

ARTICLES

Intermolecular Interactions in Strongly Polar Crystals with Layer Structures

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The compounds 2-amino-5-nitropyridine, 2-amino-5-nitro-1,3-pyrimidine, and *N*-nitro-4-amino-1-hydropyridinium nitrate have two-dimensional layer structures with the molecules in each layer held together by hydrogen bonds. Although there are strong electrostatic interactions within each layer between the molecules or ions, the dispersion interaction is the dominant interlayer interaction and the driving force to decrease the interlayer distance. The interlayer distances of 2-amino-5-nitropyridine and 2-amino-5-nitro-1,3-pyrimidine crystals are only 3.04 and 3.07 Å, respectively, which are considerably less than in graphite (3.35 Å). We find that the molecules are able to pack so as to avoid C–C contacts between layers and that the separation of the layers is determined by the size of the N atoms, which are smaller. The O atoms of neighboring nitrate anions in the *N*-nitro-4-amino-1-hydropyridinium nitrate crystal are in contact (separation 2.80 Å), but the repulsion between them is overcome by the strong attraction between the anions and cations.

1. Introduction

Understanding the details of weak nonbonding interactions is important in several fields of chemistry. Intermolecular interactions control the structures of molecular clusters,¹ crystal structures of organic molecules,² structures of host–guest complexes,^{3,4} binding properties of drugs and their receptors,⁵ and properties of liquids.⁶ In addition, nonbonding interactions play a crucial role in determining the three-dimensional structures of large molecules^{7,8} including proteins⁹ and polymers.¹⁰

Crystal engineering has attracted considerable attention, since successful control of the three-dimensional structure of crystals may lead to materials with improved electrical and optical properties.^{11–13} In this field too, detailed information on nonbonding interactions is required.^{14,15} The key to success in producing such materials is the control of the arrangement of the molecules in the crystal, which affects crucially the electronic and optical properties. An example is the design of crystals for frequency doubling, which calls not only for molecules with a high hyperpolarizability β but for their crystallization in a non-centrosymmetric space group.

The importance of hydrogen bonding in controlling the crystal structure of organic molecules has been stressed repeatedly,^{11,12,14} but less attention has been given to other interactions such as dispersion and repulsion. The dispersion interaction between a pair of atoms in interacting molecules may be substantially smaller than the electrostatic interaction between the same pair of atoms, but it is always attractive, whereas the electrostatic interactions may largely cancel out. Consequently the total dispersion interaction between molecules may be of comparable magnitude to the total electrostatic interaction, especially in interactions between large molecules. More than 20 years ago Kitaigorodsky found from the observation of crystal structures that packing considerations are important in

determining structures.¹⁶ In his view, repulsion and dispersion interactions were more important than the electrostatic interaction in determining the lattice energy. Recently high-level *ab initio* calculations have shown that the dispersion interaction plays a crucial role in stabilizing the parallel-displaced structure of the neutral benzene dimer.^{17–19} Thus, if we are to understand and predict the structure of molecular crystals, it is essential that we understand the intermolecular interactions, including dispersion.

In this paper we report an analysis of the intermolecular interactions in crystals of 2-amino-5-nitropyridine, 2-amino-5-nitro-1,3-pyrimidine, and *N*-nitro-4-amino-1-hydropyridinium nitrate. These molecules are extensively used as sources of highly polarizable cations in nonlinear optical materials. Despite considerable study of cationic species of these molecules, little is known about their intermolecular interactions. Moreover their structures show features that require investigation. The interlayer separation in the first two of these structures is significantly smaller than is expected for aromatic rings, while the third has nitrate ions packed very close together, with their oxygen atoms in contact. We seek to confirm that these structures can nevertheless be understood on the basis of standard ideas and that it is not necessary to invoke extraordinary effects. This qualitative understanding is our goal here, and we do not attempt to achieve quantitative accuracy. We find that dispersion is the dominant interlayer interaction in these crystals and is important in determining the crystal structures.

We use distributed multipoles for the analysis of electrostatic interactions. The need for this is now well established.^{20–22} Recently Coombes et al.²² commented on the importance of using anisotropic atomic multipole moments for the accurate descriptions of short-range electrostatic interactions. They reported that the distributed-multipole electrostatic model with an empirical repulsion–dispersion potential was successful in reproducing the lattice vectors and heats of sublimation of crystals of rigid organic molecules, but omission of the anisotropic multipole moments usually gave very poor and sometimes qualitatively incorrect structures.

