometimes regarded as indicating van der Waals interactions of increased strength.[35] It should be borne in mind, however, that there is no direct relationship between the length of the shortest intermolecular contact in van der Waals interaction and the energy of interaction of the corresponding molecules. Thus contracted contacts cannot be regarded as a sign of specific intermolecular interactions.

The study of hydrogen bonds occupies a unique place in the investigation of SInterC. As data on hydrogen bonds have accumulated and become more detailed, a number of geometric criteria for the existence of an H-bond have been proposed.[36–39] All these criteria are based on an examination of the distances $r(X \ldots Y)$ or $d(H \ldots Y)$ in a system XH ... Y, although in fact the strength of a bond is also determined to a large extent by its linearity, that is by the angle X–H–Y.† The general idea is that the length of the contact between atoms involved in an H-bond is shorter than the distance between the same atoms joined by only van der Waals interaction. These criteria differ, however, in the use of different VR systems and different values of δ. The general trend has been that the criteria have been made more rigid as it has been found that in some cases they 'do not work'.

The criterion of Pimentel and McClellan,[36] the first to be proposed, is based on a comparison of the length of the contact X ... Y with sum of the van der Waals radii of X and Y; δ is taken as zero. When it became possible to locate H atoms in X-ray diffraction studies, criteria based on the comparison of the lengths of the contacts H ... Y with the sum of the VR of the H and Y atoms began to be used. These are the criteria of Hamilton and Ibers[37] ($d < R_H + R_Y$ or $d < R_H + R_Y - 0.2$ Å), Zefirov[38] ($d < 2\sqrt{R_HR_Y} - 0.35$ Å), and Rahim and Barman[39] ($d < r_{XH} + R_H + R_Y$).

The use of various criteria of this kind without introducing additional information, however, may lead to erroneous conclusions, particularly when the hydrogen atoms have not been located. It has been shown[40] by infrared spectroscopy that OH ... O contacts are not H-bonds in the following crystals: citric acid[41] (O ... O 2.84 Å), methyl-α-*D*-glucopyranose[42] (O ... O 2.93 Å and H ... O 2.19 Å), *L*-ascorbic acid[43] (O ... O 2.93 Å and H ... O 2.23 Å), and tartronic acid[44] (O ... O 3.02 Å and H ... O 2.23 Å). In all these cases, the use of the criteria of Pimentel and McClellan with the VR of Bondi,[16] $d(O \ldots O) < 3.04$ Å, Rahim and Barman, $d(O \ldots O) < 3.68$ Å, Hamilton and Ibers, $d(O \ldots H) < 2.6$ Å, and a modification of the latter, $d(O \ldots H) < 2.4$ Å would have led to errors, since according to these criteria, all the above contacts should correspond to an H-bond.

† For very large deviations from linearity, for example if $\angle XHY \leqslant 90°$, the concept of H-bond apparently loses significance.

Strictly speaking, the existence and strength of an H-bond should be judged by energy calculations, for example by Poltev's method,[45,46] where account is taken of the angular dependence of the energy of the H-bond. The energy of approach (particularly when the value of the angle XHY is taken into account) unavoidably leads to the conclusion that there is no rigid boundary between the 'bond' and 'no bond' situations. This makes it obvious that any geometric criteria are arbitrary, although they may be useful for practical purposes. Moreover, the correct use of geometric parameters combined with VR is a most important (if not the principal) source of information on H-bonds. An important auxiliary role may be played by crystal-chemical (crystal-structural) considerations: the assumption that an H-bond is formed is often essential to establish the factors leading to a given mode of packing of the molecules.

The magnitude of the decrease in the length of a contact compared with the normal value, defined as $2\sqrt{R_iR_j}$ (or $R_i + R_j$) often makes it possible not only to detect an H-bond but also to deduce its strength. Thus a comparison of H-bonds of different types (NH ... Cl and OH ... O) from the differences $\Delta r_{HY} = r_{HY} - 2\sqrt{R_HR_Y}$, where the VR were taken from Zefirov and Zorkii,[11] showed that the structure of *trans*-chloro(*L*-prolinato-N,O)[(+)-α-methylbenzylamine-N]platinum(II) [47] contains pseudo-dimers of complexes formed by the stronger H-bonds NH ... Cl; the pseudo-dimers are connected in layers by the weaker bonds OH ... H.

Among the large number of H-bonds detected using VR, various types of bond which have been little studied are of particular interest. Thus an X-ray diffraction study[48] with location of the H atom has proved objectively that the crystal of (benzoylmethyl)-triphenylphosphonium bromide ($PhCOCH_2P^+Ph_3)Br^-$ contains H-bonds of the type CH ... Br^-. The geometric parameters of this bond are: C ... Br^- 3.457 Å, H ... Br^- 2.26 Å, C–H 1.20 Å, angle $CHBr^-$ 172°. The distance H ... Br is 0.41 Å shorter than the value of $2\sqrt{R_HR_{Br}} - 0.35$ Å, equal to 2.67 Å. In the crystal of (p-$CH_3OC_6H_4)_2Te(NSO_2C_6H_4CH_3$-$p$), one of the aromatic rings at the Te atom forms a short contact with the N atom (C_{16} ... N 2.96 Å, H_{16} ... N 2.25 Å, CHN 124°).[49] This contact is very short, so that it was assumed that the crystal contains a CH ... N H-bond, analogous to the familiar CH ... O bonds.

SInterC of the type Γ ... Γ, where Γ = Cl, Br, I, are fairly frequently observed in crystal structures (fluorine does not form shortened contacts[13]). The greatest of the shortened contacts increases from chlorine to iodine. The significant contacts I ... I show a practically continuous series of distances from twice the van der Waals radius to twice the covalent radius of iodine.[50] The production of Γ ... Γ SInterC is attributed to the specific interactions between the halogen atoms, that is to the greater or lesser contribution of exchange forces.

The lower limits of the distances for the contacts C–Γ ... Γ–C have been determined;[51] they are given effectively by the equation $r_{ij} = d - 0.15$ Å, where d is the length of the shortest contact in the structure of the corresponding halogen ($d = 3.28$ Å for Cl_2,[52] 3.32 Å for Br_2,[53] and 3.50 Å for I_2 [54]). Later, the 'upper limits' (r_{max}) of the distances r_{ij} for the specific interactions Γ ... Γ in organic crystals were established.[14] The angular characteristic φ—the greater of the two angles C–Γ ... Γ for each contact—was used. The data for 123 structures established that for $r_{ij} < r_{max}$, the angle $\varphi \geqslant 130°$, and that for $r_{ij} > r_{max}$, much smaller values of φ are also observed. On this basis, the value of r_{max} (3.65 Å for Cl, 3.79 Å for Br, and 4.14 Å for I) was taken as the 'upper limit' of the SI. A remarkable feature is that the relationship $r_{max} + 0.15$ Å $\simeq 2R_Γ$ is satisfied with a fairly high accuracy.

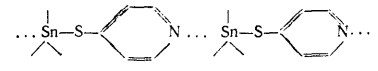
It is important to emphasise, however, that the concept of the 'upper limit' of specific interactions Γ...Γ is conditional. If $r_{ij} < r_{max}$, the interaction can be regarded as specific; if however $r_{ij} > r_{max}$, additional information is required to determine the nature of the interaction. The Γ...Γ atom–atom potentials taking account of the possible production of SI are unknown, but it is clear that with increase in the distance, the modulus of the energy of this bond decreases more smoothly than that of the covalent bond. In various crystals of organic halogen derivatives, the packing of the molecules is clearly determined by the tendency towards maximum approach of the Γ atoms. Thus the specific character of an interaction may be indicated (but not necessarily) by the characteristics of the arrangement of the molecules in the crystalline substance.

The use of VR combined with an energy calculation has shown how the successive introduction of F, Cl, Br, or I atoms into the molecule influences the packing of the molecules in the crystals of 1,5-dihalogenoanthraquinones $C_{14}H_6O_2\Gamma_2$.[55] All these crystals contain clearly defined molecular chains with similar structures. These chains resemble one another particularly closely in $C_{14}H_6O_2F_2$, $C_{14}H_6O_2Cl_2$, and $C_{14}H_6O_2Br_2$, but the ways in which they are superimposed in these structures differ considerably. When the structure is modified by the successive replacement of the H atoms in positions 1 and 5 of anthraquinone by halogen atoms, three factors are important: 1) the increase in the size of the atoms (the increase in their covalent and van der Waals radii), 2) the appearance (beginning at Cl) of SI, which to some extent may compensate the increase in the size of the atoms, and 3) the magnitude of the gap (or overlap) between the van der Waals spheres of the atoms belonging to neighbouring molecules. In particular, in anthraquinone the H atoms in positions 1 and 5 (or 4 and 8) in the chain do not give contacts close to the sum of the VR,‡ but the hydrogen atoms of neighbouring chains are in direct contact with them. The difference in the VR (ΔVR) of the F and H atoms is 0.24 Å; the difference in their covalent radii is ΔCR = 0.34 Å. Since SI are not characteristic of F atoms, their introduction into the anthraquinone molecule produces little change in the structure of the chains, but alters the way in which they are packed. The structure of $C_{14}H_6O_2F_2$ contains short contacts involving F atoms ($\Delta r_{ij} = r_{ij} - \Sigma VR = -0.12$ Å for F...H and 0.00 for F...C). Since ΔVR(Cl and F) = 0.50 Å and ΔCR(Cl and F) = 0.35 Å, the replacement of F atoms by Cl leads to a change in the packing.

