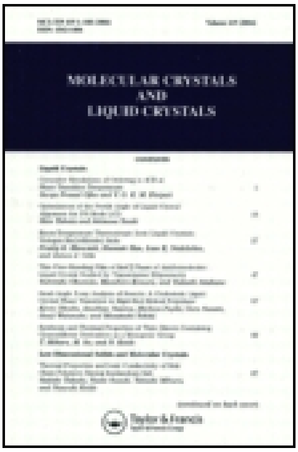

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Jack D. Dunitz (1996): Weak Intermolecular Interactions in Solids and Liquids, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 279:1, 209-218

To link to this article: http://dx.doi.org/10.1080/10587259608042191

Mol. Cryst. Liq. Cryst., 1996, Vol. 279, pp. 209–218
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WEAK INTERMOLECULAR INTERACTIONS IN SOLIDS AND LIQUIDS

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Abstract Weak intermolecular interactions are not only important in modern supramolecular chemistry, they hold the organic world together and are responsible for the very existence of liquids and solids. A characteristic feature of weak interactions is the phenomenon of enthalpy-entropy compensation. Information about weak interactions in crystals is obtained from packing patterns, which provide tests for the quality of atom-atom force fields. On melting a solid, most of the cohesive energy is retained in the liquid state, even though the optimal mutual orientation of interacting parts of molecules is now opposed by thermal disorder. For liquids, reliable structural information is hard to come by, but extensive thermodynamic data are available for certain classes of compounds.

INTRODUCTION

The earth's crust may be held together mainly by ionic forces, molecules by covalent bonds, but it is weak intermolecular interactions which hold us, along with the rest of the organic world, together. The hydrogen bond is the best known example:

> "Because of its small bond energy and the small activation energy involved in its formation and rupture, the hydrogen bond is especially suited to play a part in reactions occurring at normal temperatures. It has been recognized that hydrogen bonds restrain protein molecules to their native configurations, and I believe that as the methods of structural chemistry are further applied to physiological problems it will be found that the significance of the hydrogen bond for physiology is greater than that of any other single structural feature."[1]

Pauling's prophecy has been amply fulfilled. Hydrogen bonding has emerged as the most important organizing principle not only for the structures of biologically important molecules but also for crystal engineering.[2] A recent, comprehensive survey has been provided by Jeffrey and Saenger.[3]

ASPECTS OF HYDROGEN BONDING

Until fairly recently, the term "hydrogen bonding" was more or less restricted to interactions involving F—H, O—H, and N—H as proton donors, O and N as proton acceptors, with typical bond energies in the range 5 to 20 kcal mol^{-1} (for $[F \cdots H \cdots F]^-$). However, it is now generally recognized that C—H···O interactions also play an important role in determining molecular packing arrangements.[4] They are admittedly weaker, with energies typically less than 1 kcal·mol^{-1}, but they are of common occurrence in molecular crystals containing C, H, and O atoms. Sometimes they have remarkable consequences. For example, the highly unusual, eclipsed conformation of a C(sp^3)—CH_3 grouping in a crystalline trihydrate has been attributed to the presence of such C—H···O interactions in a cooperative system of O—H···O, O—H···N, and C—H···O hydrogen bonds.[5] And if we admit C—H···O interactions as weak hydrogen bonds, why not also others such as C—H···C(sp^2) interactions, which dominate the "herringbone" packing in crystals of small aromatic molecules such as benzene and naphthalene? [6]

While Brønsted's definitions[7]: An acid is a proton donor, a base is a proton acceptor, were clearly intended to apply to acid-base relations in solution, they may be applied with appropriate modification to hydrogen bonding in crystals, which involves proton sharing, i.e., incipient or partial proton donation and acceptance, often in characteristic patterns of cooperative interactions[2], rather than complete proton transfer. And indeed, an order of acidity and basicity based on hydrogen bonding would not differ radically from one based on acid/base equilibria in aqueous or non-aqueous solution or on proton transfer reactions in the gas phase. Hydrogen bonding in crystals (and to a lesser extent also in liquids and solutions) is characterized by a high degree of cooperativity.[7]