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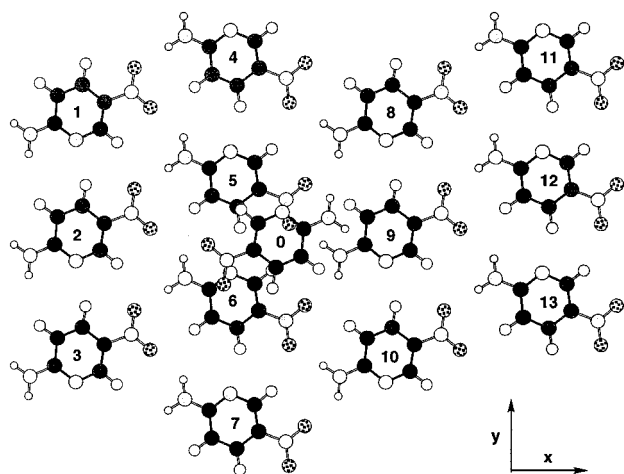


Figure 1. Structure of one layer of the 2-amino-4-nitropyridine crystal. One molecule from the next layer is also shown.

2. Method

The crystal structures reported by Aakeröy^{15,23,24} were used for the calculations, except that the positions of the hydrogen atoms were refined by HF/6-31G*²⁵ ab initio calculations on single molecules. The distributed multipoles^{26,27} were obtained from the HF/6-31G* wave function of the single molecules using CADPAC version 6.²⁸ The intermolecular interaction energies were analyzed using ORIENT version 3.2.²⁹ The calculated distributed multipoles were used for the analysis of the electrostatic interactions. The repulsion and dispersion interactions were described by simple isotropic exp-6 terms using Mirsky's parameters;^{30,31} some additional parameters not tabulated by Mirsky were obtained using a geometric mean combination rule for C_6 and harmonic and arithmetic mean combination rules for the parameters α and ρ , respectively, in the expression $\exp[-\alpha(R-\rho)]$ for the exponential atom-atom repulsion. Although Mirsky's parameters are now quite old, they are reasonably successful and are certainly adequate for a qualitative study.

3. Results and Discussion

3.1. 2-Amino-5-nitropyridine. *3.1.1. Interactions within a Layer.* Each molecule has six near neighbors in the same layer (Figure 1), but because of the crystal symmetry the six interactions are equal in pairs. For example, for molecule 5 in Figure 1, the 5-2 interaction is the same as the 5-9, 5-4 is the same as 5-6, and 5-1 is the same as 5-8. Of these in-plane interactions, 5-2 and 5-9 are the largest, at -25.36 kJ mol⁻¹; the largest component of the interaction energy in this case is the electrostatic interaction (-33.53 kJ mol⁻¹) and can be attributed largely to hydrogen bonding between the amino group of molecule 5 and the nitro group of molecule 2, but there is also a significant dispersion interaction (-15.86 kJ mol⁻¹). These figures are summarized in Table 1.

The amino group of molecule 5 is hydrogen bonded to the nitro group of molecule 1 as well as to the nitro group of molecule 2, but the 5-1 hydrogen bond is bent while the 5-2 hydrogen bond is linear, and the 5-1 interaction energy (-8.86 kJ mol⁻¹) is considerably smaller than the 5-2, the difference being mainly in the electrostatic energy (-9.24 kJ mol⁻¹ compared with -33.53 kJ mol⁻¹). The 5-4 and 5-6 interactions are only -8.19 kJ mol⁻¹. The major component here is not the electrostatic interaction (-4.62 kJ mol⁻¹) but dispersion (-14.68 kJ mol⁻¹). The sum of the intermolecular interactions between molecule 5 and the six surrounding molecules in the same layer (1, 2, 4, 6, 8, and 9) is -84.8 kJ mol⁻¹.

TABLE 1: Calculated Intermolecular Interaction Energies in the 2-Amino-5-nitropyridine Crystal (kJ mol⁻¹)

molecules	E_{es}	E_{er}	E_{disp}	E_{total}
Within a Layer				
5-2, 5-9	-33.53	24.02	-15.86	-25.36
5-1, 5-8	-9.24	8.30	-7.92	-8.86
5-4, 5-6	-4.63	11.13	-14.68	-8.19
5-(1,2,4,6,8,9)	-94.80	86.90	-76.92	-84.82
5-3, 5-10	-1.33	0.00	-0.17	-1.50
5-7	1.50	0.00	-0.08	1.42
5-11	-0.87	0.00	-0.03	-0.89
5-12	-2.05	0.00	-0.03	-2.07
5-13	-1.63	0.00	-0.03	-1.65
Between Neighboring Layers				
0-5, 0-6	-12.31	12.05	-27.44	-27.70
0-9	-0.68	2.78	-11.21	-9.11
0-(5,6,9)	-25.30	26.88	-66.09	-64.51
0-(1,2,3,4,7,8,10,12,13)	7.50	0.00	-3.77	3.73

The calculated interaction energies with more distant molecules in the plane are much smaller than these, all less than about 2 kJ mol⁻¹. The interactions between molecule 5 and the second-neighbor molecules in the same layer (3, 7, and 10-13 comprise half of this set) sum to only -12 kJ mol⁻¹.