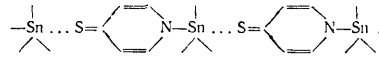
In addition to Γ...Γ SInterC, S...S InterC are fairly frequently encountered in organic crystals. Thus Zefirov and Zorkii,[34] using published data,[56] reported 14 short S...S distances, seven of which were much shorter than twice the VR of the S atom, and apparently appeared as a result of SI between the sulphur atoms.

In crystals formed by molecules or ions containing metal atoms, SI and hence SInterC involving these atoms may be produced (for example metal...metal, metal...oxygen, etc. SI). Thus the packing of the molecules in the crystals indicates the existence of the specific interactions Cu...O in copper salicylideneiminate, and Cu...Cu in copper salicylidenemethyliminate.[57] It is difficult to discuss this question, however, since there are no reliable VR values for metal atoms. For example, the published VR of the mercury atom vary from 1.5 Å [8,58] to 1.9 Å or more,[59,60] although the VR of this atom have apparently been more extensively discussed than those of any other metal.

The question of the production of SI in a structure is sometimes important for establishing the formula of a substance. For example, the use of VR detected an Sn...N specific interaction in the structure of the triphenyltin derivative of 4-thiopyridine,[61] and from this it was concluded that in the crystal the compound is an organotin derivative of pyridinethiol, and not thiopyridine, and that its structure is described by the formula



and not



If only normal intermolecular contacts are observed in a molecular crystal, the recognition of molecular agglomerates (dimers, chains, layers) of physical significance using only VR usually cannot be carried out completely correctly; in this case an energy calculation is required.[62] When SI with energies much greater than the energy of ordinary van der Waals atom–atom interactions are present, however, the agglomerates are usually distinguished quite clearly, giving a physically justified description of the structure. Thus the structure of triphenylmethyl bromide[63] consists of dimers formed by Br...Br specific interactions; the crystals contain two types of dimer, with Br...Br distances of 3.181 Å§ ($\Delta r = -0.76$ Å) and 3.466 Å ($\Delta r = -0.47$ Å). The structure of zinc 7-methylthio-8-mercaptoquinolinate[64] contains a short contact S...S 3.29 Å ($\Delta r = -0.39$ Å); these contacts join the molecules in centrosymmetric dimers.

Infinite chains −O...Sn−N−C−O...Sn−N−C−O... parallel to the long axis of the acicular crystal were detected in the structure of triphenyltin isocyanate;[65] here, the Sn...O distance is 2.81 Å ($\Delta r \lesssim -0.5$ Å). The chains can be distinguished even more clearly in the above-mentioned structure of the triphenyltin derivative of 4-thiopyridine with Sn...N 2.62 Å [61] ($\Delta r \lesssim 0.9$ Å).

The packing of the BF_3 molecules in the crystal structure of boron trifluoride at −145 °C is extremely interesting.[66] As a result of the coordinative unsaturation of the boron atom, the planar-trigonal coordination is brought up to trigonal bipyramidal by the fluorine atoms of neighbouring molecules. The BF_5 trigonal bipyramids share vertices to form infinite layers in the crystal. The intermolecular B...F distances are 2.663–2.704 Å, which is appreciably smaller than the sum of the VR of the atoms F (1.40 Å)[13] and B (2.13 Å).[16]

3. *A priori* calculation of close packing

The determination of an optimum structure by theoretical calculation generally involves the search for arrangements of the molecules with minimum energy. In the absence of specific interactions, the tendency towards close packing models with a certain accuracy the tendency towards an energy minimum, so that the minimisation of the energy can be replaced by the search for close-packed arrangements.

‡ In the work cited,[55] the numerical data were replaced by analogous quantities calculated from refined[11,13,14] VR values.

§ This SInterC is the shortest known C−Br...Br−C contact, and almost reaches the lower limit of 3.17 Å found by Zefirov.[51]

Using VR, molecules can be represented as three-dimensional bodies, and crystal structures as the packing of these bodies. As noted above, representations of this kind first appeared in works by Sidgwick,[5] Albrecht and Corey,[6] and Pauling;[7] for Kitaigorodskii[8] they provided the starting point for the development of the theory of the close packing of molecules in crystals. This theory established not only the existence of a three-dimensional system of molecules 'in contact' but also the production of intermolecular contacts according to the 'projection into cavity' principle. Zorkii,[67] who refined the formulation of the basic postulates of the theory of the close packing of molecules, pointed out that not all molecule–molecule contacts are made according to this principle, but that each structure necessarily contains 'projection into cavity' combinations which act as 'catches' fixing the structure. The existence of 'projection into cavity' contacts by itself, however, does not ensure a high packing density.

When molecules are represented as three-dimensional bodies, the question of the possibility of predicting crystal structures as close-packed arrangements of these bodies arises. In general, for three-dimensional packing, this problem is extremely complex. For the two-dimensional packing of planar molecules, it has been solved by the method of flow trajectories,[62,68,69] which makes it possible to find graphically the close-packed arrangement of figures whose outer contour is formed by intersecting circles.

Specific calculations have been carried out[62] for Ni dimethylglyoximate (Ni-DMG) and Cu salicylidenemethyliminate (Cu-SMI), in whose crystals a unique situation is produced: the planes of the molecules coincide exactly with the planes of the 'layers',¶ so that even a two-dimensional analysis can be used to discuss the possibility of an *a priori* prediction of the structure.

For both substances, a series of minima was obtained on the curves giving the dependence of the quantity $1/k$, where k is the packing density coefficient, on the parameters of the structure. In both cases the actual packing of the molecules was found to be very close to 'incompressible', that is it corresponds approximately to certain minima on the $1/k$ curves, and the packing density coefficient cannot be increased by small translations and rotations. At the same time, these structures were not the most compact; they did not correspond to the deepest minima on the $1/k$ curves. This result can be seen particularly clearly for Cu-SMI, for which it was possible to construct a packing with $k = 0.91$, which is appreciably more compact than the packing with $k = 0.87$, close to the actual packing. Thus when discussing compact molecular packing, it is necessary to be careful when using terms such as 'close-packed' and 'closest-packed'.[8,9]

If the packing of molecules in the crystals were not only incompressible but also close-packed, this would mean that the values of $1/k$ and the energy of the structure not only changed in the same sense but also were proportional to one another. Such complete mutual correspondence between a formal geometric characteristic and a thermodynamic function can hardly be expected. The arrangement of molecules in a crystal is certainly determined not only by the compactness of the packing but also by the relative orientation of the multiple moments.

At the same time, calculations have shown that there are not many examples (15–20) of closest packing corresponding to structures close to the real structures of Ni-DMG and Cu-SMI. This means that it is possible to construct a comparatively small number of hypothetical structures and to select from them the most probable structure by making use of additional methods, for example by examining the optimum arrangement of the multipoles or by using experimental data on the lattice parameters.† For structures in which the analysis of the packing cannot be reduced to a two-dimensional calculation, however, this method is naturally unrealistic.

Considerable progess in the *a priori* prediction of molecular (mainly organic) crystal structures has been achieved by using atom–atom potential functions (AAPF).[2,3,71] A remarkable feature is that VR have also played an important role in the development of organic crystal chemistry (after the theory of close packing). The VR are used to specify the equilibrium distances r_0, which appear in the parameters of the AAPF (see Fig. 1). Here, a common error is made: the sum of the VR found from the crystal structures is taken as the equilibrium distance, without taking account of the 'compression' of the molecules in the crystal. An empirical relationship between these quantities, $r_0/\Sigma VR \simeq 1.16$, has been pointed out.[72]

4. The conformations of molecules

In the mechanical model of a molecule, its conformation is regarded as resulting from the valence and non-valence interactions of the atoms.[73] The lengths of the covalent bonds, fixed in a fairly narrow range, and their directed character are the universal stereochemical factors which practically always are of decisive importance. The part played by non-valence interactions is particularly clearly revealed in three cases: 1) for non-rigid molecules, for example molecules in which rotation about single bonds is possible; 2) when there is steric hindrance; and 3) when there are intramolecular SI (they are often called attractive interactions, in contrast to steric hindrance, where forces of repulsion are most important).

In the last two cases, shortened intramolecular contacts (SIntraC) arise, and although the nature of the shortening is completely different in this case, its geometric consequences are analogous, and are revealed in the deviation of the bond lengths and more particularly the valence angles from the ideal values (the deformation of valence angles involves a much smaller expenditure of energy than the compression or elongation of covalent bonds). The use of VR makes it possible to detect SIntraC, and to follow their influence on the conformation of molecules or to conclude that effects of this kind are not observed.

¶ The characteristic features of the crystal structures of Ni-DMG and CU-SMI are due to the specific intermolecular metal–metal bonds perpendicular to the 'layer'. The word 'layer' is here put in inverted commas, since in contrast to the usual practice the word is used in the purely geometric sense. The strongest intermolecular interactions in these crystals lead to the formation of chains (perpendicular to the 'layers'), but it is in the 'layers' being considered that the tendency towards close packing should be detected.

† The two-dimensional approach (the method of flow trajectories) has also proved extremely effective for the *a priori* prediction of the packing of the chains of $PdCl_2$ and $BeCl_2$ [12,70] (in the crystal, these chains are joined to one another only by van der Waals interaction). The high symmetry and the relatively simple form of the chains obtained by modelling using VR made it possible to calculate successfully the most compact incompressible packing; the actual structure of $PdCl_2$ was found to be the third most compact, and the actual structure of $BeCl_2$ to be the most compact.