ASPECTS OF WEAK INTERACTIONS

Hydrogen bonding — even the weak C—H···C interactions mentioned above — can be described in good approximation as an essentially electrostatic phenomenon, i.e., as a first-order coulombic interaction. Other kinds of weak interaction involve mutual polarization of molecules and dispersion forces. A characteristic of weak interactions is the relative insensitivity of the bond energy on interatomic distance. Elongation of a covalent bond by say 0.2 Å reduces the binding energy by something of the order of 50 kcal·mol^{-1} (roughly half the standard bond energy). The same elongation of a typical hydrogen bond reduces the binding energy only by about 1.2 kcal·mol^{-1} (roughly 25% of the standard binding energy, taken here as 5 kcal·mol^{-1}). This is apparent from the potential energy curve shown in Figure 1(left), based on a choice of the atom-atom pair potentials listed by Gavezzotti.[8] The same increase in interatomic distance for the weak interaction described by the potential energy curve shown in Figure 1(right) weakens the interaction energy only by about 0.01 kcal·mol^{-1}(roughly 10% of the energy at the equilibrium separation). The point is that in studying weak interactions one should not adopt a too stringent distance criterion in deciding what constitutes any given type of interaction. Distributions of certain types of "nearest-neighbor contacts" in crystals show that these interatomic distances may be up to 0.6Å longer than the sum of standard van der Waals radii.[9]

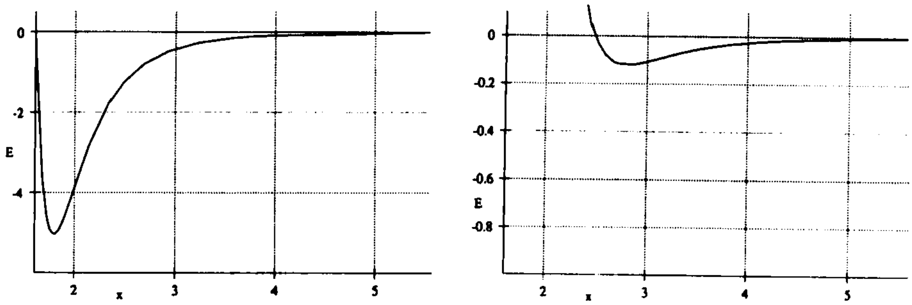

FIGURE 1. Typical potential energy curves for a OH···O(alcohol) hydrogen-bonded interaction with well depth 5 kcal·mol^{-1} and equilibrium distance 1.8Å (left) and for a non-hydrogen-bonded H···O interaction with well depth 0.12 kcal·mol^{-1} and equilibrium distance 2.8Å (right), based on atom-atom potential parameters listed by Gavezzotti.[8]

There is a more quantitative way of expressing the dependence of interaction energy on interatomic distance: the quadratic force constant $f = (\partial V^2/\partial r^2)_{r=r(\mathrm{min})}$ (the curvature at the equilibrium distance) is directly proportional to the binding energy D_0 (well depth). This relationship holds exactly for the Morse curve and for the inverse power potential and must hold closely for all "reasonable" atom-atom potential energy curves. The vibrational frequency should then be approximately proportional to $(D_0)^{1/2}$. An order of magnitude calculation shows that for a hydrogen-bonded water molecule with $(D_0) \approx 5$ kcal·mol^{-1}, the free energy contribution of the corresponding vibrational entropy at 300K, roughly 6x300xS(vib), would have roughly the same value as the bonding energy but of opposite sign, thus accounting qualitatively for the enthalpy-entropy compensation effect that is known to characterize weak intermolecular associations.