3.1.2. Interaction between Layers. The interactions with a molecule, labeled 0, in the next layer were calculated (Figure 1). The three strongest interactions are summarized in Table 1. The 0-5 and 0-6 interaction energies, which are equal by symmetry, have the largest interaction energy of -27.70 kJ mol⁻¹. This is larger than the largest intralayer intermolecular interaction, that of the 5-2 pair (-25.36 kJ mol⁻¹), which is stabilized by hydrogen bonding. There is no hydrogen bond between molecules 0 and 5, but the nitrogen atom of the aromatic ring of molecule 0 is close to the nitro group of molecule 5. There are strong electrostatic interactions between the atoms of this nitro group and some of the atoms in molecule 0, but some are attractive and others repulsive, and the total 0-5 electrostatic interaction is only -12.31 kJ mol⁻¹. The dominant contribution is the dispersion interaction, -27.44 kJ mol⁻¹.

The second largest interlayer interaction energy is calculated for the 0-9 pair (-9.11 kJ mol⁻¹). The major component of this interaction is again the dispersion term (-11.21 kJ mol⁻¹). The sum of the interactions between molecule 0 and the three nearest molecules in the next layer (5, 6, and 9) is -64.5 kJ mol⁻¹. This total includes a dispersion contribution of -66.1 kJ mol⁻¹, which is mainly responsible for the large attractive interaction between layers. The 0-2 and 0-3 interactions are repulsive (3.23 and 4.36 kJ mol⁻¹), and the 0-4, 0-7, and 0-8 interactions are attractive (-2.76 , -2.76 , and -2.18 kJ mol⁻¹, respectively). The interaction energies of other pairs are about 2 kJ mol⁻¹ or less, and the interactions with the more distant molecules (1-4, 7, 8, 10, 12, and 13) total $+3.7$ kJ mol⁻¹.

The interaction energies with molecules in the second-neighbor layer were also calculated. The largest of these is 3.31 kJ mol⁻¹ between each molecule and the corresponding molecule in the second-neighbor layer, e.g., between 5 and 5' (Figure 1). This positive interaction is mainly due to electrostatic repulsion. The interactions of molecule 5 with molecules 6' and 7' are also repulsive. The electrostatic interaction is the dominant term in all these interactions. The interactions with other molecules in the second-neighbor layer are small. In contrast to the strong attractive interaction with the first-layer molecules, the interaction with the second-layer molecules is repulsive.

The lattice energy per molecule (ignoring zero-point energy) is half the sum of the interaction energies between one molecule

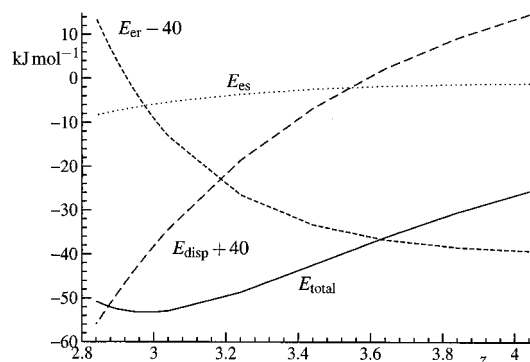


Figure 2. Variation of energy terms with distance of one molecule from two layers of the crystal.

and all the other molecules in the crystal. The sum of the interactions between one molecule and its 18 nearest neighbors in the same plane is $-97.2 \text{ kJ mol}^{-1}$, while the interaction of one molecule with the 12 nearest molecules in the first-neighbor layer on one side and the three nearest molecules in the second is $-52.6 \text{ kJ mol}^{-1}$. This leads to a lattice energy of about $(97.2 + 2 \times 52.6)/2 = 101.2 \text{ kJ mol}^{-1}$, but as this does not include a complete lattice sum, it is only a rough estimate.

To explore the separation between layers, we have calculated the interaction energy between molecule 0 and the molecules in the two neighboring layers, the first neighbor containing 16 molecules and the second neighbor containing 11 molecules, as a function of position. If the separation between molecule 0 and the first-neighbor layer is varied, the calculated interaction energy is smallest when the interlayer distance is 2.980 Å . This value is close to the experimental interlayer distance of 3.04 Å .¹⁵ Figure 2 shows the variation of the energy terms with separation; we see clearly that the electrostatic energy makes a small contribution, and the equilibrium separation arises from a balance between dispersion and repulsion.

If molecule 0 is moved parallel to the crystal planes to a new position and the distance between molecule 0 and the neighboring layer is optimized, the interlayer distance that results is always greater than the distance of 2.98 Å obtained when molecule 0 is at the position found in the crystal, and the binding energy is smaller. Thus the geometry of the energy minimum on the calculated potential energy surface agrees with the experimentally observed geometry in the crystal. This agreement suggests that the potential model is reasonably reliable, though the calculated interlayer distance is slightly smaller, at 2.98 Å , than the observed separation of 3.04 Å , implying that the balance between dispersion and repulsion is not quite correct. The optimized interlayer distance is largest ($3.24\text{--}3.28 \text{ Å}$) when molecule 0 is moved to a position where the pyridine ring of molecule 0 overlaps with the pyridine ring of a molecule in the

neighboring layer. This distance is close to the separation between layers in graphite (3.35 Å),³² though again slightly too small.