If relatively mobile fragments of a molecule are not joined by SI and there is no steric hindrance between them, free internal rotation often arises.[74] This has a significant influence on the physicochemical properties of substances, as discussed below (see section IV).

A number of examples of the distortion of valence angles as a result of the overlap of the van der Waals spheres of valence-non-bonded atoms can be considered. In the radical-ion salt $[C_{14}H_8S_4]^+ \cdot [PtBr_5S(CH_3)_2]^-$,[75] the octahedral configuration of the Pt atom is distorted by the mutual repulsion of the atoms of the methyl groups and Br. In the cobalt complex of Vitamin PP, that is nicotinamide (NA), with the composition $[Co(NA)_2(H_2O)_4](CH_3COO)_2.2H_2O$,[76] the inequality of the exocyclic angles at the C atom of the heterocyclic ring joined to the C atom of the amide group (119.5° and 122.0°) is due to the difference in the VR of the N and O atoms of the amide group, and also to the repulsion between an H atom of the heterocyclic ring on the one hand and an H atom of the amide group on the other ($\Delta r = -0.36$ Å).

The VR values have a characteristic influence on the conformations of polyethylene and substituted polyethylene polymers. The van der Waals diameter of the H atom is 2.31 Å, and the identity period along a completely *trans*-carbon chain is 2.54 Å, so that the polyethylene molecules can (and do) have a planar zigzag conformation. This period of the *trans*-carbon chain, however, does not ensure sufficient space for other atoms replacing H atoms, and more particularly for groups of atoms. For example, the van der Waals diameter of the F atom is 0.26 Å larger than the identity period, so that in polytetrafluoroethylene, a planar zigzag conformation cannot be produced. In this case the crowding is reduced by slight bending of the chain to give a slightly twisted spiral.[77] Isotactic stereoregular hydrocarbon polymers with the general formula $-(CH_2-CHR)_n-$ have similar spiral conformations,[78] since even for R = CH_3 (VR $\simeq$ 2.0 Å), crowding of the chain does not allow the production of a planar conformation.

In a number of cases, VR can be used to explain the difference in the values of the dihedral angles in related compounds. Thus the decrease by 21.4° in the dihedral angle between the planes of the benzene rings of the phenothiazine unit in the molecule of 1,3-dinitro-10-phenylphenothiazine[79] compared with the corresponding angle in non-substituted phenothiazine, equal to 153.3°, makes it possible to avoid steric hindrance in the molecule of the derivative, since the hydrogen atoms of the N-phenyl substitute 'touch' the atoms of the lateral rings of the phenothiazine unit in the *peri*-positions. The distances are H...H 2.33 Å and H...N 2.61 Å, which are very close to the values $2R_H$ = 2.31 Å and $2\sqrt{R_H R_N}$ = 2.64 Å.[11] With increase in the dihedral angle, these contacts would be shortened. The presence of a shortened N...O contact (2.719 Å) explains the folded conformation of the arabinofuranose molecule.[80]

The use of VR makes it possible not only to explain various details of the conformations of molecules but also in many cases to reach other conclusions about their structure, primarily the possibility or impossibility of conjugation, the reasons for breakdown of planarity, etc. Measurements of the dipole moments and the molecular Kerr constants have been used to study the conformation of a number of triarylphosphine oxides $(XC_6H_4)_3PO$ and the dependence of the orientation of the aryl rings relative to the phosphoryl group on the nature of the substituents.[81] From the spatial arrangement of the *d* orbitals of phosphorus, it might have been assumed that the most favourable conditions for the conjugation of these orbitals with the aryl rings are created when the angle φ is equal to zero or 90°; here, φ is the angle of rotation of the aryl rings about the P–C bonds, and the zero value corresponds to the position of the rings in which their planes pass through the C_3 symmetry axis. A graphical analysis of three-dimensional models using the VR given by Zefirov and Zorkii[11] showed, however, that the conformations with an angle of φ equal to zero or 90° are impossible, because of the overlap of the van der Waals spheres of the *ortho*-hydrogen atoms of the aryl rings. Steric hindrance is absent only for values of φ in the range 30–60°. The values of φ calculated from the anisotropy of the polarisability were as follows:

X	H	*p*-Cl	*p*-CH_3	*m*-Cl	*m*-CH_3
φ, °	55	65	60	49	52.

Assuming that the range of angles φ > 45° is more favourable than the range φ < 45°, the authors cited attributed the increase in φ when substituents are introduced into the *para*-position to the increase in the conjugation of the phosphoryl group with the aryl rings (for the *p*-chloro-derivative, slight steric hindrance predominates). In the opinion of the authors cited, the corresponding substituents in the *meta*-position lower the electrostatic repulsion, leading to a decrease in the angle φ.

A study[82] of the structure of dichlorobis(vinylbenzotriazole)-cobalt(II) showed that steric hindrance interferes with the π-conjugation of the vinyl groups with the benzotriazole rings: the terminal C atoms of the vinyl groups form extensively shortened (by 0.32 Å and 0.35 Å) contacts with the N atoms. Rotation of the free ends of the vinyl groups not towards the N atoms but in the opposite direction, however, would have led to even greater steric hindrance.

The rotation of the phenyl rings in the molecule of tricarbonyl-(1,4-diphenylbutadiene)iron $C_4H_4Ph_2Fe(CO)_3$ [83] is due to steric strain in the ligand (similar to that observed in biphenyl), as indicated by the shortening of the intramolecular non-valence distances C...C and C...H between the atoms of the phenyl rings and the butadiene system. In spite of the rotation of the phenyl groups relative to the plane of the butadiene system, however, these contractions remain fairly large: C...C 2.83–2.89 Å and C...H 2.55–2.65 Å. This strain in the ligand indicates[83] its tendency towards coplanarity and hence the presence of conjugation, which is apparently preserved despite the rotations indicated. The preservation of the planarity of a system in spite of a considerable number of contracted intramolecular contacts (compared with the sum of the VR), as for example in the cation of the salt $C_{18}H_{17}O_2^+ClO_4^-$,[84] ‡ indicates extensive delocalisation of the π-electrons.

Steric strains are sometimes reduced by their distribution among several neighbouring sites in a molecule. Thus the presence in the structure of di-(2,8-diphenylindolizin-3-yl)disulphide[85] of short intramolecular contacts S...C 3.330 Å and 3.342 Å (the sum of the VR of the S and C atoms is 3.55 Å) with the phenyl groups in positions 2 and 2′ leads to an increase in two triads of valence angles (on two triads of neighbouring carbon atoms) by 4–19° compared with the other exocyclic angles at these atoms.

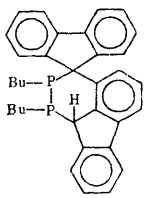
In some cases, VR have made it possible to detect an increase in the length of valence bonds as a result of steric hindrance. This effect is particularly important, since it is most directly related to the stability of chemical compounds.

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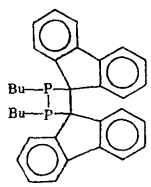
‡ In this structure the planarity of the system is preserved, despite a whole series of not only contracted but also shortened contacts, for example C...O 2.73 Å and 2.79 Å (Δr = –0.24 Å and –0.18 Å) and C...C 3.01 Å and 320 Å (Δr = –0.41 Å and –0.22 Å).

The presence of bulky substituents in the *ortho*-positions of a benzene ring influences the lengths of the bonds in the ring. Thus the presence of neighbouring phenyl and C_2F_5 groups in the molecule of 'fluoroterphenyl'[86] (shortest non-valence distances F...C 2.236 Å and 2.940 Å; length of the 'normal' van der Waals contact F...C 2.236 Å and 2.940 Å; length of the 'normal' van der Waals contact F...C 3.09 Å [13]) leads to an increase in the length of the corresponding C–C bond in the ring of 1.415 Å. Steric crowding is also responsible for the increase in the length of the C–C bond to 1.563 Å compared with 1.488–1.511 Å for the other three bonds of the type $C_{sp^2}-C_{sp^3}$ in the molecular of 2-*p*-anisidino-2,5-bis(trifluoromethyl)-3-perfluoroisobutenyl-5-monohydroperfluorohex-3-ene.[87] An even greater increase in the lengths of the bonds compared with the standard values is sometimes observed.

In the molecule of 1,2-di-t-butyl-1,2-diphosphorinane-(6,5,4-*l*,*m*)-fluorene-3-spiro-9′-fluorene[88]



extensively shortened intramolecular contacts are observed between the t-butyl groups and the phenyl rings of the fluorene fragments (C...C 3.286 Å, C...H 2.52 Å), and between the benzene rings of neighbouring fluorene fragments (C...C 3.298 Å), together with short P...C contacts (3.215 Å; sum of the VR of the P and C atoms 3.62 Å).[89] For this reason, all the P–C distances in the molecule are longer than the usual length of a single P–C(sp^3) bond, 1.85 Å;[89] here, the P–C bond length of 1.951 Å is one of the longest observed in structural studies of derivatives of three-coordinate phosphorus. Charnega and co-workers[88] also studied the molecule of fluorene-9-spiro-1-(3,4-di-t-butyl)-3,4-diphosphetane-2-spiro-9′-fluorene



which in addition to the contracted non-valence contact P...C of length 3.404 Å also contains contracts shorter than those in the previous case, C...C 3.297, 3.178, and 3.170 Å, and C...H 2.41 Å. In this molecule, the lengths of the P–C bonds in the ring are 1.904 Å and 1.911 Å, that is they are not elongated as extensively as in the previous molecule, but on the other hand, as a result of the repulsion of the fluorene groups, the bond between the spiro-carbon atoms is elongated considerably (to 1.626 Å). The central C–C bond in the molecule of 2,3-bis(trifluoromethyl)-2,3-bis(*p*-fluorophenyl)hexafluorobutane is elongated to an even greater extent (to 1.671 Å); in this case, in addition to the central bond, all the C–CF_3 bonds are also elongated (1.559–1.582 Å). In the opinion of the authors who studied this structure,[90] this increase in the length of the bonds in the 'central' unit of the molecule cannot be attributed entirely to steric hindrance.

