The Molecular Electric Quadrupole Moment and Solid-State Architecture

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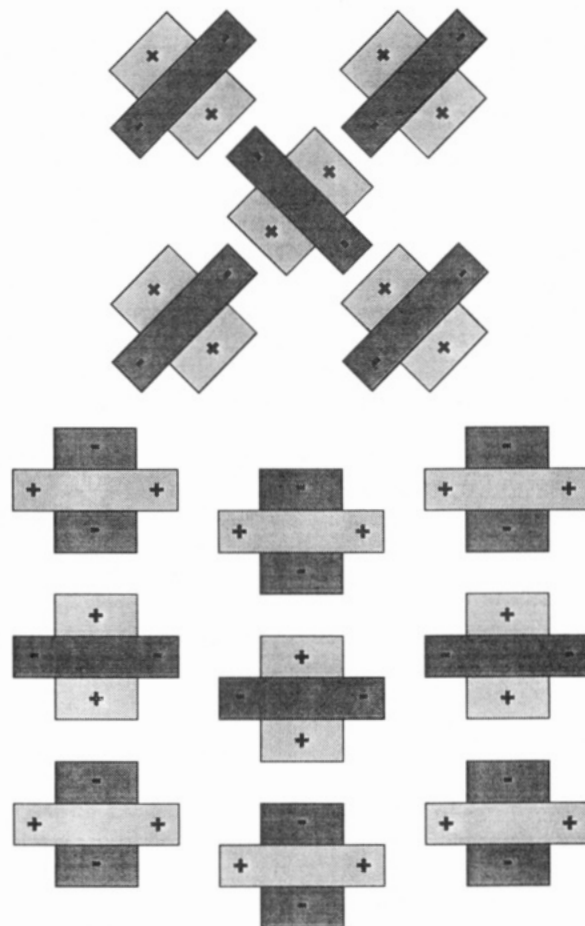*Institut Max von Laue-Paul Langevin, 156X, 38042 Grenoble, France*

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There exists some confusion on the subject of quadrupole moments. However, there are only two types commonly encountered in, for example, undergraduate chemistry and physics courses. First, there is that associated with the atomic nucleus. This is the origin of, among other things, nuclear quadrupole resonance spectroscopy and of certain hyperfine structure observed in high-resolution NMR spectroscopy. Then there is the quadrupole moment associated with the molecular charge distribution which is a property of the molecule as a whole and is termed the molecular electric quadrupole moment.

This second type of quadrupole moment is a description of the molecular charge distribution and as such has considerable importance in modeling the origin of the electrical forces which exist between molecules, particularly, in modeling how the observable bulk physical properties of the condensed phase may be related to the properties of individual molecules. For example, how might one distinguish between the boiling point of water and that of benzene or methane?

It was as an undergraduate in the much lamented Edward Davies Chemical Laboratories, Aberystwyth, that I first encountered the electrical properties of molecules, particularly, the molecular dipole moment, which is the simplest electrical property to be observed in stable molecular systems. As undergraduates, we were told how the Dutch–American physicist Peter Debye quantified the polarization within a molecule and introduced the idea of a charge separation, defining in the process a unit: 1 unit of charge separated by 1 Å, that is, 1 D (debye). In the SI system of units, a molecular dipole moment is given in coulomb meters, typical measured values being 3.33×10^{-30} C m. We were also told that Debye, who was fond of large cigars, would use the cigar he was currently smoking as a model for the molecular dipole moment, the separated electric charges residing on each end.

