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Van der Waals and Polar Intermolecular Contact Distances: Quantifying Supramolecular Synthons

Parthasarathy Ganguly*[b] and Gautam R. Desiraju*[a]

Abstract: Crystal structures are viewed as being determined by ranges and constraints on interatomic contact distances between neighboring molecules. These distances are considered to arise from environment-dependent atomic sizes, that is, larger sizes for isotropic, van der Waals type contacts and smaller sizes for more-polar, possibly ionic contacts. Although the idea of different, or anisotropic, radii for atoms is not new, we developed a method of obtaining atomic sizes that is based on a theoretical framework. Using different atomic sizes for the same atom in different environments, we were able to rationalize some structural observations and anomalies. For example, benzene with the *Pbca* structure may be described in terms of two types of C···H interactions: a longer contact largely of the van der Waals type, and a shorter, structure-determining type ($C^{\delta-}\cdots H^{\delta+}$), which we term "n-polar". Our approach is illustrated with three examples: 1) the equivalence in crystal packing of fluorobenzene, benzonitrile, pyridine *N*-oxide, and pyridine/HF 1:1 molecular complex, all of which take the not-so-common tetragonal $P4_12_12$ space group and are practically isomorphous; 2) the similarity of the *Pa3* acetylene and *Pbca* benzene crystal structures; and 3) the equivalence between an increase in pressure and an increase in the "n-polar" contacts in *Pbca* benzene; in other words, the equivalence between hydrostatic pressure and chemical pressure. In the context of crystal engineering, we describe a method whereby the topological information conveyed in a supramolecular synthon is recast in a more quantitative manner. A particular synthon, and in turn the crystal structure to which it leads, is viable within small ranges of distances of its constituent atoms, and these distances are determined by chemical factors.

Keywords: atomic radii · benzene · crystal engineering · supramolecular chemistry · van der Waals radii

Introduction

The packing of organic molecules in crystals is a subject that cannot be restricted to a particular domain of condensed-matter science.[1,2] The crystal structure of the simple and symmetrical molecule benzene poses, in itself, a considerable challenge, although it has been many years since it was determined experimentally.[3] The approach initiated by Kitaigorodskii treats organic molecules geometrically as spheres or oblate particles with characteristic radii and close-packs them in the densest-possible manner.[4–6] A second, more chemical approach uses the concept of supramolecular synthons, which are substructural units constituted by specific structure-directing interactions, and considers the crystal as a confluence of these synthons.[7,8] The geometrical approach relies on energy-landscape scenarios in discriminating between potential structures, whereas the synthon approach requires a real-space examination of molecular features to provide a packing direction.[9] These two views are not necessarily incompatible: an oblate molecule leads to directional packing, whereas the directionality inherent in a synthon requires close-packing in its final crystal structure.

The crystal structure of benzene can be understood with either the geometrical-close-packing approach or the chemical-synthon approach, depending on whether the characteristic geometrical features of the C–H···π contacts are taken as consequences or causes of the packing. Differences between the two approaches seem to surface when simple sub-

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[a] Prof. Dr. G. R. Desiraju
School of Chemistry, University of Hyderabad
Hyderabad 500 046 (India)
Fax: (+91) 40-23010567
E-mail: gautam_desiraju@yahoo.com

[b] Prof. P. Ganguly[+]
National Chemical Laboratory, Homi Bhabha Road
Pune 411 021 (India)
E-mail: patchug@gmail.com

[+] Present address:
Flat 8B, Mont Vert I
140/1A Pashan Sus Road
Pune 411 021 (India)

stituted benzenes are considered. Dunitz and Schweizer noted that different patterns of pair energies between molecules can still give the same crystal-structure type.[10] They stated that C–H···F interactions in fluorobenzene and C–H···H interactions in one of the hypothetical high-pressure forms of benzene seem to have the same "structure-directing ability". The subsequent implication of their study—that close-packing considerations rather than anisotropic interactions are important—does not, however, override well-documented observations that clearly relate the crystal structures of substituted benzenes to the nature of the substituents. Indeed, many such consistent observations, across a wide variety of compounds and functional groups, constitute state-of-the-art experimental crystal engineering today.[11]

At the heart of the problem of crystal-structure prediction (CSP) is the quantification of weak intermolecular interactions.[12] These are not negligible; they seem to have specific structural and functional roles in systems that range from the simplest molecules to complex biological systems.[13] The energy surface itself is flat with many local minima of similar energy; small errors in the atom potentials may completely change the energy landscape and give a wrong prediction.[14] The mathematical complexity in arriving at the global energy-minimized, density-optimized state is a reality: the process is lengthy and by no means reliable.[15–17]

An attractive, alternative way of considering this problem is to use information on interatomic distances.[18] We define interatomic distances in terms of core atomic sizes, r_{core} (which are much less than the corresponding Pauling atomic sizes[19]). Transferable atomic sizes, *CR*, which could be ionic or van der Waals sizes, contribute effectively to interatomic distances; for each interaction type P, the atomic size CR_{P} may be expressed as a simple linear function of r_{core} [Eq. (1)]:

$$CR_{\mathrm{P}} = C_{\mathrm{P}} r_{\mathrm{core}} + D_{\mathrm{P}} \tag{1}$$

in which C_{P} and D_{P} are atom-independent universal constants for the given bonding environment. From the formulation of Equation (1), one expects D_{P} to be the property of the atom (hydrogen) for which $r_{\mathrm{core}}=0$; in this way, any atomic property has an atom-specific contribution and a contribution from the fundamental atom, hydrogen. By its reductionist nature, Equation (1) is quite different from earlier empirical or theoretical approaches to atomic sizes. It demands, first, that the atomic size, r_{core}, is fixed for any given state of rest, even if C_{P} and D_{P} change with the nature of the bonding interaction for the given environment. This requires, in turn, a special universal condition on the chemical potential.[20–22]

Abstract in Hindi:

एक स्फटिक संरचना को निकटवर्ती अणुओं के मध्य अन्तरपरमाणविक स्पर्श दूरी के फैलावों व प्रतिबन्धनों द्वारा निर्धारित होते हुए देखा गया है | ये दूरियाँ वातावरण द्वारा प्रभावित परमाणु के आकारों से उत्पन्न समझी गई हैं | विशिष्ट रूप से ये समानुवर्ती, van der Waals प्रकार के स्पर्शों के लिए माप में लम्बी तथा एक अपेक्षाकृत अधिक ध्रुवीय, संभवतः आयनिक स्पर्शों के लिए माप में छोटी होती हैं | यद्यपि परमाणुओं के लिए भिन्न व असमानुवर्ती त्रिज्याओं का विचार नया नही है, हम जो इस परिपत्र में विकसित कर रहे है वह इन परमाणविक आकारों को प्राप्त करने की सैद्धान्तिक ढांचे पर आधारित एक विधि है | एक ही परमाणु के लिए भिन्न वातावरण मे भिन्न आकार मापों के प्रयोग से हम संरचना संबंद्धी निष्कर्षों और असंगतियों को कुछ हद तक युक्तियुक्त करने में सक्षम रहे हैं | उदाहरण के लिए, *Pbca* benzene संरचना का वर्णन संभवत: दो प्रकार की C···H संकर्षणों के आधार पर किया जा सकता है : एक लम्बी दूरी का स्पर्श जो की अधिक रूप से van der Waals प्रकार का है तथा एक कम दूरी का, संरचना निर्धारित करने वाला, $C^{\delta-}\cdots H^{\delta+}$ स्पर्श, जिसे हमने "n-polar" स्पर्श कहा है | हमारा दृष्टिकोण तीन उदाहरणों से प्रतिपादित होता है : (१) fluorobenzene, benzonitrile, pyridine *N*-oxide तथा pyridine:HF के १:१ आणविक संकर के स्फटिकों के संकुलन में समानता, ये सभी कम सामान्य tetragonal $P4_12_12$ space group धारण करते हैं और व्यावहारिक दृष्टि से सरूप हैं; (२) *Pa*3 acetylene तथा *Pbca* benzene के स्फटिक संरचनाओं की समानता ; (३) *Pbca* benzene संरचना में "n-polar" स्पर्श और दाब में वृद्धि के मध्य एकरूपता | अन्य शब्दों में द्रवस्थैतिक दाब तथा रसायनिक दाब के मध्य एकरूपता | स्फटिक अभियांत्रिकी के संदर्भ में हम एक ऐसी पद्धति का वर्णन कर रहे हैं जिससे एक supramolecular synthon द्वारा सम्प्रेषित स्थलाकृति सम्बन्धी (topological) सूचना को परिमाणात्मक ढंग से पुन: ढाला गया है | अमुक synthon, और स्फटिक संरचना जिसे वह निदेशित करता है, संघटक अणुओं के मध्य अल्प सीमा की दूरियों तक सार्थक है, और ये दूरियाँ रसायनिक कारकों द्वारा निर्धारित होती हैं |