Bonds of other types, for example P–S, may also be elongated by steric hindrance. In the molecule of 1,5-di(*p*-tolyl)-3,7-diphenyl-3,7-dithio-1,5-diaza-3,7-diphosphacyclo-octane,[91] the central fragment is the eight-membered $P_2N_2C_4$ ring. Both P atoms in the ring have the tetrahedral bond configuration characteristic of a four-coordinated phosphorus atom. The P–S bond lengths, 1.936 Å and 1.948 Å, are slightly longer than the standard value of 1.91 Å, due to the appreciable steric hindrance between the S atoms and the phenyl rings (the S...C distances are 3.11 Å, and the sum of the VR 3.55 Å).

In polynuclear coordination compounds, steric hindrance leads to an increase in the length of metal–metal bonds. Thus in the molecule of rhodium thioacetate $[Rh_2(CH_3COS)_4(CH_3CSOH)_2]$,[92] the Rh–Rh distance (2.55 Å) is much greater than the length of the Rh–Rh bond (2.3855 Å) in the analogous rhodium(II) acetate.[93] The VR of the sulphur atom (1.84 Å) is much larger than that of the oxygen atom (1.29 Å). As a result, the S...O distance in the thioacetate groups is 0.37 Å greater than the O...O distance in the acetate groups of the comparable complexes, and this, together with the electronic factor, leads to the difference in the Rh–Rh bond lengths indicated above.

Another example of the use of VR to analyse steric hindrance in molecules is given by Sadykov.[94] Here, an examination of shortened intramolecular non-valence contacts and increased valence angles gave the order of conformational strain in the molecules of matrine and its derivatives: allomatrine < sophoridine < matrine ≃ isosophoridine ≃ tetrahydroneosophoramine < *cis*-matrine.

A paper by Pasynskii and co-workers[95] gives an example of the use of VR to explain various characteristics of the conformations of molecules resulting from an attractive interaction. The use of VR in a study of the structure of $Cp_2Nb(CO)(\mu\text{-}CO)Mn(CO)_4$ detected an additional interaction between the clino-sandwich dicyclopentadienyl fragment and the pentacarbonylmanganese group. The bond between these structural fragments involves chiefly a direct Nb–Mn interaction; there is also an additional bond formed by a carbonyl group (μ-CO) acting as a bridge, and the corresponding distance Nb...C is 2.781 Å. This last value is much greater than the length of the Nb–C bond with the terminal CO group (2.06 Å), but is much shorter than the length of the van der Waals contact.

In conclusion it is useful to note that VR are very often used to reach important (and non-trivial) conclusions about the absence of any significant strain in a molecule being considered.

IV. The physicochemical properties of substances

1. The packing density coefficient. Properties determined by the effective volume, dimensions, and shape of molecules

In the absence of specific intermolecular interactions, the macroproperties of condensed phases are determined not by individual atom–atom contacts but by the integral characteristics of the molecular packing. One such characteristic, in particular, is the packing density coefficient (k). The values of k for the great majority of organic crystals lie in the range 0.65–0.77, and for substances with $k < 0.6$, a change to the vitreous state with decrease in temperature[9] or poor quality of the single crystals[96] are observed. Morphotropic jumps in homologous series are accompanied by an increase in the packing density. Substances with high packing density coefficients usually have high values of the density, viscosity, surface tension, heat of volatilisation, and melting point. An inverse dependence on k is shown by the compressibility of crystals with similar structure. Experiment has shown[9,97] that for benzene,

naphthalene, and anthracene, on going from the solid to the liquid phase, k decreases from values greater than 0.68 to 0.58, and the value in the gas does not exceed 0.5.§

Particularly compact arrangements result if the projections of a molecule fit closely into the cavities of neighbouring molecules. On the other hand, molecules with projections and cavities which do not correspond to one another are not suitable for the production of a compact arrangement. Loose molecular packing may also be due to other factors. For example, in substances containing a large number of fluorine atoms, on which appreciable negative charges are usually localised, a large number of intermolecular contacts F...F are unavoidably produced. In this case their length corresponds to the right-hand edge of the distribution curve (see section II). Thus in the crystals of perfluoro-3,3,6,6,4′,4′,4″,4″-octamethyl-1,2:4,5-dicyclobutenocyclohexa-1,4-diene ($C_{18}F_{28}$), the shortest F...F distances are 2.9–3.0 Å (VR of fluorine 1.40 Å [13]), and this explains[98] the unusually high volatility of this compound.

The analysis of intermolecular contacts is also used to interpret such properties as solubility. The low solubility of many molecular crystals is often attributed either to a high packing density or to the existence of SI. The existence of both is established using VR. Thus in the crystals of 3-carboxymethylthio-1,5-diphenylformazan,[99] the molecules are joined by H-bonds O–H...O of length 2.67 Å to form centrosymmetric dimers; between the planes of the dimers there are shortened contacts, apparently corresponding to stronger interactions, and this explains the low solubility. Similarly, the decrease in the solubility and the increase in the stability of the crystal structure of $Hg[C_9H_5(SCH_3)NS]_2$ and the isostructural zinc 7-methylthio-8-mercaptoquinolinate are attributed[59] to the existence of additional intermolecular interactions in their crystals. In fact, in this structure the molecules are connected to form dimers by a specific interaction S...S 3.35 Å (twice the VR of sulphur is 3.68 Å [15]).

A different situation is observed in the crystals of tetrakis(chloromethyl)adamantane.[100] Comparison of the intermolecular contacts with the corresponding sums of the VR showed that in this case the molecular packing is determined only by purely van der Waals forces, but at the same time it is highly compact, since the side groups occupy the spaces between the adamantane rings and ensure strong adhesion of the molecules. This adhesion, despite the absence of SI, explains the very low solubility and high melting point of the substance.

The shape of molecules, established using VR, is revealed particularly clearly in their ability to form solid solutions. Similarity in the shape and size of the replacing molecules and the molecules being replaced is a necessary and sufficient condition for the formation of substitutional solid solutions of organic compounds. Kitaigorodskii[101] proposed that the extent of this similarity be estimated using the geometric similarity coefficient ε, calculated as follows. The molecules, modelled using VR, must be superimposed to give the smallest extent of non-overlapping parts. If the overlap volume is v, and the volume of non-overlapping parts V, then $\varepsilon = 1 - V/v$. The molecules of A are soluble in a crystal of B if $\varepsilon > 0.8$ and there is no significant breakdown of the packing if a molecule of B is replaced in imagination by a molecule of A. An example is provided by the biphenyl–bipyridyl system. The molecules of these substances have very similar shapes, so that A dissolves in B, and B dissolves in A (a continuous series of solid solutions is not formed, however; the reason for this has been discussed [101]).

In addition to substitutional solid solutions, inter-block solid solutions also exist, where the dissolved molecules are localised on the surfaces of single-crystal blocks (in a mosaic crystal). Partial geometric correspondence between the molecules of the matrix and the impurity is sufficient for the formation of these solutions. Inter-block solid solutions have been used successfully[102] to produce new luminescent crystals. The matrices were naphthalene crystals, and the activating additives were anthranilic acid, methyl anthranilate, 1,4-diphenylbuta-1,3-diene, and 1,6-diphenylhexa-1,3,5-triene. Comparison of the projections of models of the additive molecules, constructed using VR, with the projection of a model of naphthalene showed that with decrease in the geometric similarity, the influence of the additives on the optical properties of napthalene decreases. Partial geometric correspondence is also a necessary condition for selecting a matrix for obtaining quasi-linear impurity spectra.[103]

To facilitate the calculation of the volume of molecules, Kitaigorodskii[8] proposed the use of the volume increments of the atoms (ΔV_i) and atomic groups. The value of ΔV_i for the atom being considered is calculated as the difference between the volume of the van der Waals sphere of this atom and the volumes of the spherical segments cut off on the given sphere by neighbouring valence-bonded atoms. The increments calculated in this way have been widely used[104–106] to calculate a whole series of important physical characteristics of polymers: density, volume expansion coefficient, vitrification temperature, temperature of the start of intensive thermal degradation, melting point, refractive index, coefficient of optical sensitivity to strain, bulk modulus of elasticity, etc. An important feature is that all these characteristics can be calculated even before synthesising the polymers, using only the chemical structure of the repeat unit. All the equations used in the calculations contain the volumes of the repeat units of the polymer $\sum_i \Delta V_i$. In particular, the density of an amorphous polymer is given approximately by the equation $d = km/\Sigma\Delta V_i$, where $k = 0.681$ (the average value of the packing density coefficient characteristic of polymers), and M the mass of the repeat unit. This calculation generally gives an accuracy of 0.001 g cm^{-3}. Similar calculations have been carried out by van Krevelen.[107]