However, if the cigar happens to be a carbon dioxide molecule, then further insight into molecular electrostatics may be gained. In CO_2, the two bond dipoles, $O(\delta-)$--$C(2\delta+)$--$O(\delta-)$, are opposed and the vector sum of the two individual moments is 0. In Figure 1a,b, we display the observed solid-state packing of an ensemble of quadrupolar molecules. Any one such "molecule" is

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Figure 1. (a) Schematic representation of the molecular conformation which maximizes the electrostatic interaction energy between molecular electric quadrupole moments for an assemblage of like-quadrupolar molecules. This pattern is termed a herringbone structure, and it minimizes electrostatic repulsion and maximizes electrostatic attraction. The molecular quadrupole moments are represented schematically as cylinders with negative charges on the ends and the balancing positive charges in the center, this denoting a negative molecular quadrupole moment (cf. benzene or carbon dioxide). (b) Schematic representation of the lowest energy interaction conformation for an assemblage of two dissimilar quadrupolar molecules, that is, an arrangement of molecules with positive and negative quadrupole moments. Here, cylinders with positive charges at the extremities balanced by negative charges at the center denote a positive molecular quadrupole moment (cf. hexafluorobenzene or carbon disulfide).

represented, figuratively, as two like charges, through which passes the main rotational axis, separated by the opposite, balancing charges lying perpendicular to the

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main rotational axis. In benzene, the vector sum of the six C(δ-)--H(δ+) bond dipoles is also 0, giving a net nonpolar molecule. In both cases, however, the molecule is better thought of as possessing a finite width. For example, the CO_2 molecule is not infinitely narrow, but ellipse-like with major and minor axes. We may then define a charge per unit area (charge by distance by distance, C m^2), that is, the molecular electric quadrupole moment, with magnitude of order 3.33 $\times$ 10^{-40} C m^2.

The first direct method for the determination of a molecular quadrupole moment was established by A. D. Buckingham.[1] He showed how an applied electric field gradient would orient molecular quadrupolar moments, in the same way that an electric field would induce an orientational torque on gaseous dipolar molecules, that is, the dipole moment of the molecule being oriented in an applied electric field, with the degree of orientation being quadratic in the applied field (the Kerr effect). However, the degree of induced orientation would in this case be linear in the applied electric field gradient. In this way, the first direct measurement of the electric quadrupole moment of the CO_2 molecule was accomplished in the early 1960s.[1] Indeed, Debye suggested at the time that the quantity, 1 unit of charge distributed over 1 Å^2, be termed the buckingham.

The SI value of the electric quadrupole moment of CO_2 is approximately -15 $\times$ 10^{-40} C m^2.[1] Thus, with a C--O distance of about 1.1 Å, we arrive at the familiar picture of this molecule as two negative charges, in fact 0.8 of an electron charge, on each extremity of the ellipse with the balancing positive charges at the waist.

The molecule is oriented in an applied field gradient because of the torque arising from the interaction of the molecular quadrupole moment with the applied field gradient. Standard electrooptic techniques, measurement of the difference in the refractive indices parallel and perpendicular to the field direction, allow a determination of the degree of induced molecular orientation and, for a known applied field gradient, a determination of the molecular quadrupole moment.

The quadrupole moment is a measure of the distribution of charge within a molecule, relative to a particular molecular axis. In CO_2, for example, one measures the distribution of charge relative to the long axis, and in benzene it is relative to the C_6 rotational axis passing through the center of the hexagonal ring of carbon atoms being perpendicular to the plane of the carbon ring. Because of the high degree of symmetry present in these molecules (they all have a C_n rotational axis with $n \geq 3$), one may relate the distribution of charge perpendicular to the main rotational axis to that along the main rotational axis, thereby gaining a complete characterization of the charge distribution in the molecule.

Consider what happens on increasing the amount of symmetry in the molecule, that is, in the charge distribution. If the molecule does not have a unique rotational axis, that is, is a spherical top, as in CH_4, then the molecular quadrupole moment is identically 0 and the molecule has an octopole moment. On further increasing the symmetry present in the molecule, a spherical top with a center of inversion (that is octahedral as in sulfur hexafluoride, SF_6), the octopole moment is 0 and the molecule possesses a hexadecapole moment. These higher molecular electric moments become weaker and of less importance in their physical manifestations, for example, the boiling points of methane and SF_6 compared to water or alcohol or benzene. For an isotropic or perfectly spherical charge distribution, as in an argon atom, there are no molecular moments, which are really measures of the departure from sphericity for molecular charge distributions.