We envisage crystallization as a process in which molecules undergo translational, rotational, and conformational changes as they approach their energy-minimized state of rest. Molecules that satisfy these local contact-distance constraints "stick together" to form a stable cluster with local (point group) symmetry. These clusters then grow and connect and eventually become viable when there is a space-group symmetry onto which they can be mapped. The problem of the crystallization of molecules may then be looked upon as one that involves finding the set of orientation of molecules and synthons that gives the intermolecular contacts allowed by Equation (1).

As a consequence of the Sanderson principle of electronegativity equalization,[23] it is well-known that the chemical potential is constant for all components of a system at rest. We may exploit this condition for a universal chemical potential, μ_{univ}, for an energy-minimized state of rest of the molecule in a crystal. It has been further shown from the density-functional definition of electronegativity that the chemical potential is required to be zero for an energy-minimized, density-optimized state.[22,24] This $\mu=0$ condition is distinguished from the $\mu \neq 0$ condition, which prevails in non-equilibrium situations.[20–22,25,26] Because of the constant chemical potential within the molecule, the atoms in a molecule at rest are also required to have $\mu=0$ as in a free atom.[22] It is assumed that Equation (1) scales the atomic sizes, r_{core}, characteristic of the free atom to the size CR_{P} such that the $\mu=0$ condition is maintained in the molecule. The advantage of such a $\mu=0$ state for a molecule, which occurs when attractive and repulsive forces cancel each other, was used effectively to obtain 1,3-nonbonded distances in gas-phase MX_n compounds.[27,28] From Equation (1), it is clear that the $\mu=0$ state may be reached in different ways (effectively, P) represented by different atomic sizes, CR_{P}. We believe that these sizes hold the key to understanding nonbonded intermolecular distances (packing) in crystals, because they represent different physicochemical situations possible for a given interatomic contact.

The simplifying feature in the $\mu = 0$ condition is that one needs only the core size of an atom, r_{core}, that satisfies this condition.[27–29] It is then especially helpful if these core sizes are obtained from a classical stationary point (see below). A molecule is then assembled atom by atom and bond by bond by using r_{core} as well as atomic sizes CR [Eq. (1)], consistent with the $\mu = 0$ condition. Complex quantum-chemical computations, which are necessary to find the balance between positive (repulsion, kinetic energy) and negative (attraction) multipart (internal energy, the entropy term, electrostatic, polarization and van der Waals interactions) contributions to the energy from different charged particles, are not required. The Gordian knot[30] of energy-landscape scenarios may be cut without substantial loss of quantitative rigor.

Results and Discussion

Atomic Sizes, Interatomic Distances, and the Nature of Intermolecular Interactions

Of crucial importance in the context of identifying synthon directors in crystals of organic molecules is a method that allows the distinction between strong and preferably anisotropic, structure-directing distances against weaker contacts of variable-to-poor directionality. Such information would be dependent on the way C_P and D_P in Equation (1) vary with changes in the nature of the intermolecular contacts (e.g., polar or neutral). The important parameter in Equation (1) is, therefore, CR_P and not the core size, r_{core}. The heart of our approach is to differentiate between "neutral" and "n-polar" intermolecular contacts and to show that synthon directors normally have "n-polar" contacts.

Core atomic sizes, r_{nZ}, for first-row elements from a classical stationary point have been obtained with a new approach (Appendix 1).[31] Such sizes are consistent with a $\mu = 0$ condition for chemical potential and satisfies the transferability condition.[21] These sizes are close to the theoretically calculated Zunger–Cohen valence-s-electron orbital radii,[19] r_s, as well as the empirical sizes, r_G.[21] The core sizes r_G were previously used to obtain 1,2- and 1,3-intramolecular distances.[20–22,27–29] The next challenge is to obtain insight into nonbonded intermolecular distances, in other words, coefficients C_P and D_P in Equation (1), for such contacts. Supramolecular synthons are qualitatively defined in terms of the connectivity of nonbonded atoms. The present work attempts to quantify synthons in terms of nonbonded distances, as described above. In effect, this amounts to obtaining intermolecular distance descriptors based on simple and chemically sensible transferable atomic sizes.

In earlier efforts,[20–22,29] charge-transfer sizes, CR^+(M) and CR^-(X), associated with positive and negative charges, respectively, were used (Appendix 2) to describe the chemical-bond distance, d_{MX}.[21] Accordingly, we used the charge-transfer sizes of atoms, which are given by Equation (2):

$$CR^{\pm} = \varepsilon_{\text{eff}}(C_1{}^{\pm} r_{\text{core}} + D_1{}^{\pm}) \tag{2a}$$

Here ε_{eff} (≈ 1.0) is an environment-dependent dielectric constant, and $C^{\pm}$ and $D^{\pm}$ are universal constants for charge-transfer bonds (Appendix 2). Both CR^+ and CR^- are sizes that are required for the (free-atom-like) $\mu = 0$ state in which attractive and repulsive contributions cancel. Using arguments related to the probability of charge transfer with conservation of spin near the insulator–metal transition, we propose that $C_1{}^+ = \pi^{2/3} \approx 2.145$ and $C_1{}^- = \pi^{4/3}/2 \approx 2.300$ when $r_{\text{core}} = r_{nZ}$ (Appendix 1, Table 3), as opposed to $C_1{}^+ = 2.13$ and $C_1{}^- = 2.37$ obtained empirically for $r_{\text{core}} = r_G$ (Appendix 2, [Eq. (A10a)]).[32] The values of D^+ ($= -2a_H/3$) and D^- ($= 2a_H$) are discussed in Appendix 2. We find these empirical values sufficient for the present. Of particular interest here are the observed nonbonded intermolecular interatomic C···C, C···X, and X···X distances in the (C_5YH_5)–X compounds (Y = C, X = H, F, CN; Y = N, X = O, HF) derived from benzene (Y = C) or pyridine (Y = N) and the way in which these distances may be related to the atomic sizes CR. For values of r_{nZ} for the elements of interest, see Appendix 1, Table 3.

Van der Waals and "n-Polar" Radii

Van der Waals (vdW) interactions underpin all intermolecular contacts in organic crystals. Typically, intermolecular contact distances are estimated as sums of vdW radii, r_{vdW},[33] such as those given by the Bondi values.The drawback in the above real-space strategy is that empirical distances such as Bondi radii are fixed and environment-independent: this does not provide the flexibility needed to account for observed variations in intermolecular distances for a given pair of nonbonded atoms. What constitutes a vdW contact may be quite different from that implied by Bondi sizes.

Van der Waals forces originate from London dispersion forces.[34] The creation at some instant of an instantaneous dipole due to excitation increases charge separation (usually considered to be a small quantity, $|\delta| < 1$) and causes an attractive interaction between temporarily induced dipoles in another atom. In such London forces, the charge or electron density is obtained probabilistically. The instantaneous or rapidly fluctuating charges involved in induced-dipole–induced-dipole interaction are different from more-static charges. For the purpose of obtaining intermolecular distances, one associates the faster fluctuation associated with vdW forces with a characteristic nonpolar or vdW size, r_{vdW}.