This equation for the density shows that the value of d depends chiefly on the ratio of the volumes and mass of the atoms in the macromolecule. A unique element in this respect is fluorine, which has a small volume and a comparatively large atomic weight. Their ratio is much greater for fluorine than for any other monovalent substituent, and when fluorine is introduced into macromolecules it leads to a sharp increase in the density. A characteristic example is provided by Teflon (polytetrafluoroethylene).[108]

If the experimental value of the density is known, the packing density coefficient of the polymer can be calculated. This calculation made it possible to explain[109] the decrease in the softening temperature of copolymers of α,ω-dimethylacryloyloctaphenyltetrasilane with methyl methacrylate (MMA) with increase in the concentration of the former in the copolymers. At the same time the value of k decreases slightly, that is slight loosening of the molecular packing of the chains is observed, leading to a decrease in the softening temperature. Comparison of the calculated and experimental

§ Since there is no periodic structure in the liquid and the gas, the quantity being considered is the ratio of the total volume of the molecules modelled using VR to the total volume occupied by the given phase.

vitrification temperatures of network copolymers can sometimes be used to establish their structure. The structures of network copolymers based on MMA and diallyl *m*-carboranedicarboxylate were determined in this way.[110]

Another example of the successful use of VR to analyse the structure of condensed phases can be found in a paper by Abramzon and Goloudina,[111] who studied monolayers of surface-active substances at a liquid–gas interface. The authors cited tried to show that under certain conditions these layers have a crystalline structure. The property of the monolayer studied was the packing density, or more accurately the free volume corresponding to one molecule or hydrocarbon chain: $V_{free}^{m(c)} = V^{m(c)} - V_0^{m(c)}$, where $V^{m(c)}$ is the experimentally determined volume occupied by the molecule (or chain), and $V_0^{m(c)}$ the characteristic volume of the molecule (or chain), calculated using the VR of the H and C atoms and the methyl group given by Kitaigorodskii.[8] The authors cited analysed the contraction isotherms for condensed monolayers of aliphatic acids and higher alcohols by comparing the values of V_{free} for the packing of the hydrocarbon chains in the monolayer and the molecules of n-alkanes. The range of existence of solid layers was then determined, and it was shown that the phase transformations in the condensed layers of the substances examined are due to changes in the packing density of the hydrocarbon chains and are similar to the phase transformations in n-alkanes. This last feature provides evidence that the condensed monolayer has a crystal structure. A similar conclusion was reached in an electron diffraction study[112,113] of films of surface-active substances. Van der Waals radii have also been used to study the structure of aqueous solutions of a number of metal thiocyanates.[114]

Particle size plays an important role in transfer phenomena, and if the particles are polyatomic ions or molecules, VR can be used to study these phenomena. An example can be found in a paper by Lesnichaya,[115] where in a study of the electrical conductivity of molten guanidinium chloride $C(NH_2)_3Cl$, a comparison of the dimensions of the guanidinium ions obtained using VR with the dimensions of the chloride ion indicated that in this case an important part in ion transfer is played by mobile protons.

The use of VR (together with other parameters of the molecules) also makes it possible to explain and to estimate quantitatively the changes in the lattice parameters on intercalation, that is when molecules or ions are introduced into the spaces between the layer in layer single crystals. Thus on the intercalation of dichlorobenzene molecules into single crystals of $(C_{10}H_{21}NH_3)_2CdCl_4$, the distance between neighbouring layers increases by 3.65 Å, and for the intercalation of chloronaphthalene molecules the corresponding increase is 3.75 Å (the unit cell parameter *c* of the single crystal increases by 7.3 Å and 7.5 Å respectively).[116] These distances correlate well with the diameter of the chlorine atom (3.80 Å), particularly if account is taken of the possibility that chlorine atoms are situated in the cavities in the layers of the single crystal.¶ A similar change is observed in the parameter *c* of a single crystal of $(C_9H_{19}NH_3)_2PbI_4$ when hexane molecules are introduced (the distance between the layers increases by the thickness of the hexane molecule).[116] In insertion compounds of graphite with the composition $C_{24}K(C_6H_6)_x$, the benzene molecules are arranged at right angles to the graphite layers;[117] in this case, however, two limiting orientations are possible: one of the C–C bonds of the benzene ring may be arranged at right angles to or parallel to the layer. Comparison of the experimentally determined distance between the graphite layers and the dimensions of the benzene molecule, a model of which was constructed using VR, made it possible to give preference to the first version.

The system of VR makes it possible to describe clearly and fairly accurately the dimensions and shapes of the cavities and channels in various crystal structures, and also the dimensions and shapes of the molecules capable of entering these cavities and channels. This is related to questions of the permeability of molecular sieves and membranes, which are of primary importance for the understanding, prediction, and practical realisation of many chemical and biological processes (in particular, transport reactions).

Zeolite crystals contain more or less extensive cavities with windows formed by the connection of *n* silicon–oxygen tetrahedra. Taking the VR of oxygen as 1.4 Å, it is possible to calculate the dependence of the diameter of the window on *n*:[118]

n	4	5	6	8	10	12
D, Å	1.2	2.0	2.8	4.5	6.3	8.0.

The value of *D* determines the size of the atoms (ions) and molecules capable of entering the zeolite cavities.

A particularly fine geometric analysis is required in the study of inclusion compounds (clathrates). Thus the formation of these compounds is prevented not only when the dimensions of the species to be introduced are too large, but also when they are too small, since mobility of the particles in the cavities is energetically unfavourable. For example, α-dextrin (cyclohexaglucan), which contains channels with a diameter of ~6 Å, can accommodate molecules of benzene derivatives containing a smaller number of substituents which are not too large; β-dextrin (cyclopentaglucan), which contains channels with a diameter of 7.5 Å, forms inclusion compounds with naphthalene derivatives, but in γ-dextrin (cyclo-octaglucan), the cavities with diameter of 9–10 Å are too large for most ordinary organic substances, and they show little tendency to form inclusion compounds.[119] Similarly, the molecules of normal alkanes can be accommodated in the channels of urea, but cannot be held in the channels of thiourea, which have a larger cross-section and cannot be filled sufficiently fully by the thin chains of normal alkanes.[119]†

The use of VR is also extremely important in the study of the cavities in globular protein molecules. To study the mechanism of the penetration of the substrate to the active centres (haemo-groups) of the enzyme catalase, an attempt was made to find intramolecular cavities and channels in the enzyme.[121] The coordinates of the atoms were used to calculate the filling function of the space within the molecule. This function takes a constant value within a sphere of radius *R* round any of the atoms, and the value zero at other points (*R* is the sum of VR of the given atom and a water molecule). The van der Waals radii were assumed to have the following values: Cα 1.95, O 1.50, N 1.55, C 1.7, S 1.8, Fe 1.35, H_2O 1.4 Å. Several fairly large cavities were found; one of them consists of a bent channel which becomes broader when it meets the surface of the molecule, where its diameter reaches 8 Å; the other end of the channel extends towards the haeme group, and ends at a distance of 7 Å from it. This cavity apparently allows the substrate molecules to penetrate to the active centres of the enzyme.

¶ Dolzhenko and co-workers[116] considered only the thickness of the aromatic ring (3.42 Å), whereas the chlorine atoms obviously play a more important role.

† Later more detailed studies of the stability of compounds of urea with n-alkanes using VR have been published.[120]

Van der Waals radii are also used in the study of adsorption phenomena. Thus in a study of the mechanism of flotation using xanthates, the dimensions of the pentyl xanthate anion and the area (28 Å^2) occupied by this anion (arranged at right angles to the surface of the mineral particle) were found. These data established that at the initial concentrations of xanthate in the pulp usually employed in flotation, the quantity of sorbent attached to the surface of the mineral particles undergoing flotation in a number of cases is sufficient for the formation of 4–5 continuous monomolecular layers with close packing of the sorbent molecules.[122]

2. The rotation of atomic groups and molecules in crystals

The physicochemical properties of substances depend on the dynamics of the molecule, in particular on the rotation of individual groups or entire molecules. Crystals in which rotation of the molecules takes place differ considerably from ordinary crystals in a number of properties, primarily their plasticity.

The possibility that molecules rotate in a crystal can be estimated using VR. A classical example (one of the first) is provided by methane. Its crystals have a cubic face-centred cell with an edge of 6.35 Å. The shortest distance between the centres of the molecules is 4.49 Å, which is exactly equal to twice the quantity $r_{C-H} + R_H$ and indicates free rotation (without free rotation, the shortest distance between the centres of the molecules would be smaller, since according to the principle of close packing the van der Waals spheres of the H atoms should enter the cavities of neighbouring molecules). A similar calculation using VR was carried out[8] to prove the possibility of coordinated rotation of the molecules of methyl-, ethyl-, and propylmercury chlorides round one of the axes in the crystals. A particular case of the rotational-crystalline state is provided by the H-phase of n-alkanes, in which the molecules rotating about their long axis form a hexagonal arrangement corresponding to the close packing of cylinders.

Not only whole molecules, but also individual groups, may rotate in a crystal. Using the mean-statistical VR values of the atoms of fluorine and chlorine, Antipin and co-workers[123] found that in the structure of 2-trichlorophosphazo-2-trifluoromethylperfluoropropane $Cl_3P=N-C(CF_3)_3$ the trifluoromethyl groups mesh with one another like gears. This should restrict their movement mainly to twisting vibrations about the C–C bonds. An analysis of the non-valence contacts using VR made it possible to estimate the relative contributions of intramolecular and intermolecular forces to the barrier to the reorientation of these groups. The possibility of the rotation of other groups in molecules in crystals has been discussed, for example, in papers by Bokii and co-workers[124] and Gachegov and Soifer.[125]

In some systems, free rotation about a σ-bond is restricted by the approach of non-bonded substituents which would be impossible according to the corresponding VR values. In these cases the conformers are in fact isomers, and can be separated. Sometimes, steric hindrance to free rotation leads to the appearance of optical isomerism, and it becomes possible to separate the optical antipodes.