To date, there are no direct methods for the experimental determination of octopolar or hexadecapolar molecular moments. Their magnitudes, but not their phases, are determined, indirectly, from collision-induced absorption spectra, for example, the pressure-induced infrared absorption spectrum of methane. However, as the non-SI units of these properties tend to be named after the discoverer of the method of direct measurement, there is, perhaps, some incentive for further investigation.

The charge distributions of the simple aromatic molecules benzene and hexafluorobenzene are of particular interest. The quadrupole moments of these two molecules have been measured directly using the Buckingham technique of vapor-phase electric field gradient induced birefringence. The quadrupole moment of benzene is large and negative, -29.0 $\times$ 10^{-40} C m^2,[2] and that for hexafluorobenzene is large and positive, 31.7 $\times$ 10^{-40} C m^2.[2] The large negative value for benzene can be interpreted with the familiar picture of delocalized charge above and below the plane containing the six carbon atoms. In hexafluorobenzene, the electron charge density is now, due to the strong electronegativity of the fluorine atoms, contained in the plane of the carbon ring and the sign of the quadrupole moment changes, making the molecule less susceptible to chemical, electrophilic attack, an observation made and retained by every generation of organic chemistry students. Interestingly, whereas the quadrupole moments of C_6H_6 and C_6F_6 are both large, that of 1,3,5-trifluorobenzene is almost the arithmetic mean of the values of the other two, 3.1 $\times$ 10^{-40} C m^2,[3] demonstrating the bond additivity of this particular molecular property.

In any scheme of molecular interactions, it is the first nonvanishing electrical moment which will dominate the electrostatic interaction of a pair of molecules. However, the ability to predict, for example, the solid-state packing of molecules and to comprehend the observed molecular dynamics from a knowledge of the electrical properties of the isolated molecules and the measured solid-state spectra is a goal much sought after, but not easily realized. Although the strength of the various intermolecular interactions may be approximated, the problem is not straightforward.

Such structure–property relationships have been investigated in the aromatic solids benzene and hexafluorobenzene and in the binary mixture benzene/hexafluorobenzene. This latter is the simplest member of a very large class of layered organic compounds sometimes referred to as charge-transfer complexes. It