TYPES OF WEAK INTERACTION

Hydrogen bonding is undoubtedly the best studied and most important type of weak interaction (we interpret it here in its most general sense, as including all types of X-H...Y interactions, Other types of weak interaction can arise from:

(a) Dipole-dipole interactions, A good example is the structure of dimethylsulfoxide[10], which is virtually determined by such interactions among the S=O bonds (Figure 2). Interactions among overall molecular dipoles are usually much less important than local interactions among bond dipoles, Indeed, inferences based on interactions among molecular dipoles are not to be trusted. The repulsive nature of local dipole-dipole interactions across rotation axes and mirror planes helps to explain the low frequency of occurrence of these symmetry elements in molecular crystals.[11]

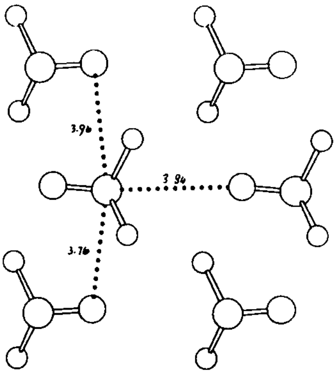

Figure 2. Structure of a layer of molecules in the dimethylsulfoxide crystal (interatomic diatances in Å).

(b) Quadupole-quadrupole interactions. The cubic crystal structures of carbon dioxide[12] (Figure 3) and of acetylene[13] illustrate the favorable arrangement of like quadrupolar

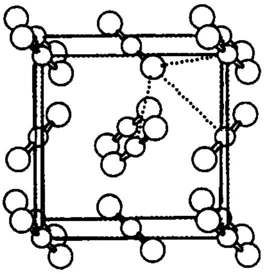

Figure 3. Crystal structure of carbon dioxide (cubic space group Pa3). The molecules sit on the threefold axes. Cubic acetylene has a very similar structure.

molecules in three dimensions. The molecules sit on the threefold axes of space group Pa3, such that each terminal atom in one molecule is equidistant from the centers of three surrounding molecules.

At low temperatures, cubic acetylene transforms to an orthorhombic structure in space group Acam.[13] With cell dimensions 6.20, 6.02, and 5.58 (C_2D_2 at 15K), the structure is pseudo-tetragonal with layers that closely resemble the favorable arrangement of like quadrupolar molecules in two dimensions, i.e., each C—D bond points nearly at the center of a neighboring molecule. However, closer examination reveals that although the D atom is equidistant (2.74Å) from the two atoms of the C,C-triple bond, the C—D bond actually points amost exactly at one of these atoms (C—D···C angle 178°). This inequivalence of the two C atoms leads to the loss of tetragonal symmetry. Even for such small molecules, the packing optimizes local interactions at the expense of the global quadrupole-quadrupole interaction.

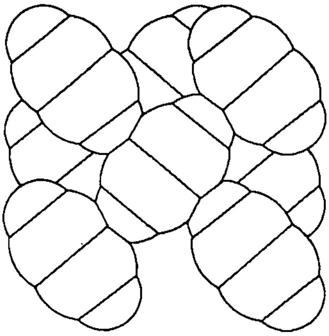

Figure 4. Layer of molecules in the orthorhombic low-temperature structure of acetylene.[13]

Benzene and hexafluorobenzene have almost the same molecular quadrupole moments but of opposite sign (around 30 x 10^{-40} C m^2, negative for C_6H_6, positive for C_6F_6).[14] The molecules are roughly the same shape and size, and since the interaction energy should not depend on the sign of the quadrupole moment, the quadrupole-quadrupole interaction alone should lead to the same stable packing arrangement for both. In fact, the structures of benzene I[15] and benzene II (high-pressure modification)[16] are completely different from that of hexafluorobenzene[17]. Only the orthorhombic benzene I structure has a slight resemblance to the cubic structures of CO_2 and C_2H_2; its space group Pbca is a sub-group of Pa3.