3. Organic conductors

In the case of isotropic metallic and ionic conductors, the conductivity is characterised by a fairly well studied three-dimensional band structure. Organic substances (charge-transfer complexes, radical-ion salts) usually show one-dimensional, or less frequently two-dimensional, conductivity, the interpretation of which requires an analysis of the molecular packing using VR. Various regular features of this conductivity, usually related to the stacked packing and the magnitude of the interplanar distance (the distance between the parallel planes of the molecules in contact), have been established.[126–128]

The one-dimensional character of the properties of most organic conductors is due to the characteristic features of their structures: the large planar molecules are arranged in stacks in such a way that the overlap of the electronic wavefunctions along the stacks is smaller by several powers of ten:[127] the conductivity electrons (π-electrons) move more readily along the stacks than between them.

The most familiar one-dimensional organic conductors are 7,7,8,8-tetracyanoquinodimethane (TCNQ) and its radical-ion salts, whose conductivity at room temperature reaches $10-10^2\ \Omega^{-1}\ cm^{-1}$. A characteristic feature of the crystal structures of these salts is the existence of a conducting system consisting of infinite stacks of TCNQ molecules, and the interplanar distance between the stacks is practically the same throughout the stack (3.22–3.26 Å) [126] and shorter than twice the VR of the carbon atom (3.42 Å). The increase in the interplanar distance TCNQ...TCNQ to 3.43 Å in the salt Pb^+TCNQ^- leads to a decrease in the conductivity to $10^{-2}\ \Omega^{-1}\ cm^{-1}$ (the other characteristics of the conducting quasi-one-dimensional structures are preserved).[129]

For other compounds with a quasi-one-dimensional electronic system, such as the radical-cation salts of tetrathiotetracene (TTT), tetraselenotetracene (TSeT), and tetrathiofulvalene (TTF), the condition for the production of high metallic conductivity is again the presence of conducting chains, that is regular radical-cation or radical-anion stacks with an interplanar distance which is the same throughout the stack and which is shorter than the ordinary van der Waals distance, and with neighbouring radicals superimposed in identical fashion. Important features for the stabilisation of the metallic state apparently include not only strong interactions within the conducting chain but also an additional strong interaction between the chains, as indicated by the contracted (compared with the sum of the corresponding VR) intermolecular contacts.[126]

Among the radical-cation salts of TTT and TSeT with a high conductivity ($10^3\ \Omega^{-1}\ cm^{-1}$ at room temperature), three complexes can be distinguished: $(TTT)_2I_3$, $(TSeT)_2Cl$, and $(TSeT)_2I$. In their crystal structures,[126] the shortest interplanar distances in the conducting stacks are 3.32, 3.37, and 3.40 Å respectively, whereas in the complexes of TTT these distances lie in the range 3.32–3.63 Å (twice the VR of sulphur is 3.68 Å), and in the TSeT complexes they lie in the range 3.37–3.53 Å (twice the VR of selenium is 4.00 Å [7]). Moreover, the structures of these three compounds contain extensively shortened intermolecular contacts: Se...Se 3.47 Å and 3.45 Å [in the stacks of $(TSeT)_2Cl$ and $(TSeT)_2I$ respectively] and S...S 3.38 Å [between the stacks in $(TTT)_2I_3$]. Similarly, in the regular radical-cation stacks of TTF in TTF–halogen complexes with different stoichiometry, the average interplanar distance (3.55 to 3.61 Å) is less than twice the VR of sulphur. The conductivity of almost all the complexes with non-stoichiometric compositions is $\sim 300-550\ \Omega^{-1}\ cm^{-1}$ at room temperature.[126]

The discovery of the superconductivity of tetramethyltetraselenofulvalene hexafluorophosphate $(TMTSF)_2PF_6$,[130] and then of a whole series of related compounds $(TMTSF)_2A$, where A = ClO_4, AsF_6, SbF_6, etc.,[131,132] with superconducting transition temperature $T_c \simeq 1$ K, provided the starting point for a new stage in the study of organic conductors. These studies demonstrate the importance of VR in another field of the study of conductivity in organic conductors.

In the crystals of $(TMTSF)_2A$ the planar molecules form stacks extending along the X axis. For almost all pairs of Se atoms from neighbouring molecules along the X axis (within the stacks) and along the Y axis (between the stacks), the Se...Se distances (~ 3.9 Å)

are shorter than twice the VR of selenium. This suggests that the electrons can move fairly freely in the *XY* plane. This is confirmed by measurements of the anisotropy of the conductivity and the upper critical value of the magnetic field intensity.[128] The anions A are situated in the cavities formed by the packing of the zigzag conducting TMTSF chains. This quasi-one-dimensional metallic system is stabilised by pressure. If the VR of fluorine is taken as 1.4 Å, the diameter of the AsF_6 ion is close to 6.4 Å, and if the VR of oxygen is taken as 1.29 Å, the diameter of the ClO_4 ion is about 5.6 Å. The effect of the replacement of the AsF_6 ion in the $(TMTSF)_2AsF_6$ structure by the smaller ClO_4 ion is analogous to that of pressure; this 'chemical compression' gave the first organic superconductor at atmospheric pressure, $(TMTSF)_2ClO_4$.[131] The 'chemical compression' taking place when AsF_6 is replaced by PF_6 leads to equalisation of the lengths of the Se...Se contacts along the *X* and *Y* axes;[133] as a result, the difference in conductivity in these two directions is decreased. In the $(TMTSF)_2ClO_4$ crystals, the ratio of the dimensions of the cavities and the ClO_4 anions occupying them determines the types of ordering of the anions with decrease in temperature, and this has a significant influence on the change in properties.[127]

Superconductivity was later detected in a family of compounds, (BEDT-TTF)A. The molecule of BEDT-TTF (bis-ethylenedithiolotetrafulvalene) has eight S atoms in the conjugation chain. The change from TMTSF to BEDT-TTF made it possible to create organic conductors with even lower anisotropy. The crystalline salts of this family show a wide range of physical properties; they are capable of behaving as dielectrics, organic metals with a metal–dielectric transition, organic metals stable over a wide temperature range, and superconductors. In the investigation of the reasons for the difference in the conductivity of these substances, particular attention is paid to the intermolecular contacts S...S (of length ~3.7 Å or less) in and between the stacks.[134–139].

In the study of the conductivity of radical-ion salts, intermolecular (interionic) contacts S...S have been examined in other crystals, in particular in the structure of the tetraethylammonium salts of bis(1,3-dithiol-2-thione-4,5-dithiolato)gold(III).[140] Structures whose molecules contain both thio- and seleno-fulvalene rings, including the structure of bis-ethylenedithiodimethyldithiadiselenafulvalene tri-iodide,[141] in addition to S...S contacts, contain intermolecular Se...Se and S...Se contacts, close to the sums of the corresponding VR. Cation–anion contacts close to or shorter than the sums of the corresponding VR have also been analysed, for example S...I contacts with a length of 3.85 Å or less.[142]

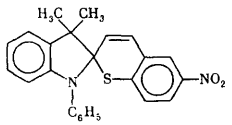
V. Chemical reactions

The reactivity of a substance is often influenced by steric factors. In this connection, steric effects of the following types will be examined: 1) steric hindrance leading to the elongation of covalent bonds or to the distortion of valence angles, 2) the shielding or complete blocking of the active centre of a molecule, 3) steric factors determining the angle of nucleophilic of electrophilic attack, and other forms of the influence of steric factors on chemical processes.

The elongation of a covalent bond as a result of crowding in the molecule facilitates the rupture of this bond in a chemical reaction. Thus in the molecule of fluorene-9-spiro-1-(3,4-di-t-butyl)-3,4-diphosphetane-2-spiro-9'-fluorene[88] (see section III), the increase in the length of the bond between the spiro-atoms to 1.626 Å leads to a considerable decrease in its strength, and when the compound is brought into solution, the cyclic structure breaks down with the rupture of this bond, as confirmed by the EPR spectra.[143]

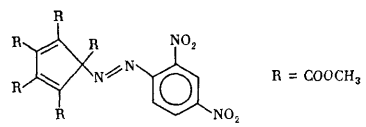
In the structure of 2,3-bis(trifluoromethyl)-2,3-bis(*p*-fluorophenyl)-hexafluorobutane,[90] the bonds in the central part of the molecule, in particular the central C–C bond (1.671 Å), are elongated considerably. Although in the opinion of the authors cited this cannot be due entirely to steric hindrance, the latter plays an important role, since the distances between the fluorine atoms of CF_3 groups in contact is 2.43–2.59 Å, which is much smaller than twice the VR of fluorine (2.80 Å). The authors cited[90] compared the properties of this compound with those of its analogue not containing F atoms (bicumyl), and noted the increased tendency of the fluoro-derivative to undergo dissociation to form radicals; for bicumyl this is not observed even at 200 °C. Similar easy rupture of an elongated single bond C–C 1.638 Å is also observed in the sterically crowded molecule of the thermally unstable 5,6-dibutyl-5,6-diphenyldecane (containing a number of short intramolecular contacts H...H of length 2.06–2.11 Å).[144]

Another example of a decrease in the strength of a bond elongated as a result of steric hindrance is provided by the molecule of 1'-phenyl-3',3'-dimethyl-6-nitrospiro(indoline-2,2'-[2H-1]-benzothiopyran).[145]



In this molecule, the length of the bond $C_{spiro}-S$ (1.866 Å) broken on photoexcitation is much greater than that of the corresponding bonds in six-membered heterocyclic compounds (1.80–1.83 Å [146]). The increase in length is due to the fact that the non-valence contact between the S atom of the benzothiopyran fragment and the C atom of one of the methyl groups of the indolene fragment (C...S 2.99 Å) according to Zefirov and Zorkii,[34] is 0.56 Å shorter than a normal S...C contact. In the opinion of the authors cited,[145] the photochemical properties of this molecule are explained by the vibrational mechanism of the rupture of the $C_{spiro}-S$ bond, which is elongated and weakened even in the ground state, and whose vibrations should be excited first.