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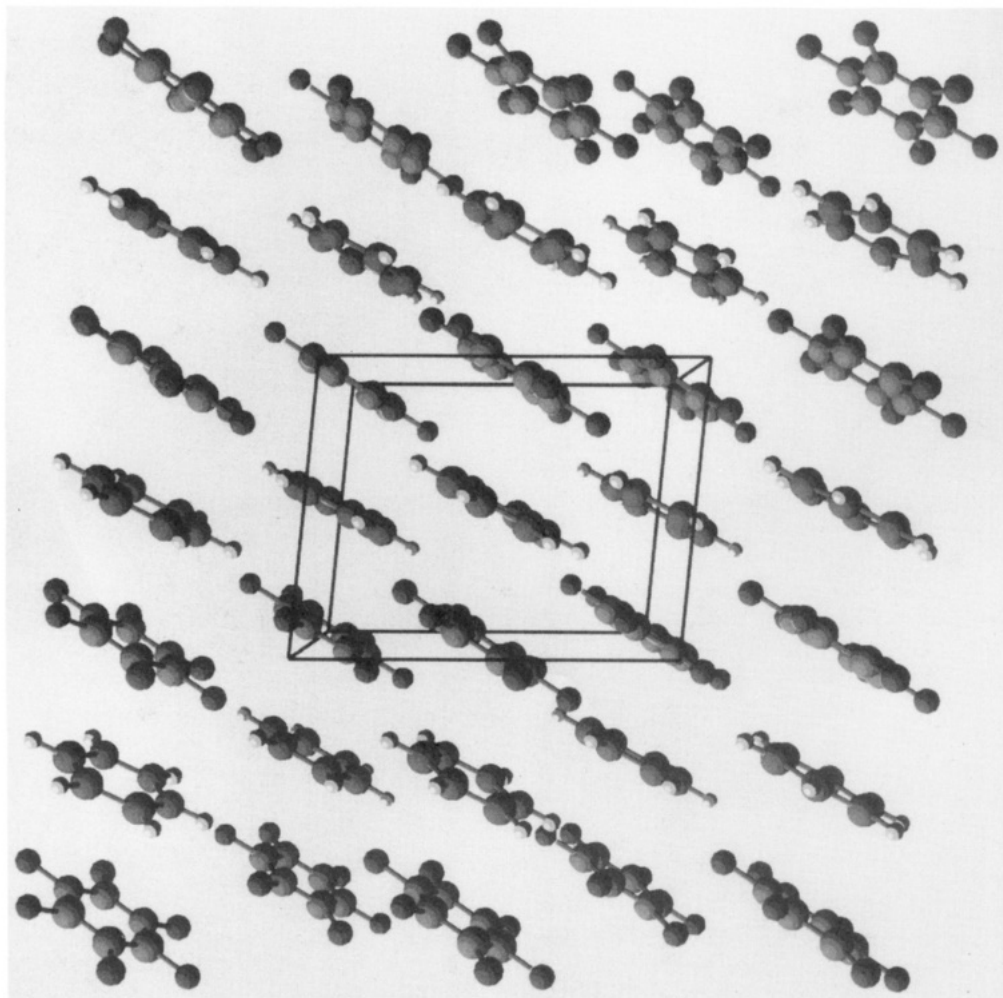
Figure 2. The structure of solid C_6H_6/C_6F_6, in its lowest temperature phase ($T < 205$ K) viewed along the b crystallographic axis, as revealed by neutron and synchrotron diffraction experiments. This structure is seen to be an example of that described in Figure 1b.

is produced by mixing equal amounts of the two component liquids at room temperature. Gas-phase investigations of the benzene/hexafluorobenzene dimer, with molecular beam electric resonance spectroscopy, revealed that the dimer is possessed of an induced dipole moment of 0.44 D.[4] That is, almost $1/8$ of an electron transferred over a typical intermolecular spacing of 3.7 Å. With such a strong intermolecular polarization, the existence of a new solid, with physical properties distinct from those of solids composed of the constituent molecules, is perhaps to be expected.

The description of these materials as charge-transfer solids arose from early ideas concerning the slighlty stronger intermolecular interactions which are displayed in these materials. For example, both benzene and hexafluorobenzene are liquids at room temperature, but the binary mixture is a solid at this temperature. It was suggested that there was a delocalized donor–acceptor or π–π* bond between the benzene and hexafluorobenzene.[5] However, a transfer of charge and the resulting orbital changes is too dramatic a description for what is actually happening. The internal vibrations of the complex show only a small frequency shift when compared to those of the pure solids.[6,7] A

few bands are split, but these are only asymmetry splittings resulting from the very different crystal structrues. The maximum difference in frequency for the vibrations of the benzene molecule in solid benzene and in solid C_6H_6/C_6F_6 are ± 5 cm^{-1}.[6,7] If appreciable charge had been transferred from benzene to hexafluorobenzene, the π electron density withdrawal from the benzene would result in a weakening of the ring framework, effecting, for example, the ring-breathing mode. Similarly, π electron density flow to the anti-bonding orbital of hexafluorobenzene would facilitate ring-breathing modes on the C_6F_6 ring. The absence of such frequency shifts in C_6H_6/C_6F_6 confirms the absence of appreciable intermolecular charge transfer, leaving a strong intermolecualr polarization as the additional contribution to the binding energy of the solid.