HALOGEN-HALOGEN INTERACTIONS

The crystal structures of the halogens make an interesting series. They have the same space group and essentially the same layer-packing arrangement as low-temperature acetylene. In the halogen crystals the interlayer contact distances are roughly equal to the van der Waals diameters, but within the layers there is an increasingly strong tendency towards a specific, highly directional Hal···Hal interaction. For iodine this has gone so far that the shortest intermolecular I···I distance is 3.50Å, or about 0.8Å less than the van der Waals diameter. From Figure 5 it is apparent that the iodine structure does not fit simple electrostatic models with charges on the atoms or interactions between molecular quadrupoles. Some sort of polarization or charge transfer is clearly at work. It looks as if the molecule is acting as an electron acceptor along the direction of the I—I bond and as electron donor perpendicular to the bond — or vice versa; from the halogen crystal structures alone one cannot decide.

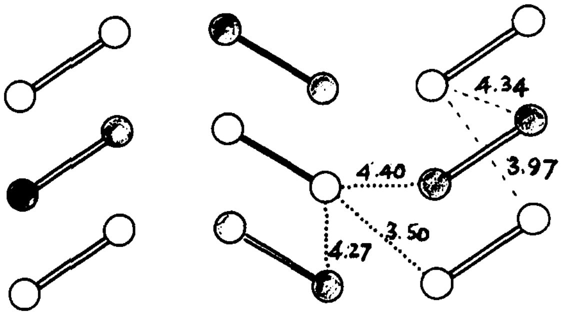

Figure 5. Crystal structure of iodine[18]. Molecules in different layers are shaded differently.

HIGHLY DIRECTIONAL INTERACTIONS

The answer comes from the structures of molecular complexes formed by electron donors and halogen molecules, studied many years ago by the Oslo school.[19] The first such complex to be studied was the 1:1 complex formed by molecular bromine and 1,4-dioxane[20], shown schematically in Figure 6. The remarkably short O···Br distance of 2.71Å (compared with 3.35Å, sum of van der Waals radii) is along the direction of the Br—Br bond (at 2.31Å, slightly longer than the distance in gaseous bromine) and roughly in the direction expected for a tetrahedral lone pair on the O atom. Clearly the bromine molecule is acting as an electron acceptor along the direction of the Br—Br bond. From the extensive list of complexes studied, the same conclusion applies to the other halogens and also to Hal—C bonds. In more modern HOMO/LUMO parlance, the interactions are interpreted as n:σ^*, the σ^* orbital of the Hal—X bond functioning as electron acceptor.

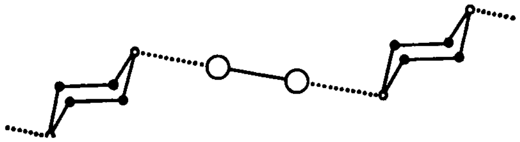

Figure 6. Schematic view of the crystal structure of the 1:1 complex formed by molecular bromine and 1,4-dioxane

The directionality of non-bonded contacts has been examined for several C—X systems and interpreted in terms of orientation-dependent van der Waals surfaces, rotation ellipsoids with the short radius along the C—X bond.[21] However, such a picture would be complicated by the need to construct a different surface for different types of contact atoms, depending on their electron donor abilities. From recent work at the Cambridge Crystallographic Data Centre, C—Cl···O contact distances tend to be shorter in the C—Cl bond direction and longer perpendicular to it, but C—Cl···H distances show practically no orientation dependence.[22] Similarly, electron donors (nucleophiles) tend to approach divalent sulfur along one of the X—S directions whereas electron acceptors (electrophiles) tend to approach nearly perpendicular to the X—S—Y plane.[23]

Allowance for the highly directional nature of weak intermolecular interactions has hardly begun to be made in force fields for atom-atom potential calculations, which adhere, for the most part, to spherical atom models as far as the non-bonded atoms are concerned. Further information about such interactions should be important not only for crystal engineering but also for chemistry. Just as hydrogen bonding can tell us about acid-base relationships, so the wider study of how molecules approach one another in crystals can inform us about the incipient stages of chemical reactions in general.[24]

CRYSTALS AND LIQUIDS

We have seen that in crystals weak intermolecular interactions are strongly directional and that the mutual orientation of neighboring groups is important in achieving stable packing arrangements. On melting to a liquid, there is usually only a slight change in packing density but the breakdown of periodicity means that the regular, favorable orientation neighboring molecules is partly lost. Only a statistical, temperature dependent preference is retained. In general, the enthalpy of fusion ΔH(fus) is much less than the enthalpy of vaporization ΔH(vap); in other words, even if the preferred mutual orientation of groups is largely lost, most of the cohesive energy of the system is retained.