An additional useful perception is the idea of a characteristic "n-polar" (n = negative) size associated with the more-static charge.[35] We identify this "n-polar" size with the size CR^- [Eq. (2a)] of an atom expressed in terms of r_{nZ} (Appendix 1) by Equations (2b) and (2c):

$$CR^- = 2.300 r_{nZ} + 2a_H \tag{2b}$$

$$CR^- = 2.300 r_{nZ} + 105.8 \text{ (in pm)} \tag{2c}$$

Here 105.8 in pm is $2a_H$, the Bohr radius of the hydrogen atom (Appendix 2, Equations (A7)–(A10)). The assumed values of C_1^+ ($=\pi^{2/3}\approx 2.144$) and C_1^- ($=\pi^{4/3}/2\approx 2.300$) are close to those in Equation (A10b). The actual values of $C_1^{\pm}$ were obtained from geometrical arguments on the basis of the probability of spin conservation. These arguments are not included herein, and the values of $C_1^{\pm}$ are used in an empirical sense to establish the viability of using "n-polar" and vdW sizes as an aide for synthon identification.

In general, for the intermolecular interatomic distances between two atoms X and Y, $d_{XX'}$, it is sufficient to use [Eq. (3)] (from [Eq. (2c)]):

$$d_{XX'} = \varepsilon_{XX'} C^- \{K_X r_{nZ}(X) + K_{X'} r_{nZ}(Y)\} \qquad (3)$$

The term $\varepsilon_{XX'}$ (≈ 1) may be viewed as an effective dielectric constant for the nonbonded intermolecular distances, which takes into account fine changes in the environment due to changes in molecular size or electric polarizability. Importantly, all the sizes described in Equations (2) and (3) are to be used only in the context of intermolecular nonbonded distances for a $\mu = 0$ condition.[20–22,27,28]

The X···X′ distance in Equation (3) when $K_{XY} = K_{\text{“polar”}} = 1$ is given by the sum of the "n-polar" sizes, CR^- [Eq. (2c)], associated with a negative charge. When $K_{XY} = K_{vdW} \approx 1.125$ (see below), the sizes correspond to the "vdW" sizes, r_{vdW}. When the attractive force associated with the static charge is stronger than the instantaneous dispersion interactions, one expects CR^- to be less than r_{vdW} ($K_{\text{“polar”}} < K_{vdW}$). The possible existence of two different values of K in Equation (3) was found in a study of 1,3-nonbonded distances in X–M–X linkages of gas-phase MX_n compounds ($n \leq 4$).[27,28] In that study, it was observed that there are two sets of 1,3-distances that could be explained in terms of $K = 1$ and 1.08 (with $r_{core} = r_G$). The value $K = 1.08$ was associated with Bondi or vdW sizes. Clear evidence of such variations has also been observed consistently by structural chemists; for example, there are two well-demarcated populations for Br···N≡C and Cl···N≡C contact distances in crystals that correspond to longer van der Waals separations, and polar $Br^{\delta+}\cdots N^{\delta-}$ and $Cl^{\delta+}\cdots N^{\delta-}$ contacts corresponding to shorter separations.[36]

The value of K_{vdW} may be obtained on empirical grounds.[31] Van der Waals forces determine the binding between rare-gas atoms in the solid state. Because of this, the nearest-neighbor interatomic spacing, $d_{XX}(RG)$, in rare-gas crystals may be assumed to be $2r_{vdW}$. From fits of Equation (3) to $d_{XX}(RG)$, we find as a first approximation that $K_{vdW} = 1.125$. Thus, we may write [Eq. (4)]:

$$r_{vdW} = K_{vdW} CR^-(X) \approx 1.125(2.30 r_{core}(X) + 2a_H) \qquad (4)$$

in which $K_{vdW} = 1.125$. We plotted in Figure 1 the calculated values of CR^- [Eq (2b)] and r_{vdW} [Eq. (4)] versus the empirical Bondi radii obtained from nearest-neighbor nonbonded intermolecular distances, which are regarded as a reliable benchmark for vdW sizes.

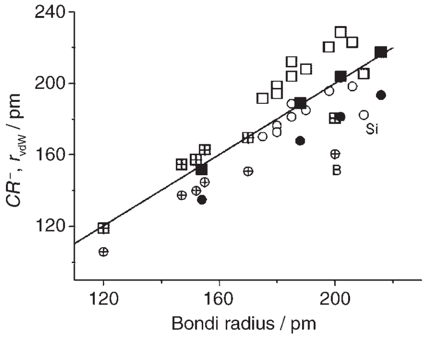

Figure 1. Plot of calculated "n-polar" size CR^- [Eq. (2c)] (circles), and van der Waals size r_{vdW} [Eq. (4)] (squares), versus the Bondi size.[33] Filled symbols = rare-gas elements, symbols with cross inset = first-row insulator elements (B, C, N, O, F), open symbols = other elements. The diagonal line represents CR^- or r_{vdW} = Bondi size. B and Si show large deviations.

One may now examine the alternative interpretations of a crystal structure in which the intermolecular X···X′ distances are represented either by vdW sizes ($K_{XX'} = K_{vdW}$) or by "n-polar" ($K_{XX'} = K_{\text{“polar”}} = 1$) sizes in [Eq. (3)]. The distinction between "n-polar" and vdW nonbonded intermolecular contacts is a new tool that we exploit to understand the subtle differences in the crystal structures of benzene and some monosubstituted benzenes. We were able to analyze effectively the directionality of the supramolecular synthons and discriminate between alternative crystal structures for a given molecule. Some conclusions from Figure 1 are:

1) The distinguishing feature of crystals of first-row insulator elements (C, N, O, F) in organic compounds is that the intermolecular distances at ambient pressures and temperatures correspond predominantly to longer vdW contacts. This justifies the notion that organic compounds are soft materials.
2) A decrease in volume on applying external pressure could result in some intermolecular contacts becoming "n-polar" as $CR^- < r_{vdW}$.
3) There could also be changes from vdW contacts to "n-polar" contacts as a function of internal, namely, chemical, pressure. The substitution of the H atoms of the benzene molecule by other (necessarily larger) atoms would cause an expansion of the lattice. This could result in internal pressure as intermolecular contacts that involve other H atoms would resist such an expansion. One would expect this internal pressure to be localized around the central atom.
4) The only constraint on atomic sizes is that they satisfy the $\mu = 0$ condition. This may be achieved in different ways for different contacts in different directions for the same atom. It is not necessary, in our model, to associate an atom with the same size (say, either r_{vdW} or CR^-) for all intermolecular contacts with it, and this is borne out by common experience. For example, the occurrence of longer head-on collinear C–Cl···Cl–C linkages (type I) in

halogenated compounds as opposed to shorter side-on contacts (type II)[37] is a neat manifestation of these effects.

5) The above method of distinguishing between "n-polar" and "neutral" vdW contacts is general and may eventually be applied to all atoms once a proper core atomic size is obtained for each atom. This is already under consideration by us. For the present, we considered mainly atoms of second-row elements as the synthon concept has so far been mainly applied to the crystal engineering of organic molecules.

Benzene and Substituted Benzenes

The understanding of the crystal packing of molecular solids requires an elucidation of criteria that control different interactions and the conditions in which they might prevail in the final crystal structure. We described the pattern-forming characteristics of functional groups, or the hierarchy of supramolecular synthons, in terms of both the so-called strong and weak interactions.[8,38] An area-filling tiling of a two-dimensional surface by hexagons is one of the simplest examples of the tessellation of a plane. Such a tessellated 2D lattice is used as a projection of a 3D packing of spheres when spheres (in contact) are located at each point of the lattice.