This new solid structure melts at a higher temperature, 298 K, than the solids composed of the pure components, both at 278 K. However, it is a structure which displays structural instabilities. Whereas pure solid benzene and pure solid hexafluorobenzene do not undergo any first-order structural phase transitions below their melting points, only a second-order transition arising from the onset of thermally driven

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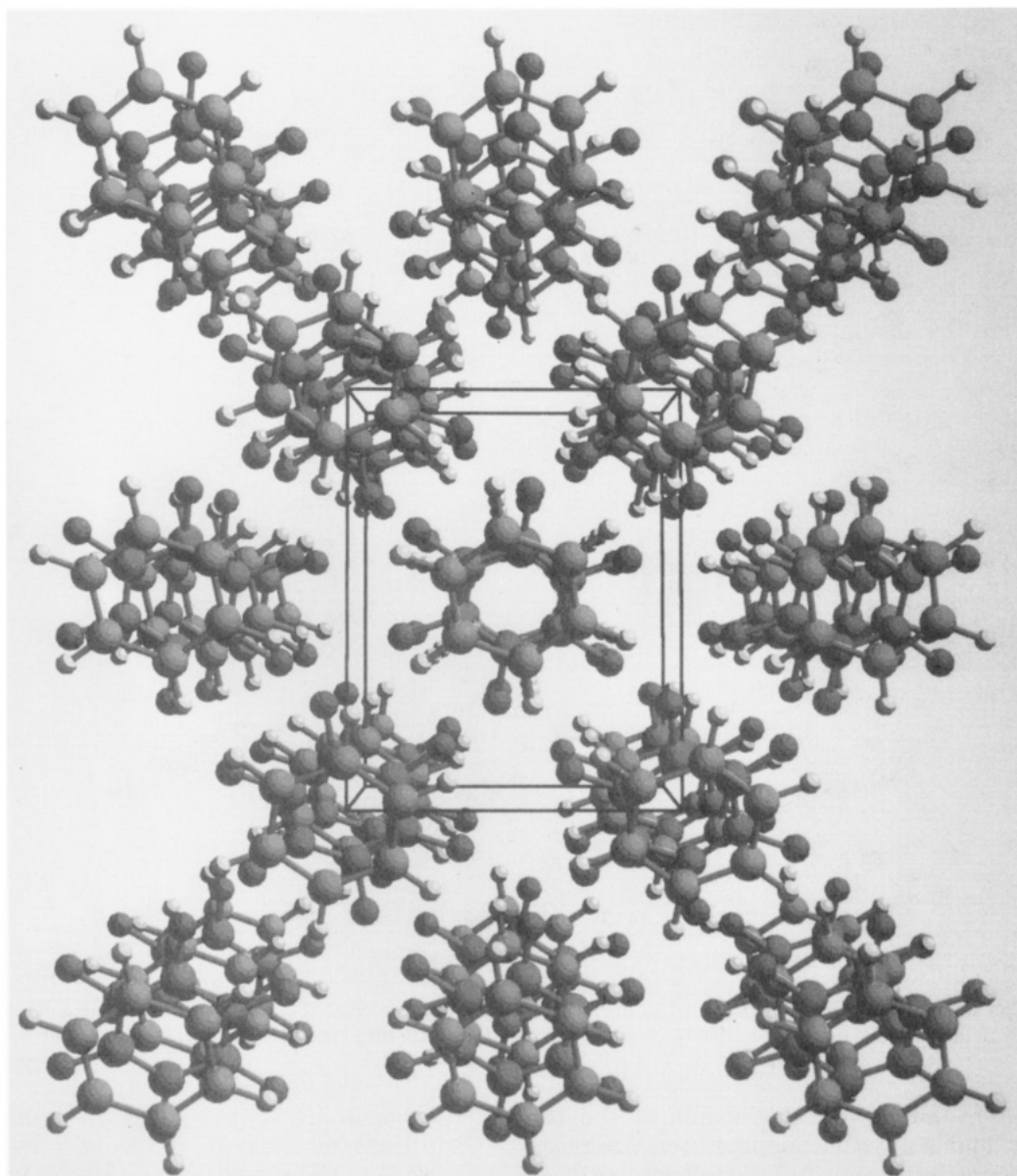
Figure 3. The structure of solid C_6H_6/C_6F_6, in its lowest temperature phase ($T < 205$ K), viewed down the c crystal axis, that is, along the long stacks of alternating benzene and hexafluorobenzene molecules.