We can now understand why the interlayer separation is so much smaller in 2-amino-5-nitropyridine than in graphite. Given the structure of one plane of molecules, the position of a molecule in the next plane will be such as to maximize the attraction due to dispersion without incurring an excessive penalty from repulsion. Figure 1 shows that the position of molecule 0 is such that there are no C–C contacts between the planes; the only heavy-atom contacts are N–N contacts, and the N atom is significantly smaller than the C atom (Pauling van der Waals radius of 1.50 Å , compared with 1.70 Å for the C atoms in graphite).³³

Kitaigorodsky reported that the mutual arrangement of the molecules in a crystal is always such that the projections of one molecule fit into the hollows of adjacent molecules from the observations of organic crystals.¹⁶ Our finding agrees with this general rule. A molecule locates in the position in the crystal where the repulsion is small and the layers are able to pack close together. The analysis of intermolecular interactions shows that molecules pack in such a way as to maximize the attractive dispersion interaction.

3.2. 2-Amino-5-nitro-1,3-pyrimidine. *3.2.1. Interactions within a Layer.* The general pattern here is that same as for 2-amino-5-nitropyridine. The main interactions are listed in Table 2. Each molecule has six near neighbors in the same layer (Figure 3). Because of the crystal symmetry the 10–9 interaction is the same as the 10–11 and the 10–6 is the same as the 10–15. The 10–5 is the largest in-plane interaction, at $-40.39 \text{ kJ mol}^{-1}$; the largest component of the interaction energy in this case is the electrostatic interaction ($-64.29 \text{ kJ mol}^{-1}$) and can be attributed largely to two linear hydrogen bonds between the amino hydrogen atoms and the ring nitrogen atoms, but there is also a significant dispersion interaction ($-27.37 \text{ kJ mol}^{-1}$).

There are two bent hydrogen bonds between the ring hydrogen atoms and the ring nitrogen atoms of molecules 10 and 14. The 10–14 interaction energy ($-27.95 \text{ kJ mol}^{-1}$) is considerably smaller than the 10–5, the difference being mainly in the electrostatic energy ($-23.96 \text{ kJ mol}^{-1}$ compared with $-64.29 \text{ kJ mol}^{-1}$). The 10–9 and 10–11 interactions are $-16.59 \text{ kJ mol}^{-1}$. The major component here is also the electrostatic interaction ($-20.44 \text{ kJ mol}^{-1}$) and can be attributed largely to the hydrogen bonding between the amino group and the nitro group of these molecules. The 10–6 and 10–15 interactions are only $-8.80 \text{ kJ mol}^{-1}$. Here the dispersion interaction ($-7.17 \text{ kJ mol}^{-1}$) is slightly larger than the electrostatic interaction ($-6.97 \text{ kJ mol}^{-1}$). The sum of the interactions

TABLE 2: Calculated Intermolecular Interaction Energies in the 2-Amino-5-nitro-1,3-pyrimidine Crystal (kJ mol^{-1})

molecules	E_{es}	E_{er}	E_{disp}	E_{total}
Within a Layer				
10–5	–64.29	51.28	–27.37	–40.39
10–14	–23.96	7.96	–11.94	–27.95
10–9, 10–11	–20.44	12.52	–8.66	–16.59
10–6, 10–15	–6.97	5.34	–7.17	–8.80
10–(5,6,9,11,14,15)	–143.07	94.96	–70.97	–119.12
10–(1,2,3,4,7,8,12,13,16,17,18,19)	5.25	0.00	–0.67	4.57
Between Neighboring Layers				
21–14	–6.66	15.03	–28.61	–20.24
21–15	–4.18	3.36	–12.50	–13.33
21–10	1.16	4.38	–15.42	–9.87
21–(10,14,15)	–9.68	22.77	–56.53	–43.44
21–(5,6,9,11,13,16–19)	–1.19	0.01	–3.36	–4.55

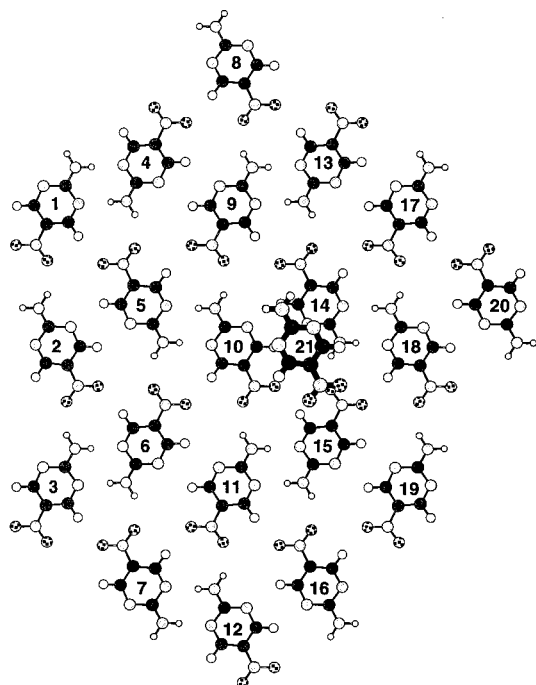


Figure 3. Structure of one layer of the 2-amino-5-nitropyrimidine crystal. One molecule from the next layer is also shown.

between molecule 10 and the six surrounding molecules in the same layer (5, 6, 9, 11, 14, and 15) is $-119.1 \text{ kJ mol}^{-1}$.