Benzene does not form a planar 2D honeycomb lattice whereby the H atoms are arranged in a triangular lattice in which the orientations of all the benzene rings are identical (Figure 2). Such a structure is characterized by the H_3 synthon (similar to, say, an I_3 synthon in iodobenzenes[39]), which is a triangular supramolecular motif. The actual structure of benzene at ambient and higher pressures is more complex and is distinct from the structure in Figure 2.[3,40–43] What are the features that bring about such a change? It is apparent that stereoelectronic features associated with the size of atoms are important. An examination of intermolecular distances in terms of r_{vdW} and CR^- gives a wealth of quantitative insight not noted before.

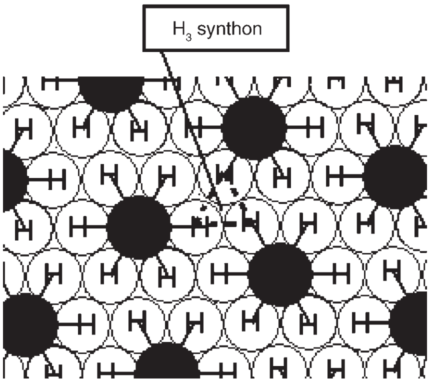

Figure 2. Ideal tessellation of a plane with hexagonal benzene tiles. The black circles are benzene rings. The H_3 synthon is indicated.

On the Structure of Benzene

As stated above, the experimental *Pbca* structure of benzene (phase I) is different from the symmetrical tessellated hexagonal structure in Figure 2 with H_3 synthons. As the layer structure in itself seems to be unproblematic, the difficulty in its adoption would appear to arise in the stacking of layers. The intermolecular C···C contacts in *Pbca* benzene are much longer than $2r_{vdW}(C) = 340$ pm; the shortest C···C contact is > 370 pm $> 2r_{vdW}(C_{arom})$. The absence of C···C vdW contacts is surprising in a supposedly geometry-controlled structure; in such a structure, the probability of C···C vdW contacts should be high because the C atom is larger than the H atom. The propensity for forming C···C contacts is expressed in the traditional dictum that "like prefers like" for vdW forces.[44] Indeed, such structures, which emphasize C···C (and not H···H) contacts, are seen in some higher condensed aromatic hydrocarbons. Dunitz and Gavezzotti also found that the best pairwise interactions in benzene occur when the two neighboring rings are parallel with a center-of-mass separation of 341 pm.[6] Despite this, C···H interactions are preferred in crystalline *Pbca* benzene. It would seem then that space-filling rather than better interactions is the more important constraint ("nature abhors a vacuum"), and this concern is valid at the molecular level, now expressed as Casimir forces (quantum vacuum).[45]

As $r_{vdW}(C) > r_{vdW}(N) > r_{vdW}(O) > r_{vdW}(F) > r_{vdW}(H)$, the formation of a layered structure with π···π stacking in C_6X_6 compounds with X = N, O, F, H would necessarily ignore X···C and X···X contacts. To the extent that these latter contacts are significant, the benzene molecules must reorient themselves. Furthermore, such reorientation is expected to be most prominent when the size difference between C and X is the greatest, namely, when X = H, that is, in benzene itself. One of the more frequently discussed contact patterns in benzene is the so-called C–H···π geometry in which one H atom is approximately equidistant from the six C atoms of a neighboring molecule (dotted lines in Figure 3).[46] However, the C–H···C_π distance of 305 pm is much larger than the value expected (290 pm) for a vdW contact (Table 1). On the other hand, C···H contacts in benzene that are shorter than the vdW value do exist, with distances of about 285 pm ($r_{vdW}(H) + r_{vdW}(C) = 289$ pm; Table 1) and nearly parallel to the *b* axis (Figure 2). Accordingly, two types of C–H···C contacts are present: a longer one, which may be classified as a weak vdW interaction, and a shorter one, which has more "n-polar" character and is structure-determining.

In acetylene, in which the notion of a directed C–H···π interaction might find more favor, the relevant distance is greater than 309 pm. To reconcile this with the idea of a structure-directing C–H···π synthon, one would have to associate a larger "vdW" size with a C atom that has π electrons or is part of an aromatic ring, $r_{vdW}(C_\pi) = 180$–185 pm. It could also be that there is considerable thermal motion (or wobbling; see below) of the atoms so that the intermo-

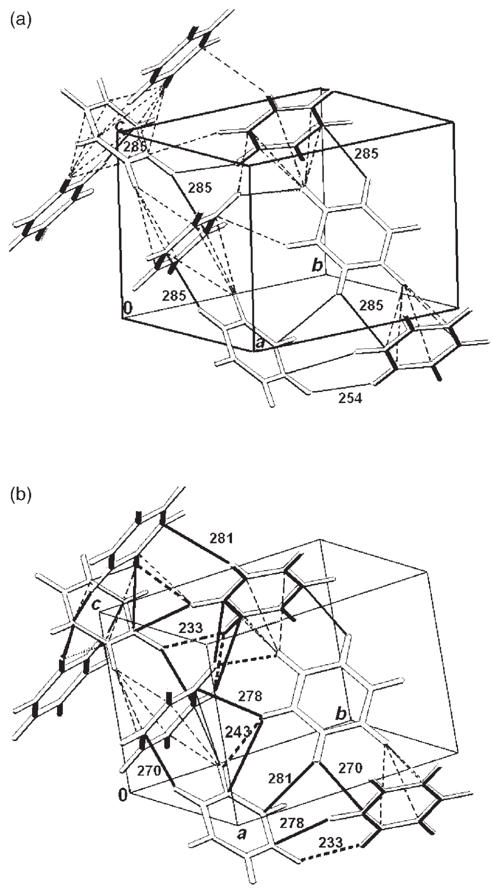

Figure 3. a) Structure of benzene (*Pbca*) at ambient temperature and pressure. The dotted lines indicate X···X′ contacts (mainly 90° C–H···π contacts of 307–310 pm) longer than the sum of the vdW radii ($r_{vdW}(X)+r_{vdW}(X')$). The bold lines indicate distances (285 pm) less than $r_{vdW}(X)+r_{vdW}(X')$. b) Hypothetical *Pbca* structure of benzene at 1.1 GPa in which the atomic coordinates at 1 atm have been changed but the intramolecular distances are retained. The bold and dotted lines have the same meaning as in a). The bold dashed lines indicate H···H contacts of 235–245 pm ($2r_{vdW}(H)=238$ pm). Distances are in pm.

Table 1. "N-polar" and van der Waals radii of some elements.

Atom	r_{nZ} [a.u.]	CR^- [pm] $n_v^{[a]}=0$	 $n_v^{[a]}=1$	r_{vdW} [pm]	r_{Bondi} [pm][33]
H	0.00	106	90	119	120
C	0.37	151	128	170	170
N	0.32	145	123	163	155
O	0.28	140	119	157	152
F	0.26	137	116	155	147
Cl	0.53	170	144	192	175
Br	0.62	181	154	204	185
I	0.74	196	165	220	198

[a] n_v is the number of "extra-bonding" valence electrons that contribute to a decrease in the size CR by a term $F_S=[1+\{S(S+1)\}^{1/3}]$,[28–30,36–38] in which $S=n_v/2$. The term F_S accounts for the decrease in bond length with an increase in bond order ($=n_v+1$). Thus, $F_S\approx 1$, 1.18, 1.25, 1.31, 1.38, 1.42 for $n_v=0$, 1, 2, 3, 4, 5, respectively. The term F_S could also account, for example, for short intermolecular distances less than $2CR^-$.

lecular distances effectively increase. In the end, one may ascribe the packing equally well to structure-directing C–H···π contacts of 300–305 pm or to the need to optimize space-filling.