molecular rotations, solid benzene/hexafluorobenzene undergoes three structural solid-state phase transitions in addition to the same second-order phase transition (6-fold molecular rotations) below its melting point; 205, 247, and 275 K.[8] The question naturally arises, why for similar molecules packed into solids which are held together by similar intermolecular forces should such drmatic differences in lattice dynamics occur?

Figure 1a,b is a schematic representation of the electrostatic interaction of electric quadrupole moments. The model of like charges repelling one another and unlike charges attracting one another is perfectly valid for systems containing many separated charges, that is, molecules. When the indiviual molecules interact to form a condensed phase, they will try to minimize their repulsive interactions and maximize their attractive interactions, the balance point of these two opposing forces being the familiar energy minimium, for example, the Lennard-Jones 6–12 potential. In Figure 1a we see how an assemblage of one type of

molecule, that is, one type of electric quadrupole moment, condenses to form a herringbone arrangement of molecules. The two molecular orientations present in this picture (slipped parallel, the orientation of a molecular pair along a vertical axis in this figure, and T-shaped pairwise, diagonal orientations of aromatic rings) are the two lowest energy configurations for the electrostatic interactions of quadruple moments of the same sign, for example, pure solid benzene, pure solid hexafluorobenzene, or solid carbon dioxide. That is, this arrangement of like electric quadrupole moments maximizes the electrostatic interaction energy. In Figure 1b we see how two quadrupolar molecules, of differing sign, for example, solid C_6H_6/C_6F_6, interact to produce, as the lowest energy configuration, a linear stacked structure, where a positive electric quadrupole moment is found parallel and next to a negative electric quadrupole moment.

In Figure 2 we see the structure of solid C_6H_6/C_6F_6, in its lowest temperature phase viewed along the b crystallographic axis, as revealed by neutron and

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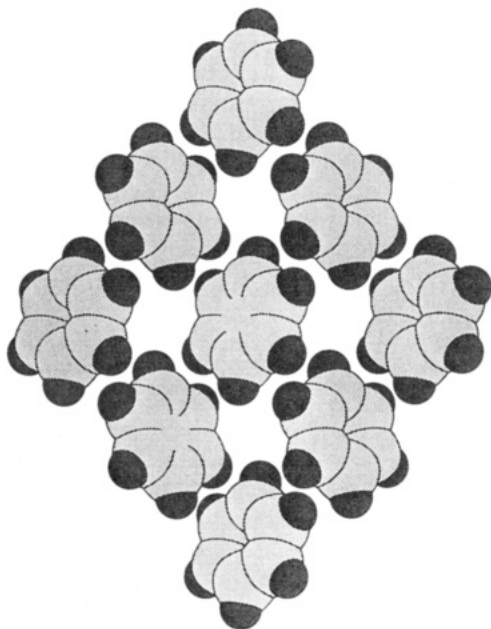
Figure 4. The structure of solid benzene as determined by neutron diffraction viewed down the *c* crystal axis. This structure is seen to be an example of that described in Figure 1a.