The calculated interaction energies with more distant molecules in the plane are much smaller than these, all less than 2 kJ mol^{-1} . The interactions between molecule 10 and the second-neighbor molecules in the same layer (1–4, 7, 8, 12, 13, 16–19) sum to only 4.6 kJ mol^{-1} .

3.2.2. Interactions between Layers. The interactions between the same set of molecules and a molecule in the next layer, labeled 21 in Figure 3, were calculated. Some of the calculated interaction energies are summarized in Table 2. The 21–14 interaction has the largest interaction energy, $-20.24 \text{ kJ mol}^{-1}$. The dominant contribution is the dispersion term, $-28.61 \text{ kJ mol}^{-1}$, and the electrostatic term is only $-6.66 \text{ kJ mol}^{-1}$. The second largest interlayer interaction energy is $-13.33 \text{ kJ mol}^{-1}$ for the 21–15 pair, and the third largest is $-9.87 \text{ kJ mol}^{-1}$ for the 21–10 pair. The major component of these interactions is again dispersion (-12.50 and $-15.42 \text{ kJ mol}^{-1}$, respectively). The interaction energies of other pairs are less than about 2 kJ mol^{-1} . The sum of the interactions between molecule 21 and three nearest molecules in the next layer (10, 14, and 15) is $-43.4 \text{ kJ mol}^{-1}$. This total includes a dispersion contribution of $-56.5 \text{ kJ mol}^{-1}$, which is mainly responsible for the large attractive interaction between layers. The interactions with the more distant molecules (5, 6, 9, 11, 13, 16–19) total -4.6 kJ mol^{-1} .

The interactions of the original set of molecules with a molecule in the second-neighbor layer were also calculated. The largest of these in magnitude is $-1.92 \text{ kJ mol}^{-1}$.

We have calculated the interaction energy between a molecule and the molecules in the two neighboring layers, each containing 15 molecules, as a function of position. If the separation between the molecule and the first layer is varied, the calculated interaction energy is smallest when the interlayer distance is 2.966 \AA . This value is close to the experimental interlayer distance of 3.07 \AA ;²³ again it is slightly too small. The variation of the electrostatic energy with separation is small, and as before, the equilibrium separation arises from the balance between dispersion and repulsion.

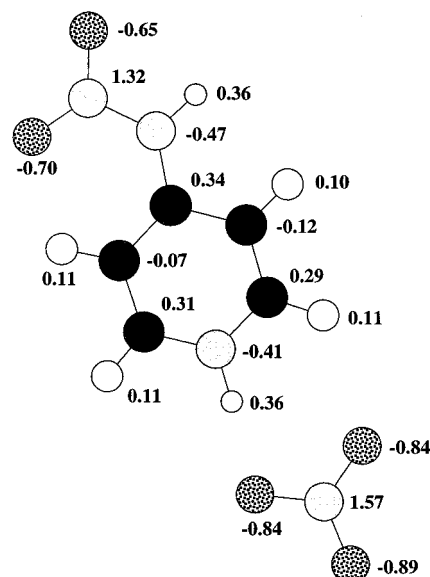


Figure 4. Charge distribution in *N*-nitro-4-amino-1-hydropyridinium nitrate.

TABLE 3: Calculated Intermolecular Interaction Energies in the *N*-Nitro-4-amino-1-hydropyridinium Nitrate Crystal (kJ mol^{-1})

molecules	E_{es}	E_{er}	E_{disp}	E_{total}
10–14, 10–15	286.25	2.72	–3.44	285.54
10–10'	–401.12	59.91	–26.08	–367.28
10–11', 10'–9	–350.83	51.90	–26.42	–325.35
10–15', 10'–14	–318.73	10.70	–11.10	–319.13
5'–10', 6'–10'	138.93	7.04	–11.86	134.12
10–(14,15,10',11',15)	–498.18	127.95	–70.48	–440.68
10'–(9,10,14,5',6')	–792.82	136.59	–87.32	–743.52

The arrangement of the 2-amino-5-nitro-1,3-pyrimidine molecules in the crystal is such that there are no C–C contacts between the planes; the only heavy-atom contacts are again N–N contacts as in the crystal of 2-amino-5-nitropyridine (Figure 3). It is clear that molecules locate in positions in the crystal where the repulsion is small, so that the interlayer distance is minimized and the attractive dispersion interaction is maximized.