The increase in entropy on melting ΔS(fus) is associated mainly with the loss of orientational order as well as with the increased conformational freedom of flexible molecules, which is largely frozen in the solid state. For spherical molecules, e.g., those of the inert gases, where there is no orientational order to lose, ΔS(fus) is close to 3.3 e.u. (1 e.u. = 1 $\text{cal·mol}^{-1}\text{·K}^{-1}$) even though the melting temperatures and ΔH(fus) values vary greatly*. In general, the interpretation of entropies of fusion is complicated by the possibility of order-disorder phase transitions in the solids.

COHESIVE ENERGIES OF LIQUIDS

A convenient measure of the cohesive energy of a liquid is provided by the standard enthalpy of vaporization at 298.15K, $(\Delta H^o{}_v)_0$**(to obtain the actual energy we should subtract the constant RT = 0.592 kcal·mol^{-1}). Some interesting regularities may be noted. For example, the $(\Delta H^o{}_v)_0$ values for benzene, hexafluorobenzene, pentafluorobenzene, and the three difluorobenzenes are almost equal (8.1 - 8.7 kcal·mol^{-1})[25], as are the boiling points (353-367K). This may suggest that the major part of the cohesive energy is provided by the mutual attractions of the aromatic rings of the different molecules, and that the peripheral H or F atoms have little effect. Replacement of H or F by CH_3 (isoelectronic with F) raises the cohesive energy by about 1 kcal·mol^{-1}.

When $(\Delta H^o{}_v)_0$ for a homologous series of hydrocarbon derivatives is plotted against chain length an almost perfect linear relationship is obtained with slope approximately 1.1 kcal·mol^{-1}, as has also been noted elsewhere.[26] The intercept (zero chain length) is close to RT for linear and cyclic alkanes but has a more positive value for other functional groups. When $(\Delta H^o{}_v)_0$ values for molecules of the same chain length (e.g., n-pentane, diethylether, methylpropylether, 1-bromobutane, 1-butanol, etc.) are compared, we obtain by difference an estimate of the contribution of the various functional groups to the cohesive energies of the liquids. In this way, we obtain estimates (in kcal·mol^{-1}) of about

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*Some authorities state that the molar entropies of fusion of spherical molecules are "close ro R", but the actual values seem to be closer to 1.65 R.

**Note that this is not the same as $(\Delta H_v)_b$, the enthalpy of vaporization at the normal boiling point of the liquid.

0.1-0.3 for ether O, 1.1 for -NH-, 2.2 for $-NH_2$, 1.7 for -Cl, 2.4 for -Br, 5.0 for -CN and 6.1 for -OH, which fit reasonably well with estimates from other sources.

CONCLUSIONS

For solids, we need better atom-atom potential energy functions. We have a wealth of information about the directional properties of weak interactions but very little thermodynamic data with which to test packing energy estimates. The phenomenon of polymorphism shows that the crystal form stable at room temperature is not necessarily that with the best packing energy; the entropy cannot be neglected. Recall that calculated packing energies generally refer to the sublimation enthalpy at 0K, a quantity that is hardly ever experimentally available.

For liquids, we have a wealth of thermodynamic data from which averaged interaction energies can be estimated but we lack structural information about the relative orientations of neighboring molecules. To what extent are the orientations that occur in the crystal preserved in the liquid just above the melting point? To what extent are these destroyed as the liquid is warmed towards its boiling point?

There is much to be learned.

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