synchrotron diffraction experiments.[9] The binary solid C_6H_6/C_6F_6 may be described as being composed of alternating layers of benzene and hexafluorobenzene molecules, this being the most stable configuration for the electrostatic interaction of electric quadrupole moments of opposite sign, as seen in the stacked structure of Figure 1b. What is also readily observed, particularly in Figure 3 (the same structure as in Figure 2 but viewed along the *c* crystallographic axis, which almost coincides with the molecular C_6 rotational axis), is the interpenetration of the C–H and C–F bonds of molecules in neighboring columns. That is, at these low temperatures (this is the lowest temperature phase of this material, $T < 205$ K, the actual measurements being made at 25 K) the bonds on one type of molecule closely approach neighboring aromatics, indeed, aromatics of the other type. Thus C–H bonds on a benzene molecule are directed toward and come very close to F atoms of the C–F bonds of a hexafluorobenzene molecule in the layers above and below. It is possible, therefore, to envisage a network of weakly polarized hydrogen bonds as the means of stabilizing the lattice. The same model may be invoked for solid benzene; here a consideration of the crystal structure, as determined by neutron diffraction experiments,[10] Figure 4, shows that the solid is made up of slipped parallel and T-shaped pairwise orientations of aromatic rings, a herringbone structure as seen in Figure 1a. In solid benzene these weakly polarized intermolecular bonds arise because the C–H bond, the positive end of the electric quadrupole moment, points into the π cloud of a neighboring molecule, the negative end of the electric quadrupole moment.

In this analysis of the relationship between crystal structure and molecular properties, we have only considered the lowest order, intermolecular electrostatic interaction and have not considered the contribution of London dispersion forces or second-order induction forces of the type interacting quadrupole induced dipole moments. However, in a detailed analysis of the origin of the lowest temperature phase transition seen in C_6H_6/C_6F_6, we demonstrated that the induced dipole–induced dipole interaction energy, arising from the induction interaction between the vibrating molecules making up the solid, is of order a few millielectron volts,[11] whereas the quadrupole–quadrupole electrostatic interaction energy between neighboring, parallel benzene and hexafluorobenzene molecules, 3.77 Å apart,[9] is 150 meV.[11]

The dispersion interaction energy between two identical molecules, of polarizability α and ionization potential I, separated by a distance r, scales as $(I/2)\{\alpha^2/r^6(4\pi\epsilon_0)^2\}$ in SI units. If we consider benzene and hexafluorobenzene to have the same ionization potential (≈ 9 eV) and similar polarizability,[2] then with $r = 3.77$ Å[9] we find the dispersion energy to be of the same order of magnitude as the quadrupole–quadrupole interaction. However, we point to the success of our model involving electrostatic molecular quadrupole–quadrupole interactions only, in rationalizing the observed crystal structures in a number of aromatic solids, in justification of its use.

We may summarize these observations by saying that the change of polarity between the electric quadrupole moments of benzene and hexafluorobenzene can determine the overall structure of the solid, C_6H_6/C_6F_6. Similarly, we point to the electric quadrupole moment as the origin of the anisotropic intermolecular forces which determine the structure of pure solid benzene, these electrical moments being particularly large in these molecules. This model allows us to explain the columnar-like structure of alternating benzene and hexafluorobenzene molecules observed in experiment. What it does not allow us to predict so easily is the relative orientations of two neighboring columns, that is, the nearest neighbor orientations; see Figure 3.

Molecules such as benzene and hexafluorobenzene have no permanent electric dipole moment. However, they do have, or rather they may be represented as having, bond dipole moments. That is, for the aromatic molecules, partial charged structures may be constructed to represent the positive and negative molecular quadrupole moments. Over very short intermolecular distances, it may well be that we are justified in discussing the interaction of molecules much larger than or of the same size as the dimensions over which we are interested in investigating, in terms of the molecular quadrupole moment, but must instead consider the bond moments and their interactions. It is perhaps with such local models that we may be able to unravel the orientational ordering and dynamics of the columns of benzene and hexafluorobenzene molecules which constitute the binary complex. Such a model has, for example, been successful in rationalizing the barriers to 6-fold rotation of these molecules in the lowest temperature phase of C_6H_6/C_6F_6.[11]

We see, therefore, that relatively simple ideas of electrostatics are reflected in the observed solid-state architecture of materials composed of small polyatomic molecules. But what of the question of the relative

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stability of one type of quadrupolar structure over the other? Is the instability of the solid structure composed of stacked interacting quadrupole moments of differing sign, that is, its susceptibility to structural phase transitions arising from thermal fluctuations, a consequence of this particular arrangement or of the level of thermal molecular agitation within the solid?