At room temperature and pressure, the *Pbca* structure of benzene has a molar volume of 118.5 $\text{Å}^3\text{mol}^{-1}$, but this volume decreases quickly to 114 and 107.8 $\text{Å}^3\text{mol}^{-1}$ at 0.3 and 1.1 GPa, respectively, while retaining the same space group.[42] We calculated the intermolecular distances in these hypothetical high-pressure *Pbca* structures by retaining the relative molecular orientations of normal-pressure *Pbca* benzene and without changing the intramolecular geometry. The new intermolecular contacts in the hypothetical 1.1-GPa structure of *Pbca* benzene are shown in Figure 3. As expected, the number of molecules in close contact increases with pressure. The C···H distances of 271–275 pm at 1.1 GPa are close to $\{r_{vdW}(H)+CR^-(C)\}$ (270 pm) and $\{r_{vdW}(C)+CR^-(H)\}$ ($\approx$276 pm) (Table 1). The H···H distance (235 pm) in this high-pressure phase is also just under $2r_{vdW}(H)=238$ pm (Table 1). The interatomic distances in phase I of benzene at 1.1 GPa are thus close to a transition to a phase with "n-polar" C···H or H···H contacts. The structure of benzene between 1.4 and 4.5 GPa is described as a yet-unrefined phase II structure.[42]

In the experimental high-pressure phase III (Figure 4), there are intermolecular C···C distances (indicated by thin and thick lines) that are 346–350 pm long; these distances

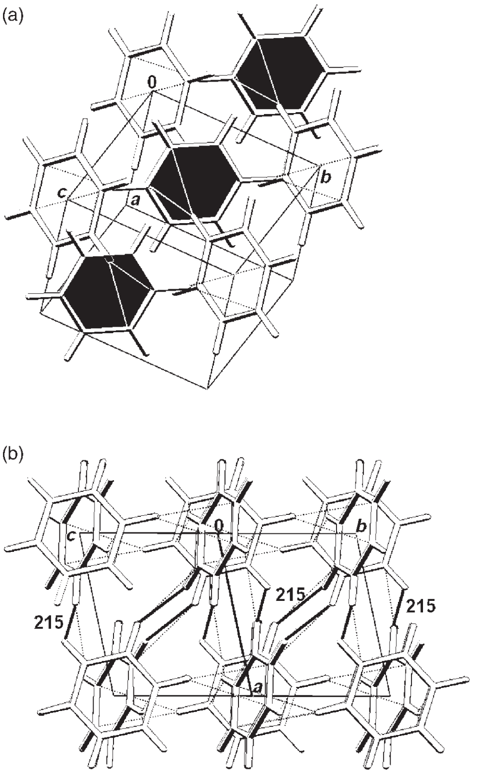

Figure 4. Packing of benzene molecules in the high-pressure $P2_1/c$ structure.[40–43] The shaded and unshaded hexagons correspond to different inclined layers. The solid lines indicate "n-polar" H···H contacts, the dotted lines represent C···H contacts. Distances are in pm. Parts (a) and (b) show two different perspectives of the unit cell for clarity. In (b) the horizontal molecules lie along [110].

are just over $2r_{vdW}(C) = 340$ pm (Table 1). Close-packed layers are discernible (Figure 4) in the (010) planes of phase III of benzene, and these layers are stacked. What is interesting is that the H···H contact distances (215 pm) are much less than $2r_{vdW}(H)$ (240 pm); rather, these distances are close to $2CR^{-}(H)$ (211 pm). This feature is in accord with the notion (see above) that in such anisotropic systems, increasing pressure introduces "n-polar" intermolecular contacts. This conclusion is actually not inconsistent with the observation by Dunitz and Schweizer[10] that "the C−H···F−C interactions in the fluorobenzene crystal have about the same structure-directing ability and influence on the intermolecular energy as a typical C−H···H−C interaction in crystalline benzene", except that we would suggest that these contacts are anisotropic in both cases. In other words, their possible innuendo that the C−H···F−C interaction is not polar and that it is not the cause of the structure-directing synthon is not sustained by our analysis. We would rather assert that the nature of the H···H interaction in benzene has changed from isotropic to anisotropic in going from the normal-pressure form to the high-pressure form. Notably, the high-pressure form they allude to is a hypothetical form, isomorphous to PhF, obtained by simulation. However, our comment that the nature of some interactions change from vdW to "n-polar" upon going from normal to higher pressures is a general one and is borne out by our analysis of an experimental high-pressure form of benzene (phase III). It is therefore no surprise to us that some H···H contacts in the (hypothetical and simulated) high-pressure form of benzene, which is isomorphous to PhF, are rather short.

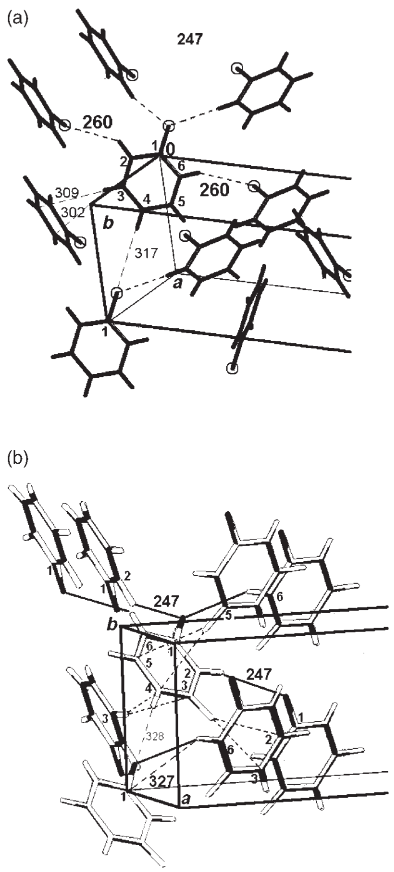

Figure 5. Near-neighbor contacts in a) fluorobenzene ($P4_32_12$) and b) pyridine *N*-oxide ($P4_12_12$). Distances are in pm. The substituent position is at C1 in both cases.

Monosubstituted Benzenes and the C−H···F−C Hydrogen Bond

Thalladi et al. provided arguments for an "ionic" C−H···F−C structure-directing synthon based on the close similarities (almost isomorphic) between the crystal structures of fluorobenzene (PhF; 231 K), pyridine/HF 1:1 molecular complex (Py·HF; 223 K), pyridine *N*-oxide (PyO; 338 K) and benzonitrile (PhCN; 259 K).[47] As the N···H···F, C−H···O, and C−H···N hydrogen bonds in Py·HF, PyO, and PhCN, respectively, are well-known structure directors, it was argued that the C−H···F−C contact in fluorobenzene is also of similar character. Among these four molecules, we may distinguish between the single-atom-substituent PhF and PyO and the two-atom-substituent Py·HF and PhCN.

The packing of PhF and PyO is shown in Figure 5. The C−F distance (136 pm) in C_6H_5F is marginally longer than the N−O distance (133 pm) in pyridine *N*-oxide. The shortest H···F distance in PhF (260 pm) and H···O distance in PyO (247 pm) involves H atoms adjacent to the substituent. In PhF, this contact (260 pm) is shorter than the sum of the vdW radii (270 pm), and it is comparable to $\{r_{vdW}(H) + CR^{-}(F)\} = 256$ pm or, alternatively, $\{r_{vdW}(F) + CR^{-}(H)\} = 259$ pm. In PyO, the 247-pm contact is close to the sum of the "n-polar" radii of H and O $\{(CR^{-}H) = 106,\ CR^{-}(O) = 140\ \text{pm})\}$. The O1···C6 contact of 327 pm (the so-called orthogonal contact) is of the vdW type, being exactly equal to the sum of the vdW radii. This could indicate that it is O1···H6 that is structure-directing, whereas the O1···C6 contact fulfils a space-filling role.