3.3. *N*-Nitro-4-amino-1-hydropyridinium Nitrate. **3.3.1. Interactions within a Layer.** The crystal structure of *N*-nitro-4-amino-1-hydropyridinium nitrate is shown in Figure 5, and the calculated charge distributions of the anion and cation are shown in Figure 4. The nitro-amino group in the cation is nearly neutral, and the aromatic ring carries a positive charge. The nitrate anions are located close to the positively charged aromatic rings in the crystal, and there is a hydrogen bond between the ring NH and one of the O atoms of the nitrate ion.

The calculated interaction energies are summarized in Table 3. The primed labels refer to the cations and the unprimed ones to the anions. Each nitrate anion has two neighboring anions and three neighboring pyridinium cations (Figure 5). The interactions between neighboring nitrate anions, e.g. 10–14, are all equal by symmetry. The total interaction is $285.54 \text{ kJ mol}^{-1}$ and is largely electrostatic ($286.25 \text{ kJ mol}^{-1}$). The interactions of each anion with the three neighboring cations are strongly attractive: -367.28 for 10–10', -325.35 for 10–11', and $-319.13 \text{ kJ mol}^{-1}$ for 10–15'. The largest component of the interaction energy is again electrostatic (-401.12 , -350.83 , and $-318.73 \text{ kJ mol}^{-1}$, respectively). The sum of the interactions between nitrate anion 10 and the surrounding two anions and three cations is $-440.7 \text{ kJ mol}^{-1}$.

Likewise, each pyridinium cation has two neighboring cations

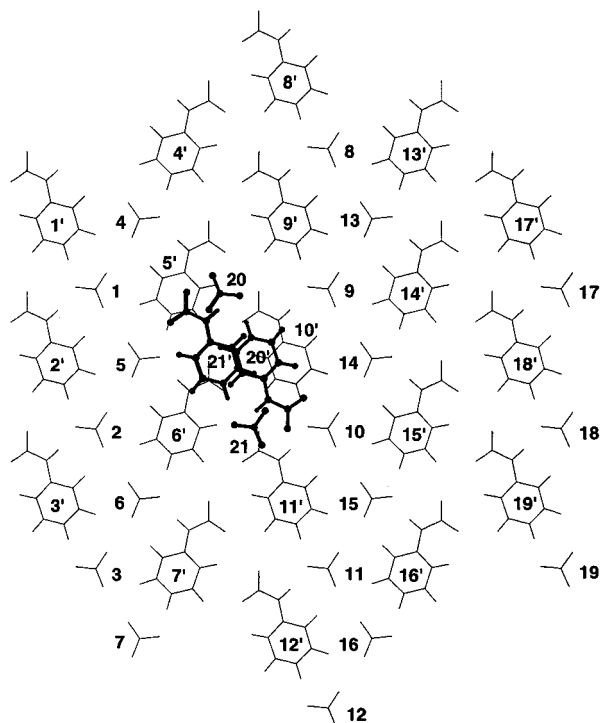


Figure 5. Structure of one layer of *N*-nitro-4-amino-1-hydropyridinium nitrate. One molecule from the next layer and one from the second-neighbor layer are also shown.

and three neighboring nitrate anions. The 5'–10' and 6'–10' interactions are the same (134.12 kJ mol⁻¹). The largest component of the interaction energy is electrostatic (138.93 kJ mol⁻¹). The 10'–14' interaction (and the 10'–15', which is equal by symmetry) is more repulsive than the 5'–10' interaction (192.17 kJ mol⁻¹ compared with 134.12 kJ mol⁻¹), even though the ions are somewhat further apart. There is an attractive electrostatic attraction between the oxygen atoms of the nitro group of 10' and the aromatic ring of 5' which mitigates the overall electrostatic repulsion. The sum of the interactions between a pyridinium cation and the surrounding two cations and three anions is -743.5 kJ mol⁻¹.

The interaction between ions decays only slowly with distance, so there are substantial electrostatic interactions between more distant ionic species. For example, the 10–1, 10–1', 10'–1, and 10'–1' interactions are 83.72, -69.51, -99.41, and 81.35 kJ mol⁻¹, respectively. However, the sum of these is only -3.85 kJ mol⁻¹, and in general the total interaction of an anion–cation pair with another distant anion–cation pair is small. It is predominantly dipole–dipole in nature, so it decays with distance like $1/R^3$, and an accurate calculation of the lattice energy would require Ewald summation. We have not carried out such a summation, however, as it would not affect the qualitative picture of the interactions.