Steric hindrance leading to the distortion of valence angles is also important, since under certain conditions it may initiate a chemical reaction at the corresponding site. An example is provided by an X-ray diffraction study[147] of 5-(2,4-dinitrophenylazo)-1,2,3,4,5-pentamethoxycarbonylcyclopentadiene.



As a result of steric hindrance (the shortest intramolecular distances C...N between valence-non-bonded atoms are 3.00 Å and 2.91 Å, whereas $2\sqrt{R_C R_N}$ = 3.20 Å), the valence angle CCN at the four-coordinate C atom is increased to 120°. The authors cited regard this feature as the factor responsible for the vigorous decomposition of the substance when heated to 100–110 °C. Moreover, the strain at this atom should facilitate the dissociation of the molecule in solution (at the C–N bond) to give an ion pair, whose recombination can take place at any of the carbon atoms of the cyclopentadiene ring.

The shielding of an active centre was dealt with by Bel'skii and co-workers,[148] who established by X-ray diffraction that in the molecule of 2,6-dicyano-3-trifluoromethyl-5-phenylaniline the distance between the H atom in position 4 of the aniline ring and one of the F atoms of a neighbouring trifluoromethyl group is 2.30 Å, and the distance from the H(4) atom to the nearest H atom of the phenyl substituent is 2.42 Å. Thus the hydrogen atom in position 4 is shielded by the trifluoromethyl and phenyl groups. As a result, electrophilic substitution cannot be carried out in position 4; in spite of numerous attempts, the authors cited could not obtain any 4-substituted aniline derivative of this type, whereas 3,5-dimethyl-2,6-dicyanoaniline readily undergoes electrophilic substitution.

It has been proposed[149] that the shielding of the metal atom in compounds MR_n can be estimated quantitatively using the solid angles, with vertices at the M atom, containing the inscribed R substituents, modelled by van der Waals spheres. The degree of shielding is characterised by the sum of these angles (the quantity Q), or more accurately by its approach to the total solid angle $4\pi \simeq 12.56$ rad. In the compounds $(R_3E)_2Hg$, where E = Si, Ge, Sn, the degree of shielding increases in the order R = Me, Ph, C_6F_5, which correlates with the decrease in reactivity, in particular the tendency to undergo oxidation. The fact that the value of Q is close to 4π indicates that the ligand environment of the metal is compact and hence stable. This explains, for example, the high thermal stability of $Ti(CH_2SiMe_3)_4$ and $V(CH_2SiMe_3)_4$, for which Q is 11.7 rad and 12.6 rad respectively, and the low stability of $TiMe_4$ (Q = 8.8 rad, decomposition temperature −40 °C) and $TiPh_4$ (Q = 9.3 rad, decomposition temperature −10 °C). It was suggested[149] that the value of Q can also be used to estimate the possible existence in principle of molecules of the type MR_n. A value in excess of 12.56 rad indicates steric strain, and a value which is much higher shows that the molecule cannot exist, for steric reasons. For example, in the hypothetical molecule $Ta(CH_2SiMe_3)_5$, the value of Q is 14.7 rad,[149] which is much greater than 4π. In fact, this compound has not yet been synthesised, despite repeated persistent attempts.[150] Another compound which has not been obtained is $(\pi\text{-Cp})_2CrCl_2$,[151] for which Q = 14.02 rad.

The VR of fluorine has been used[152] to illustrate that the ion NF_6^- cannot exist, in contrast to the PF_5 molecule and the PF_6^- ion. In the last two cases the overlap of the van der Waals spheres of the F atoms is extremely slight, whereas in the hypothetical NF_6^- ion it would be too great (summation of the covalent radii gives the distances P−F 1.74 Å and N−F 1.34 Å).

VR have also been used[153] for qualitative and quantitative estimates of the accessibility of the reaction centre in trityl ethers of sugars with the general formula Ph_3C-O-R, where R represents different sugars. A study of the spatial environment of the nucleophilic active centre—the ether oxygen atom—using Stuart–Briegleb models, based on X-ray diffraction data,[154,155] showed that in all the molecules studied the active centre is open only on the side of the vertex of the angle at the ether oxygen atom (the opposite side is completely shielded by one of the phenyl rings of the trityl group). Assuming that the glycosylating agent approaches the active centre chiefly along the bisector of the angle indicated on the side of its vertex, the authors cited[153] compared the degree of shielding of the ether oxygen atom in this direction in different molecules Ph_3C-O-R. For this purpose, three-dimensional models of the molecules were projected in the direction of the bisector of the $C-O-CPh_3$ angle. Analysis of the projections showed that in all cases the trityl group shields ~40% of the area of the active centre. In the molecule of 3-O-acetyl-4-O-trityl-1,2-O-[1-(*exo*-cyano)-ethylidene]-β-*L*-ramnopyranose, however, the active centre is shielded for the most part only by the trityl group (the shielding by H atoms is slight, and this shielding is easily removed by the conformational mobility). At the same time, in other molecules of this type, the active centre is more extensively shielded, both by the trityl group and by the O and C atoms of the sugar residue. To estimate quantitatively the degree of shielding of the active centre by the method proposed by Zakharov and co-workers,[149] three-dimensional models of the molecules were projected on a cylinder whose axis coincided with the bisector of the $C-O-CPh_3$ angle. According to the calculations, the above molecule allows practically free approach of the glycosylating agent to the active centre, whereas in the other cases, contact between the reagents is possible only for a definite relative orientation, so that the probability of effective collisions of the reacting molecules is lowered. This facilitates the competing reaction of isomerisation to give the glycosyl cation, which gives the 1,2-*cis*-bonded anomers.

An interesting example of the use of VR to analyse the chemical properties of molecules was described by Chernega and co-workers.[156] The sterically strained molecule of $(Me_3Si)_2N-P=N'-C_6H_2(t\text{-}Bu)_3$ (I) contains exclusively shortened contacts P...C (t-Bu) (3.26 Å and 3.37 Å; sum of the VR 3.60 Å [7]), and also a shortened Si...N contact (3.23 Å; sum of the VR 3.60 Å [7]). As a result the P=N′ (1.566 Å) is ~0.02 Å longer than the corresponding bonds P=N′ (1.544 Å and 1.545 Å) in the compounds $(Me_3Si)_2N-P=N'-SiMe_3$ (II) and $(Me_3Si, Me_3C)N-P=N'-CMe_3$ (III). Nevertheless, the reactivity of the first compound towards proton-donor reagents (alcohols, amines) is much lower than that of the last two compounds, and, moreover, compound I can be heated to 250 °C with no sign of dimerisation, in contrast to known λ^3-aminoiminophosphines, including compounds III and II, that is it has an exceptionally high thermal stability. This can be attributed to the fact that the atoms which elongate and weaken the P=N bond shield it at the same time. To investigate the magnitude of this shielding and how it changes when R′ = 2,4,6-$(t\text{-}Bu)_3C_6H_2$ is replaced by R″ = $SiMe_3$, the authors cited[156] used the program CRON [149] to calculate the projections of these substituents on a cylinder of unit radius with axis coinciding with the P=N′ bond. The calculations showed that the shielding of the P=N′ bond by R′ is ~1.5 times greater than that by R″. The greatest difference in the degree of shielding is observed in the region adjoining the P atom, that is on the side of the centre at which proton-donor reagent attack takes place. The sum Q of the solid angles with vertex at the P atom, calculated by the methods described,[149,157] is 4.4 rad for the substituent R′, and 2.4 rad for R″.

An analysis of the non-valence interatomic contacts has been used[158] to determine the angles of electrophilic and nucleophilic attack in reactions involving a divalent sulphur atom. The angular distribution of 169 S...X contacts smaller than the sum of the VR in organic, organometallic, and inorganic compounds of divalent sulphur (Y−S−Z) was studied. The authors cited suggested that when the attacking atom X is electrophilic, it approaches the S atom along a direction forming an angle of ~20° with the perpendicular to the Y−S−Z plane; if however, the X atom is nucleophilic, then with certain exceptions it approaches the S atom along the continuation of one of the valence bonds.

Another example of the influence of geometric characteristics, analysed using VR, on the chemical properties of molecules is provided by an X-ray structural study[159] of 2,10-diacetoxy-13-thia-bicyclo[7,3,1]-*cis*-tridec-5-ene sulphide and 2,9-dichloro-13-thia-bicyclo[8,2,1]-*cis*-tridec-5-ene sulphoxide (Fig. 3). In both molecules, the intramolecular distances between the S atom and the opposite C

atoms forming double bonds in the macrocyclic rings are only slightly greater than the value characteristic of the van der Waals contact C...S (3.55 Å), by 0.14 Å and 0.22 Å in the first case, and by 0.24 Å and 0.44 Å in the second. Moreover, in both cases the lone pairs of electrons of the S atoms are directed towards the C=C double bond. As a result of this conformation, the molecules being considered are 'prepared' for *trans*-annular transformations, which take place with these compounds under the influence of various reagents.