A feature of the packing in these monosubstituted benzenes is the presence of four distinct rows of molecules along [001]. In PyO there are inter-row C4···H5 distances (Table 2 and Figure 5 b) of 284 pm that resemble the shortest C···H contacts in *Pbca* benzene. In PhF the shorter interchain C···H contacts of 304 pm (Table 2 and Figure 5 a) are close to the C−H···π distance in *Pbca* benzene. We suggest that the "n-polar" H···O distance in PyO results in internal pressure that favors other short interatomic contacts. Accordingly, one might assert that the H···O contact in PyO (m.p.: 338 K) is more ionic ($R_{ob,vdW} = 0.89$) than the H···F contact in PhF (m.p.: 231 K; $R_{ob,vdW} = 0.95$) and is comparable to the short H···H distance in 1.1-GPa *Pbca* benzene ($R_{ob,vdW} = 0.90$). Significantly, all these contacts are best described by "n-polar" atomic sizes.

We now consider the structures of the two-atom-substituent Py·HF and PhCN[47] (Figure 6). The shorter intermolecular contact distances are given in Figure 6 and Table 2. There are C−H···F−C and C−H···N contacts from C−H groups adjacent to the substituent, similar to the corresponding features in PhF and PyO, which accounts for the

Table 2. Comparison of the intermolecular distances (d_{MX}) from a reference molecule to its near neighbor (n.n.) with the sum of calculated r_{vdW} for the two atoms.

Atom label[a] Ref.	n. n.	r_{nZ} [a.u.] Ref.	n.n.	d_{MX}(obs) [pm]	d_{vdW} [pm]	$R_{ob,vdW}$[b]
PyO						
O1	H6	0.282	0	247	277	**0.89**
O1	C6	0.258	0.366	327	323	1.01
H4	O1	0	0.282	328	277	1.19
C4	H5	0.366	0	284	288	0.99
PhF						
F1	H6	0.258	0	260	273	**0.95**
H4	F1	0	0.258	318	273	1.16
C3	H5	0.366	0	304	288	1.05
C4	H5	0.366	0	309	288	1.07
PhCN						
N1	H6	0.318	0	276	282	0.98
N1	H5	0.318	0	283	282	1.00
C1′	H5	0.366	0	287	288	1.00
H4	N1	0	0.318	266	282	**0.95**
C3 (C4D)	C1 (C4)	0.366	0.366	350	338	1.03
Py·HF						
F1	H6	0.258	0	258	273	**0.94**
H4	F1	0	0.258	233	273	**0.85**
C3	C6	0.366	0.366	368	338	1.09

[a] For numbering of atoms, see Figures 5 and 6. [b] Observed distance in vdW units ($R_{ob,vdW}$ = ratio of observed distance and calculated vdW distance). Interatomic distance is "n-polar" when $R_{ob,vdW} = 1/1.125 \approx 0.888$; $R_{ob,vdW} \approx 0.944$ indicates the average of "n-polar" and r_{vdW} distances.

isostructurality of the four compounds. The *ortho*-F⋯H2 (or H6) distance of 258 pm in Py·HF is close to the corresponding F⋯H2 (or H6) distance of 260 pm in PhF (Table 2). Because of the presence of an additional atom in the two-atom-substituent compounds, there is internal pressure that compresses the longer intermolecular contacts involving H4 atoms (H4⋯F1; Table 2) along the C1−C4 axis. The intramolecular C1⋯F distance of 247 pm in Py·HF is shortened (by 125 pm) to 122 pm in PhF. The intermolecular H4⋯F1 distance in Py·HF (233 pm) is shortened by 86 pm relative to PhF. The additional 39-pm shortening (125–86 pm) can, in principle, be accommodated by a decrease in the tetragonal lattice *a* parameter of $39/\sqrt{2} \approx 28$ pm. The actual *a* unit-cell parameter is 606 pm for Py·HF and 580 pm for PhCN. Accordingly, the shortening of the intermolecular H4⋯F1 distance in Py·HF relative to PhF can be almost-wholly explained by the lengthening of the intramolecular C1⋯F distance in the former.

Similar considerations apply in PhCN, in which the two-atom substituent also imposes internal pressure on the H4⋯N1 distance. The intramolecular C1⋯N distance of 253 pm in PhCN is 131 pm longer than the C1⋯F distance in PhF. The longer *a* unit-cell parameter of PhCN (636 pm) relative to that in PhF (580 pm) should account for 79 pm $\{(\sqrt{2})(636–580)\}$ of this lengthening. Accordingly, the H4⋯N1 distance in PhCN should be 52 pm shorter (131–79 pm) than the corresponding distance in PhF (318 pm; Table 2). The observed H4−N1 distance of 266 pm is in excellent agreement with this estimate. This value is considerably shorter than the vdW distance and must be considered to have more "n-polar" character than the *ortho*-H⋯N1 contact. Thus, in comparison to the single-atom substituent, the two-atom substituent introduces internal pressure.

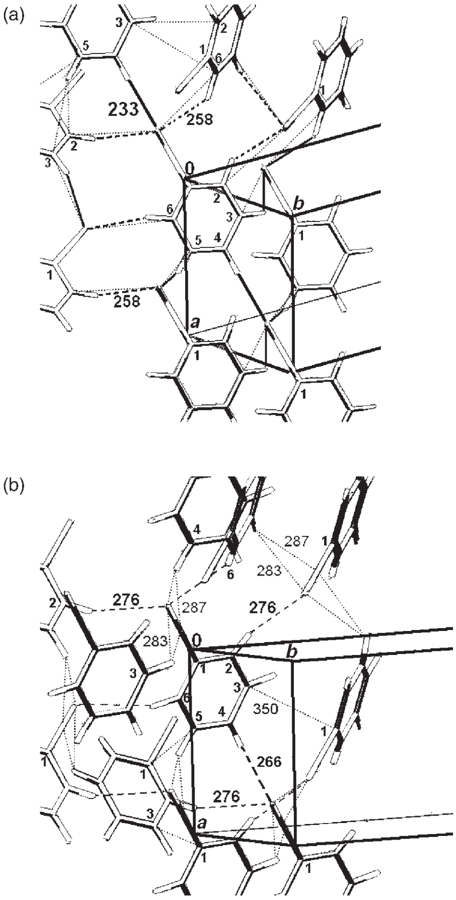

Figure 6. Important near-neighbor distances (pm) in a) pyridine/HF 1:1 molecular complex and b) benzonitrile.

A difference between PhCN and Py·HF is that the intervening sp-hybridized C atom (C1′) in the nitrile linkage of PhC≡N has a larger r_{vdW} value than the terminal N atom, whereas the intervening H atom in the C1−HF linkage of Py·HF is smaller than the terminal F atom. As a result, the CN group is involved in extra contacts. The most prominent of these are the vdW contacts of the CN group in PhCN with near neighbors (e.g., N1⋯H5 or C1′⋯H5; Table 2 and Figure 6b). Among the four compounds considered here, the shortest intermolecular C⋯C contact of 350 pm (still longer than $2r_{vdW}(C) = 340$ pm) is found in PhCN. Even so, PhCN has an *ortho*-H⋯N≡C distance (276 pm) that is shorter than expected for a vdW contact. Therefore the *ortho*-N1⋯H2 (or H6) contacts may be considered as synthon directors. Interestingly, the "n-polar" *ortho*-H⋯F contacts in PhF and the *ortho*-H⋯N contacts in PhCN, which are synthon directors in these compounds, also seem to play the same role in 1-fluoro-4-cyanobenzene (Figure 7), which has

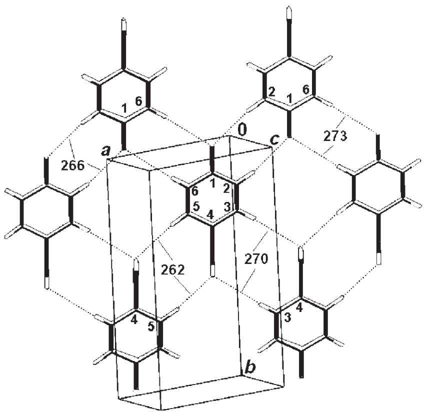

Figure 7. Crystal packing in 1-fluoro-4-cyanobenzene, showing *ortho*-H···F and *ortho*-H···N contacts with distances in pm.

activated H atoms, although its crystal structure is different.[48]

Distance analysis therefore helps in associating contacts shorter than the sum of the vdW radii with the synthon directors proposed by Thalladi et al. for monosubstituted benzenes. All the elements in the four molecules considered (PhF, PyO, Py·HF, and PhCN) are either hydrogen or insulator first-row elements. The introduction of "ionic" character as in PyO or Py·HF decreases contact distances to "n-polar" and results in a concomitant contraction of cell volume. Equivalently, the number of shorter "n-polar" contacts is expected to increase as external pressure is applied. For anisotropic molecules such as these, a decrease in volume may be accompanied by a preferred contraction in just one direction, and this would increase the anisotropy in the crystal. In effect, the number of equivalent orientations is expected to decrease.