Quasielastic neutron scattering techiques, in particular, fixed window scattering[12] (that is, the measurement of the scattering law at very low energy transfer), have been used extensively to investigate the motion of the benzene molecules in both pure solid benzene and solid C_6H_6/C_6F_6, over the same temperature range. It is observed that, at temperatures above 150 K and in both solids, the benzene molecules have sufficient energy to undergo 6-fold reorientations, that is, the molecules are observed to rotate within the solid, giving rise to a second-order phase transition. The frequency of this rotational motion, for the benzene molecules in both soilds, is found to be temperature dependent and to follow an Arrhenius-like behavior. The Arrhenius parameters, that is, a temperature-dependent activation energy, E_a, and a temperature-independent preexponential frequency, ν_0, were found to be very similar. In fact, for pure benzene, up to its melting point (278 K), $E_a = -12.5$ kJ/mol and $\nu_0 = 77$ cm^{-1},[12] and for solid C_6H_6/C_6F_6 in its lowest temperature phase, that is, up to 205 K, $E_a = -12$ kJ/mol and $\nu_0 = 73$ cm^{-1}.[12] Consequently, at the temperature of the first structural phase transition seen in C_6H_6/C_6F_6, 205 K, the benzene molecules in solid benzene and in solid benzene/hexafluorobenzene will have the same level of angular or librational excitation. Consequently, the individual molecular dynamics is not the only cause of the structural instability seen in solid C_6H_6/C_6F_6 and not in solid pure benzene or solid pure hexafluorobenzene.

That the first structural phase transition occurs at a temperature substantially higher than this onset of thermally activated rotation tells us that a certain amplitude of rotational motion is required before the lattice becomes unstable. The presence of some hysteresis in the temperature of this first structural phase

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transition can be rationalized with this necessity for a certain magnitude of rotational excitation in individual molecules before the solid lattice becomes sufficiently unstable to thermal fluctuations as to change. Indeed, it is from a study of the softening of the vibrations of the chains of molecules in these solids (the phonons) as a function of temperature that one discovers the differing stability of the various molecular arrangements, herringbone as opposed to stacked.[11]

Whereas in pure benzene, electric quadrupole moments of like polarity interact to give a solid composed of slipped parallel and T ordered pairs of molecules, in C_6H_6/C_6F_6, the opposite polarity of the quadrupole-quadrupole interaction produces stacked chains of alternating, parallel benzene and hexafluorobenzene molecules, the one structure being more stable to thermal excitations, particularly, excitations transverse to the main chain direction, than the other. Just as stacking columns of bricks one on top of another is not a sound technique for constructing buildings, it also fails to give stable extended molecular structures. Solid benzene and solid hexafluorobenzene, on the other hand, having more complex structures of overlapping and interpenetrating layers of molecules, have greater stability, even with the same level of individual molecular librational excitation. They are not so susceptible to lattice distortions and have no structural phase transitions below their melting points.

Such investigations, involving the modeling of intermolecular forces in terms of molecular electric quadrupole moments, have shown that it is possible to interpret the structure and the dynamics of solids such as C_6H_6/C_6F_6 in terms of the electrostatic interactions of the constituent molecules. This conclusion allows predictions about other aromatic layered compounds. A survey of the literature shows that most of the organic "donor–acceptor" or "charge-transfer" complexes have at least one solid-state phase transition in the same temperature range as C_6H_6/C_6F_6. Such insights into the organization and behavior of polyatomic molecules in crystal structures have profound implications for our ability to design and produce new materials with unique mechanical, optical, or electronic properties.