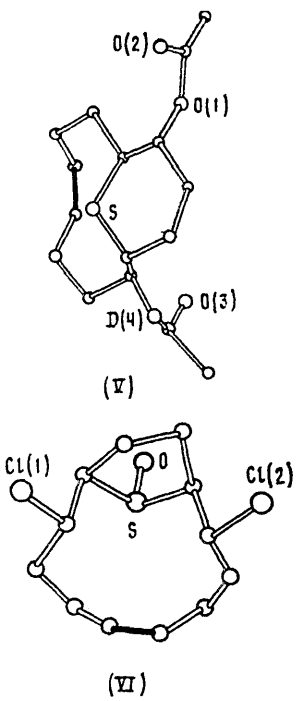
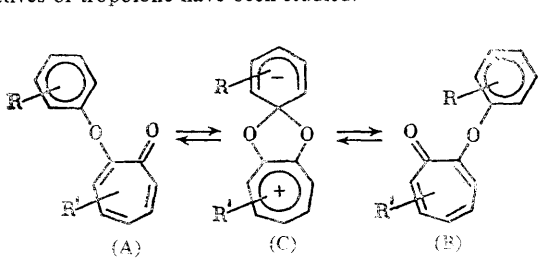


Figure 3. Conformations of the sulphide and sulphoxide molecules[159] (the double bonds are black).

In recent X-ray diffraction studies, the change in the geometry of molecules with similar compositions in an appropriately selected series of compounds is regarded as providing a model of the three-dimensional change in a molecule during a chemical reaction (mapping the course of chemical reactions). These studies have been described by Furmanova and Kompan.[160] The parameter used to follow the 'movement' of the system along the reaction path is often the distance between two atoms which initially are not bonded but which are joined by a valence bond as a result of the reaction.

In particular, the arylotropic rearrangements in O-nitroaryl derivatives of tropolone have been studied:[161,162]



By varying the number of positions of the substituents in the six- and seven-membered rings, a series of compounds was obtained, illustrating the course of the reaction (A) ⇄ (B), including the formation of the intermediate [the spiro-complex (C)]. In the molecule of S-(2′,4′,6′-trinitrophenyl)thiotropolone,[161] which has the *trans*-configuration, the torsional angle C(O)−C−S−C(Ar) (the angle φ) is 170°, the O...C(Ar) distance is greater than 4 Å, and the steric requirements for intramolecular *trans*-arylation are not satisfied. In O-(2′-nitro-4′-trifluoromethylsulphonylphenyl)-3,5,7-trimethyltropolone,[161] the aryl ring is rotated towards the carbonyl O atom (φ = 77°), and the distance O...C(Ar) 2.94 Å is practically equal to the normal van der Waals contact 2.97 Å, that is this structure is already prepared for the tautomeric transformation. The crystal of O-(2′,4′,6′-trinitrophenyl)tropolone,[161] contains two crystallographically independent molecules with similar geometric parameters; the O...C(Ar) distances in them (2.56 Å and 2.52 Å) are extensively shortened, indicating an attractive interaction between these atoms, that is the start of the formation of a new bond; the angle φ has the value 28.9° and 10.2° respectively. The O...C(Ar) distance is shortened to an even greater extent (to 2.45 Å) in the molecule of O-(2′,6′-dinitrophenyl)-3,5,7-trimethyltropolone,[162] where φ = 2°. The angle between the straight line O...C(Ar) and the plane of the aryl ring is 107.5°, and there is appreciable breakdown of the coplanarity of the covalent bonds at the C(Ar) atom, which is displaced from the plane of the atoms joined to it by 0.09 Å towards the carbonyl O atom. All this is characteristic of nucleophilic attack at an sp^2 carbon atom. Finally, the molecule of O-(2′,4′,6′-trinitrophenyl)-3,5,7-trimethyltropolone [162] has the structure of the spirocyclic intermediate of type (C) [in it, both O...C(Ar) distances are 1.47 Å].

Another example of the analysis of a reaction path using X-ray diffraction data is given by Sitkina and co-workers,[163] who regarded the molecule of 4-chlorophenylamino-3-acetoxy-1-methylindole-2-carboxaldehyde as a geometric model of the initial stage of the formation of the transition state of the inverse dark reaction of O → N transfer of the acyl group in O-acylated imines. In this molecule, the distance between the nucleophilic N atom and the migrating C atom is shortened to 3.02 Å (normal contact N...C 3.20 Å), indicating a weak attractive interaction.

Some of the above examples can be regarded as illustrating the influence of the three-dimensional structure of molecules, in particular the shielding of the reaction centres, on the rate of a chemical reaction.

The quantitative dependence of the reaction rate constant k on steric factors is given by the Taft equation[164] $\lg(k/k_0) = \Delta E_S(X)$, where $E_S(X)$ is a parameter characterising the steric effect of the substituent X. E_S is linearly dependent on the VR.[165] Subsequent studies[166] examined the parameter ν_X, the difference between the VR of the substituent X and the H atom: $\nu_X = R_X - R_H = R_X - 1.20$ Å. Using this parameter, the rate of esterification of substituted carboxylic acids by methanol or ethanol was described[167] by the modified Taft equation $\lg k = \psi\nu_X + h$, where ψ and h are empirical constants.

The changes in the reactivity of the chlorides of phosphoric and thiophosphoric acids $P(O)Cl_3$, $(RO)_nP(O)Cl_{3-n}$, and $(RO)_nP(S)Cl_{3-n}$, where n = 1, or 2, in the stepwise alcoholysis of aliphatic alcohols ROH (R = Me, Et, Pr, Iso-Pr, Bu, iso-But) have been analysed.[168] Assuming that the change in the reactivity of the reagents is due to steric factors, the authors cited took as a measure of the steric effects the values of ν given by Charton.[169] The relative reactivity in series with identical substituents in the two reagents is effectively described

by the equation $\lg k = av + b$, and in series with independent variation of the groups RO in the chlorides and R'O in the alcohols it is described by the equation

$$\lg k = av(\mathrm{OR}) + bv(\mathrm{OR}') + c,$$

where a, b, and c are constants.

The rate constants of bimolecular reactions have been calculated successfully[170] using the equation

$$k_{12} = \frac{(\sigma_1 + \sigma_2)^2}{4M^{1/2}} 0.1838 \cdot 10^{27} \exp(-B/T)T^{1/2}\left\{1 - \frac{C}{T}\left[1 + \frac{B}{T} - \frac{B^2}{T^2}\right]\right\},$$

where σ is the diameter of the species, calculated using the VR; M the reduced molecular mass $M_1M_2/(M_1 + M_2)$; and B and C are parameters calculated by the method described by Evdokimov.[170] The values of k were found (with a deviation of ~30% from the experimental values) over a wide temperature range up to 8000 K for the reactions

$$\mathrm{N} + \mathrm{O_2} = \mathrm{NO} + \mathrm{O},\ \mathrm{O} + \mathrm{O_3} = 2\mathrm{O_2},$$
$$\mathrm{Cl} + \mathrm{H_2} = \mathrm{HCl} + \mathrm{H},\ \mathrm{CO_2^{\cdot}} + \mathrm{N_2} = \mathrm{CO_2} + \mathrm{N_2^{\cdot}}$$

and other reactions. The results give correctly the temperature dependence of the rate constants.

VR are often used to determine the steric conditions under which solid-phase reactions of a particular type are possible. Thus in a study of the photo-isomerisation of naphthoquinone derivatives in the crystalline state[171] it was found that intramolecular transfer of the hydrogen atom takes place at distances comparable with the sum of the VR of the interacting atoms. According to data given by Shklover and co-workers,[172] solid-phase polymerisation in which a bond is formed between the atoms A and B of neighbouring molecules is possible if the distance R_{AB} does not exceed the quantity $(R_A + R_B + 0.5)$ Å.

An analysis of the intermolecular contacts in a hypothetical layer of molecules of 4,4'-diazidobiphenyl ($N_3-C_6H_4-C_6H_4-N_3$) (the structure of this layer was found by calculation using the method of flow trajectories and atom–atom potentials) made it possible to interpret the mechanism of the solid-phase polymerisation, accompanied by photolysis with the removal of two N_2 molecules and the formation of a nitrene radical.[173] The distance between the central N(1) atom of the azide group of one molecule and the N(2) atom joined to the aromatic ring of a neighbouring molecule is 3.0 Å, that is it is equal to the VR of the nitrogen atom. At the same time, the distance between N(2) and the nearest H atom of a neighbouring molecule (4.4 Å) is much greater than the length of the normal contact between these atoms (2.64 Å). This structure of the crystal should facilitate the reaction of the nitrene with the azide group of a neighbouring molecule and creates definite hindrance for the reaction with the removal of hydrogen; this is confirmed by analysis of the photolysis products.

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Van der Waals radii have been known for more than 50 years. They first appeared in crystal chemistry, and have subsequently found extensive application in the most varied branches of physical chemistry, in particular in the study of the mechanism of chemical reactions. The present review is the first attempt to present this topic systematically, and it naturally does not deal with all methods (and all conceivable methods) of using this simple and extremely effective concept. The material presented, however, demonstrates the variety of chemical applications of van der Waals radii.

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