Equivalence of Benzene and Acetylene

A further interesting analogy is provided by the equivalence of *Pbca* benzene and *Pa*3 acetylene. The packing in these structures are dominated by C···H contacts because the C atom is much larger than the H atom. One may examine, in this context, the effect of pressure on the number of different orientations in a unit cell for rodlike molecules. O'Keeffe and Andersson showed that the densest packing of rods is hexagonal close-packing,[49] a recent example being Gd_2TeO_6.[50] Long linear hydrocarbon chains align themselves close to such hexagonal close-packing. Linear molecules such as N_2 and CO_2 (but not Cl_2), which do not have a dipole moment, are less densely packed, being at the nodes of a face-centered cubic lattice. Solid Cl_2 has a layered structure characteristic of anisotropy. In acetylene, the intermolecular contacts ($T \approx 140$ K) are long with all H···C distances greater than 309 pm ($r_{vdW}(H) + r_{vdW}(C) = 290$ pm), all C···C distances greater than 385 pm ($2r_{vdW}(C) = 340$ pm), and all H···H distances greater than 325 pm ($2r_{vdW}(H) = 240$ pm) (Table 1). The acetylene molecules are therefore rather loosely packed, and any structure-directing synthon seemingly requires the C–H···π interaction with the C···H distance close to that in benzene. One may recognize four symmetry-equivalent directions along [111].[51,52] Nagai and Nakamura associated such an arrangement with the lowest quadrupole energy.[53] At lower temperatures, the crystal structure of acetylene becomes orthorhombic.[54] As low temperatures are equivalent to high pressures, this transition is similar to the phase I→phase III transition in benzene at high pressures.[42]

The orientation vectors in crystals of acetylene and benzene are equivalent. This is seen when the unit-cell dimensions of benzene and acetylene are normalized. By this we mean that we change the dimensions of the crystals of benzene to cubic (*Pbca* benzene is quasi-face-centered-cubic), thus keeping the unit-cell volume the same, and that we next contract the cell to that of acetylene. The atomic positional coordinates of benzene are concomitantly revised. Figure 8 is the projected view down the [111] direction of the superimposed unit cells of the two compounds (experimental cell for acetylene, contracted "cubic" cell for benzene). It can be immediately seen that the axes of the acetylene molecules are nearly perpendicular to the planes of the benzene rings. Examination of Figure 8 shows that the C···H interactions in benzene are replaced by H···C interactions in acetylene at somewhat similar locations. *Pbca* benzene and *Pa3* acetylene are therefore equivalent, but the latter is a "looser" structure. This similarity, like that between PhF, PyO, PhCN, and Py·HF, illustrates that crystal structures are found in domains that may be populated by molecules that can have intermolecular contact distances within certain ranges.[55] The C···H contacts in acetylene are of the vdW type, whereas some of the C···H contacts in *Pbca* benzene tend to have ionic character; however, this does not prevent both molecules from adopting what is essentially the same structure. A recent study on the crystal structure of the 1:1 benzene/acetylene molecular complex[56] is pertinent in that it illustrates this "looseness" of the acetylene molecule relative to benzene. In this 1:1 solid, the acetylene molecules are literally inserted in the benzene lattice and undergo a "wobbling" motion so that the molecular axis of acetylene is

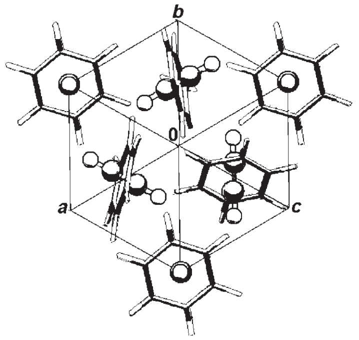

Figure 8. Superposition of the [111] orientations of *Pbca* benzene ("pseudocubic") and cubic acetylene, showing the near coincidence of the normals of the benzene-ring planes with the axes of the acetylene rods.

perpendicular to the benzene planes in a time-averaged sense.

Conclusions

Similarities in supramolecular synthons may be quantified with a new (even if currently phenomenological) method of obtaining intermolecular distances based on atomic sizes. It was found that intermolecular interactions in solids range from van der Waals to a shorter, more polar variety. The intermolecular distances are derived from different atomic sizes, *CR* [Eq. (1)]. The smaller distances are associated with smaller "n-polar" atomic sizes, whereas the longer are associated with van der Waals sizes. Our scheme for atomic sizes is thus able to accommodate chemical distinctions between interactions. Van der Waals interactions are associated with geometry-based close-packed structures, whereas the shorter "ionic" interactions are characteristic synthon descriptors and may be termed "structure-determining". We conclude by stating that equivalences between crystal structures of different molecules, as revealed through these distance descriptors, are strongly suggestive of chemical similarities between the participating interactions.

At the heart of the issue for a molecular crystal—as opposed to, say, an inorganic crystal, which may be viewed as an assembly of spherical objects of different sizes—is the notion of anisotropy or synthon directionality, which follows from the arbitrary shape of the typical organic molecule. This directionality introduces an element of polarity in the intermolecular contacts, the so-called "n-polar" contacts. Alternatively, external (hydrostatic) or internal (chemical) pressure increases "n-polar" contacts in crystals, which accounts for the similarity, say, between PhF and the computed high-pressure structure of benzene. Such correlations between "polar" contacts and anisotropic molecular shape are expressed naturally and effectively in terms of synthon directionality. This methodology was illustrated by the following examples: 1) comparison between PhF and the group of compounds constituted by PhCN, PyO, and Py·HF, all of which have very similar crystal structures in the tetragonal $P4_12_12$ space group; 2) comparison between *Pa3* acetylene and *Pbca* benzene; 3) comparison between experimental ambient-pressure *Pbca* benzene and hypothetical high-pressure *Pbca* crystals.

We emphasize that the values of C_P and D_P, which contribute to atomic sizes in Equation (1) and add to give interatomic distances, change with the nature of the interaction. In this study, we have only addressed intermolecular contact distances of the "n-polar" and "neutral" type. This general classification is also applicable to other compounds, including inorganic ones. There are, however, other common interactions such as bonding (charge-transfer or neutral) interactions, hydrogen bonds, nonbonded interactions, multiple bonds, and 1,3-nonbonded interactions, all of which require (different but fixed) changes in C_P, as observed empirically.[20–22,27–29]

Appendix 1

Atomic Sizes

Our model for atomic sizes delineates core regions from valence regions differently.[19,57] The arguments given below for the size r_{nZ} are valid for main-group elements, including rare-gas elements but excluding Li, Na, Ca, Sr, and Ba. The model is based on the notion that atomic sizes, r_{atom}, are important only in the context of external interactions; hence, models for such sizes must incorporate such interactions. The novelty in the method is to assume that such interactions are described by emission and absorption of a virtual photon[58] or by a virtual electron–hole pair, e^-h^+. This external interaction is represented by adding an electron–hole pair to the atom [Eq. (A1)]:

$$Z(\eta) + (e^-h^+) = (Z)h^+ - e^- = [n_{\mathrm{val}} + Z_{\mathrm{RG}(\eta-1)}](h^+e^-) \qquad \text{(A1)}$$

Z is the atomic number for an atom in the ηth row of the periodic table ($\eta = n-1$, in which n is the principal quantum number of the outermost valence electron). n_{val} is the number of electrons in the "valence shell", and $Z_{\mathrm{RG}(\eta-1)}$ is the atomic number of the rare-gas element in the ($\eta-1$)th row. The actual strength of the interaction represented by $e^- - h^+$ (positronium atom) is not critical in our model for the atomic size. We only require the additional interaction of h^+ ("virtual positron") with the "valence-shell" electrons and the "inner-shell" electrons with the rare-gas configuration.