The characteristic and rather remarkable feature of the crystal structure is the very short distance between the oxygen atoms of neighboring nitrate anions.²⁴ This distance is only 2.80 Å, which is just twice the Pauling van der Waals radius of 1.40 Å,³³ and less than twice the Bondi van der Waals radius of 1.52 Å,³⁴ so these atoms are in contact. It is tempting to postulate some unfamiliar attractive interaction that might overcome the expected electrostatic and exchange repulsion. However the interaction between neighboring nitrate anions is very large and repulsive—571.1 kJ mol⁻¹—just as one would expect. It is the even stronger attractive interaction with neighboring cations that overcomes this repulsion and makes the structure stable overall. Also, the nitrate anions are twisted in the crystal to decrease the repulsion between oxygen atoms, as shown in Figure 6.

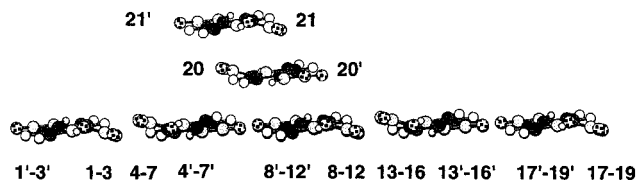


Figure 6. View along a layer of *N*-nitro-4-amino-1-hydropyridinium nitrate. One molecule from the next layer and one from the second-neighbor layer are also shown. Note the puckering of the layer, especially the way that neighboring nitrate ions are twisted away from each other.

3.3.2. Interactions between Layers. The interactions of the same set of ions with an anion and a cation in the next layer, labeled 20 and 20' in Figures 5 and 6, were calculated. As expected, the ion–ion interactions are large: 195.97 kJ mol⁻¹ for the 20–5 pair, 250.56 kJ mol⁻¹ for 20'–10', and -293.34 kJ mol⁻¹ for 20–5'. However the attractions and repulsions largely cancel, and the total interlayer interaction is not large. The total interaction energy of the anion–cation pair 20 and 20' with the 19 anions and 19 cations considered in the neighboring layer is only -109.0 kJ mol⁻¹; of this, -90.7 kJ mol⁻¹ is dispersion and -48.2 kJ mol⁻¹ is electrostatic.

The interactions with an anion and a cation in the second neighboring layer, labeled 21 and 21' in Figures 5 and 6, were calculated. Some ion–ion interactions are still larger in magnitude than 150 kJ mol⁻¹. The total interlayer interaction is slightly repulsive, in contrast to the interaction with the first neighboring layer: the total interaction energy of the anion–cation pair 21 and 21' with the 19 anions and 19 cations in the original layer is +30.5 kJ mol⁻¹. Of this, +36.8 kJ mol⁻¹ is electrostatic.

We have calculated the interaction energy of an anion–cation pair with the molecules in the two neighboring layers, each containing 19 anions and 19 cations, as a function of position. If the separation between these ions and the first layer is varied, the calculated interaction energy is smallest when the interlayer distance is 2.94 Å. This value is close to the experimental interlayer distance of 3.06 Å;²⁴ as before, it is somewhat too small. Once again, the variation of the electrostatic energy with separation is small, and equilibrium separation arises from the balance between dispersion and repulsion. We note again that a quantitative calculation would require Ewald summation of the electrostatic interactions, but we would not expect this to modify the qualitative picture.

4. Conclusion

The 2-amino-5-nitropyridine and 2-amino-5-nitro-1,3-pyrimidine crystals have layer structures with molecules in each layer held together by hydrogen bonds. The dominant intermolecular interaction within the layers in these crystals is electrostatic, mainly associated with hydrogen bonding. On the other hand, the interaction between layers is dominated by dispersion, even though these molecules have polar functional groups and there is an attractive electrostatic contribution.

The separations between the layers of 2-amino-5-nitropyridine and 2-amino-5-nitro-1,3-pyrimidine, at 3.04 and 3.07 Å, respectively, are significantly smaller than in graphite (3.35 Å). This is due to the fact that the aromatic ring of a molecule in one layer can pack into a region in the next layer which is occupied by nitrogen and oxygen atoms, which are smaller than carbon atoms.

We find that the interlayer equilibrium separation arises from a balance between dispersion and repulsion and that the electrostatic term varies little with separation between layers. We have also found that the position of a molecule relative to

the neighboring layer is controlled mainly by repulsion and the molecule locates in the position in the crystal where the repulsion interaction is small and the layers are able to pack closer to maximize the attractive dispersion interaction. Thus the repulsion and dispersion interactions have important roles to play in controlling the crystal structures of these molecules, and electrostatic interactions between layers are much less important.

The *N*-nitro-4-amino-1-hydropyridinium nitrate crystal also has a layer structure. The interactions between ions are dominated by the electrostatic interaction, but the electrostatic interactions between layers largely cancel out, and surprisingly the total interlayer interaction is dominated by dispersion, just as in the crystals of neutral 2-amino-5-nitropyridine and 2-amino-5-nitro-1,3-pyrimidine. Thus it is important to take account of the dispersion interaction to understand and predict the structures not only of crystals of neutral polar molecules but also of ionic crystals.