Valence Size

The n_{val} electrons of the "valence shell" is treated together as a negative charge $(n_{\mathrm{val}})^-$ that interacts with h^+ with mass $M_{\mathrm{nv}} \gg m_\mathrm{h} \approx m_\mathrm{o}$, in which m_h and m_o are the mass of h^+ and free electron, respectively. The additional interaction energy, $E_{\mathrm{val}}{}^+$, of the light external hole h^+ with $(n_{\mathrm{val}})^-$ is given in an ("inverted"; heavy negative charge and light hole) Bohr-like model by Equation (A2):

$$E_{\mathrm{val}}{}^+ = (\eta/r)^2/2m_\mathrm{o} - n_{\mathrm{val}}e^2/r \qquad \text{(A2)}$$

It is sufficient to visualize Equation (A2) as a one-dimensional equation (see Equation 3.12 of reference [59] and discussions thereon). The 1D first "Bohr size", r_{nv}, is obtained by Equation (A3):

$$r_{\mathrm{nv}} = a_\mathrm{H}/n_{\mathrm{val}} = 1/n_{\mathrm{val}} \text{ (in a.u.)} \qquad \text{(A3)}$$

in terms of the first Bohr size, a_H, for principal quantum number $n_{(h+)} = 1$ of the hole. The size r_{nv} is thus obtained for a classical stationary state, consistent with the transferability condition $\mu = 0$ for the chemical potential. Effectively, all atoms are treated as pseudo-hydrogen atoms in a manner reminiscent of the pseudopotential method.[19]

Inner Size, $r_{RG(\eta-1)}$

We make the simple statement that for a 1D number density, N_{1D}, of inner-shell electrons interacting with the external hole, h^+, in the direction of interaction, dN_{1D}/N_{1D} is the rate of growth in 1D size per particle of the "inner shell" due to such interactions. The total change, ΔN_{1D}, is given by Equation (A4):

$$\Delta N_{1D} = \int_1^{N_{1D}} (dN_{1D}/N_{1D}) = \ln(N_{1D}) = \ln(Z_{inner})^{1/3} \tag{A4}$$

in which Z_{inner} is the appropriate number of "inner-shell" electrons in the given direction.

The logarithmic dependence is reminiscent of the Beer–Lambert relationship between absorption coefficient and number of particles (photons) absorbed. The ΔN_{1D} inner-shell electrons occupy in pairs a "Bohr" size, a_{Bohr}, such that the size per electron $r_{inner} = \xi a_{Bohr}$, in which ξ could arise as a statistical factor. Thus, we may expect for $Z_{inner} = Z_{RG(\eta-1)}$ [Eq. (A5)]:

$$r_{RG(\eta-1)} = \xi a_{Bohr} \Delta N_{1D} = \xi a_{Bohr} \ln\{(Z_{RG(\eta-1)})^{1/3}\} \tag{A5}$$

Total Core Size, r_{nZ}

From Equations (4) and (6), we obtain, to a first approximation [Eq. (A6)]:

$$r_{nZ} = 1/n_{val} + \xi(a_H/2)[\ln(Z_{RG(\eta-1)}{}^{1/3})] \tag{A6}$$

Equation (A6) for r_{nZ} has no adjustable parameter (when $\xi = 1$), does not depend on the nature (s or p) of the valence electron, is consistent with the spherical symmetry of an isolated atom, and is simply related to its row number, η, and its atomic number, Z $(= n_{val} + Z_{RG(\eta-1)})$.

The calculated values of r_{nZ} from Equation (A6) are shown for the first-row main-group elements (except Li), the halogens, and the rare-gas elements and are compared in Table 3 with the values of r_G and the Zunger–Cohen valence-s-electron orbital radii, r_s (from reference [27]). The values of r_{nZ} are given to three decimal places as no adjustable parameters are involved in Equation (A6).

Table 3. Atomic radii for various elements.

Atom (η)	n_{val}	$Z_{RG(\eta-1)}$	Atomic radii [a.u.] r_{nZ}	r_s	r_G
H			0		0
Be (2)	2	2	0.616	0.64	0.59
B (2)	3	2	0.449	0.48	0.41
C (2)	4	2	0.366	0.39	0.32
N (2)	5	2	0.316	0.33	0.26
O (2)	6	2	0.282	0.28	0.22
F (2)	7	2	0.258	0.25	0.18
Cl (3)	7	10	0.527	0.5	0.52
Br (4)	7	18	0.625	0.58	0.62
I (5)	7	36	0.74	0.76	0.78
Ne (2)	8	2	0.241	0.22	
Ar (3)	8	10	0.509	0.46	
Kr (4)	8	18	0.607	0.56	
Xe (5)	8	36	0.722	0.75	

Appendix 2

Interatomic Distances

The M−X bond distance, d_{MX}, for charge-transfer interactions is empirically given by Equations (A7)–(A9):[21]

$$d_{MX} = CR^+(\mathrm{M}) + CR^-(\mathrm{X}) \tag{A7}$$

$$d_{MX} = C^+ r_{core}(\mathrm{M}) + C^- r_{core}(\mathrm{X}) + D^+(\mathrm{M}) + D^-(\mathrm{X}) \tag{A8}$$

$$d_{MX} = 2.24 r_G(\mathrm{M}) + 2.49 r_G(\mathrm{X}) + 74 \text{ (in pm)} \tag{A9}$$

Equation (A9) is interesting as interatomic distances at NTP may be written[20–22] simply in terms of a core atomic size and the bond length of the H_2 molecule ($d_{H-H} \approx 74.2$ pm at NTP) when the charge-transfer description is applicable.[21] It has been shown that the bond length of the H_2 molecule may be expressed in terms of the Bohr radius, a_H, of the hydrogen atom with $d_{H-H} = \varepsilon_{eff} \times 4a_H/3$, in which ε_{eff} (≈ 1.05) is the effective dielectric constant.[22] We may now rewrite Equation (A9) as Equations (A10a)and (A10b):

$$d_{MX} = \varepsilon_{eff}[C_1{}^+ r_G(\mathrm{M}) + C_1{}^- r_G(\mathrm{X}) + D^+ + D^-] \tag{A10a}$$

$$d_{MX} \approx 1.05[2.13 r_G(\mathrm{M}) + 2.37 r_G(\mathrm{X}) + 4a_H/3] \tag{A10b}$$

in which $C_1{}^\pm$ and $D_1{}^\pm$ are the values of $C^\pm$ and $D^\pm$ when $\varepsilon_{eff} = 1$. It has been found that $D^+ = -2a_H/3$ and $D^- = 2a_H$, so that $d_{H-H}(\varepsilon_{eff} = 1) = 4a_H/3$. We may thus write (assuming $r_G \approx r_{nZ}$; Appendix 1) Equation (A10a) as Equation (A11):

$$d_{MX} = \varepsilon_{eff}[C_1{}^+ r_{nZ}(\mathrm{M}) + C_1{}^- r_{nZ}(\mathrm{X}) + 4a_H/3] \tag{A11}$$

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