The neighboring nitrate anions in the *N*-nitro-4-amino-1-hydropyridinium nitrate crystal are separated by oxygen–oxygen distances of 2.80 Å, so that they are in contact. This does not however imply any sort of unusual attraction between them; there is in fact a strong repulsion between the neighboring anions, which however is overcome by the anion–cation attraction.

We conclude that no unusual effects need to be invoked to understand the unusual features of these crystal structures. It is encouraging that, here as elsewhere, the well-understood electrostatic, dispersion, and repulsion terms of the theory of intermolecular forces are sufficient to describe the energetics of crystal structures.

References and Notes

- (1) Buckingham, A. D.; Fowler, P. W.; Hutson, J. M. *Chem. Rev.* **1988**, 88, 963.
- (2) Wright, J. D. *Molecular Crystals*; Cambridge University Press: Cambridge, 1987.
- (3) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, 112, 5525.
- (4) Askew, B.; Ballester, P.; Buhrand, C.; Jeong, S.; Parris, K.; Williams, K.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1989**, 111, 1082.
- (5) Williams, D. H.; Westwell, M. S. *Chemtech* **1996**, 17.
- (6) Jorgensen, W. L. *J. Chem. Soc.* **1984**, 106, 6638.
- (7) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monographs; American Chemical Society: Washington, DC, 1982.
- (8) Dale, J. *Stereochemistry and Conformational Analysis*; Verlag Chemie: New York, 1978.
- (9) Hunter, C. A.; Singh, J.; Thornton, J. M. *J. Mol. Biol.* **1991**, 218, 837.
- (10) Tsuzuki, S.; Uchamaru, T.; Tanabe, K. *J. Phys. Chem.* **1993**, 97, 1346.
- (11) Desjariu, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, 1989.
- (12) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 1304.
- (13) Aakeröy, C. B.; Nieuwenhuyzen, M. K. *J. Am. Chem. Soc.* **1994**, 116, 10983.
- (14) Aakeröy, C. B.; Seddon, K. R. *Chem. Soc. Rev.* **1993**, 22, 397.
- (15) Aakeröy, C. B.; Nieuwenhuyzen, M. in preparation.
- (16) Kitaigorodsky, A. I. *Molecular Crystals and Molecules*; Academic Press: New York and London, 1973.
- (17) Hobza, P.; Selzle, H. L.; Schlag, E. D. *J. Am. Chem. Soc.* **1994**, 116, 3500.
- (18) Tsuzuki, S.; Uchamaru, T.; Mikami, M.; Tanabe, K. *Chem. Phys. Lett.* **1996**, 252, 206.
- (19) Jaffe, R. L.; Smith, G. D. *J. Chem. Phys.* **1996**, 105, 2780.
- (20) Fowler, P. W.; Buckingham, A. D. *Chem. Phys. Lett.* **1991**, 176, 11.
- (21) Willock, D. J.; Leslie, M.; Price, S. L.; Catlow, C. R. A. *Mol. Cryst. Liq. Cryst.* **1993**, 234, 499.
- (22) Coombes, D. S.; Price, S. L.; Willock, D. J.; Leslie, M. *J. Phys. Chem.* **1996**, 100, 7352.
- (23) Aakeröy, C. B.; Nieuwenhuyzen, M. In preparation.
- (24) Aakeröy, C. B.; Nieuwenhuyzen, M. In preparation.
- (25) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, 28, 213.
- (26) Stone, A. J. *Chem. Phys. Lett.* **1981**, 83, 233.
- (27) Stone, A. J.; Alderton, M. *Mol. Phys.* **1985**, 56, 1047.
- (28) Amos, R. D. *CADPAC: The Cambridge Analytic Derivatives Package, Issue 6*, Tech. rep., University of Cambridge, 1995, A suite of quantum chemistry programs developed by R. D. Amos with contributions from I. L. Alberts, J. S. Andrews, S. M. Colwell, N. C. Handy, D. Jayatilaka, P. J. Knowles, R. Kobayashi, K. E. Laidig, G. Laming, A. M. Lee, P. E. Maslen, C. W. Murray, J. E. Rice, E. D. Simandiras, A. J. Stone, M. D. Su, and D. J. Tozer.
- (29) Stone, A. J.; Dullweber, A.; Hodges, M. P.; Popelier, P. L. A.; Wales, D. J. *Orient: a program for studying interactions between molecules, version 3.2*; University of Cambridge: Cambridge, 1995.
- (30) Mirsky, K. In *Computing in Crystallography*; Schenk, R., Olthoff-Hazenkamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, 1978; p 169.
- (31) Stone, A. J. *The Theory of Intermolecular Forces*; International Series of Monographs in Chemistry; Clarendon Press: Oxford, 1996.
- (32) Franklin, R. E. *Acta Crystallogr.* **1951**, 4, 253.
- (33) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
- (34) Bondi, A. J. *J. Phys. Chem.* **1964**, 68, 441.