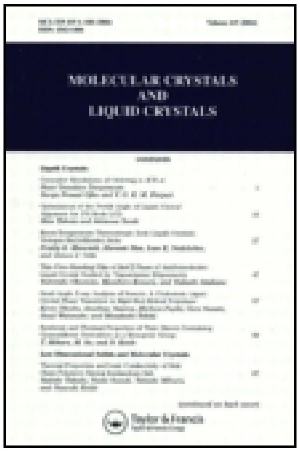

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Theoretical Analysis of the Packing and Polimorphism of Molecular Crystals Using Quantum Mechanical Methods: The Packing of the 2-Hydro Nitronyl Nitroxide

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THEORETICAL ANALYSIS OF THE PACKING AND POLIMORPHISM OF MOLECULAR CRYSTALS USING QUANTUM MECHANICAL METHODS: THE PACKING OF THE 2-HYDRO NITRONYL NITROXIDE.

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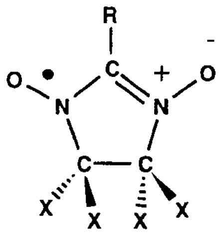
Abstract The crystal packing of molecular crystals can be rationalized using quantum mechanical ab initio methods. This work describes the principles in which this approach is based, applying the basic principles to the 2-hydro nitronyl nitroxides. Two forms of packing analysis using ab initio methods are described. The first one is based on the use of the molecular electrostatic maps for the molecules. The second one uses the information about the strength of the molecular interactions present in the crystal provided by accurate ab initio computations from model systems. Using this information it is possible to rationalize the packing in terms of primary, secondary and so on structures. For the 2-hydro nitronyl nitroxide radical the $C(sp^2)$-H···O contacts should be the driving force behind the primary structure of the packing, while the $C(sp^3)$-H···O contacts should be responsible of the secondary structure. The N-O···O-N contacts are found to be repulsive.

INTRODUCTION

It is commonly accepted that the presence of magnetism in a molecular crystal and its dimensionality depends on the way the crystal packs, that is, on the distance and relative spatial orientation of the molecules which constitute the crystal.[1] Small changes in the molecular structure create changes in the crystal packing which give rise to a modification in the macroscopic observed magnetic properties. This is the commonly accepted justification for the wide variation of magnetic properties found within families of compounds. Therefore, understanding and controlling the factors which govern the packing of these crystals is a key step towards the design of molecular magnetic crystals. This is the aim of this work, where our attention is focused in rationalizing the packing of the simplest member of the nitronyl nitroxide family of radicals, the 2-hydro nitronyl nitroxide radical (hereafter identified as HNN), using the information from ab initio quantum mechanical methods and from the distance analysis of the crystal.

The nitronyl nitroxide radicals is one of the most interesting families in the field of organic ferromagnetism. Their general formula is:



In this rather large family, the HNN radical is the member with R=H. It was first synthesized by Ullman et al.[2] and a recent study[3] has allowed to find two crystal phases (thereafter identified as the α-HNN and β-HNN phases) which show an antiferromagnetic behavior. A thermal analysis of the α-HNN phase[3,4] in the 40-160 °C range shows the presence of an irreversible transition to the more stable β-HNN phase at 60.2 °C. At 105.4 °C the α-HNN crystals begins thermal decomposition.

Why to select the HNN radical as the focus of our study and not another member of the nitronyl family showing ferromagnetism?. There are various reasons for this choice, the first one being the size of the molecule, which allows to use highly accurate ab initio methods and test options at a lower computational cost. Furthermore, this radical presents an interesting and well documented polymorphism which it is interesting to study. Last but not least, the HNN molecule is a good model to understand the packing properties of the five member ring part of the nitronyl nitroxide family. This information can then be combined with the packing behavior of the R group to predict the expected packing of any molecule of the nitronyl nitroxide family.

PACKING STRUCTURE AND INTERMOLECULAR FORCES

According to the modern ideas about the design of molecular crystals,[5] except in some simple cases, it is possible to predict only one packing structure from a theoretical analysis. Instead one should expect to find a set of structures, which hopefully contains the experimental ones. Each of these minimum structures is one of the polymorphs the crystal can present, often a set of 10 structures which differ by less than 2 kcal/mol from the most stable one for each symmetry group of the crystal. Consequently, we are facing a problem of multiple minima (each polymorph) separated by small or large energetic barriers. The experimental structures are not necessarily the most stable ones, as kinetic and other factors can play an important role in the way the crystal grows in a saturated solution. The problem is similar to that of finding the minimum structures in a molecule or molecular aggregate.

Computationally, the problem of finding one minimum for the molecular crystal is one of locating the geometrical arrangement of the molecules which minimizes the packing potential energy of the crystal, which is normally written as a sum over all the pairs of the possible pair intermolecular interactions:

$$E = \sum' E_{ij}(r_{ij})$$

being $E_{ij}(r_{ij})$ any of the intermolecular interactions between atoms i and j located at a distance r_{ij}. To lower the computational cost, in many cases the geometry of the interacting molecules is considered to be frozen, based on the fact that for weak intermolecular interactions the geometrical distortions in the interacting molecules is small.

The shape of the $E_{ij}(r_{ij})$ intermolecular potential results from the addition of the following four components: repulsive (V_{rep}), electrostatic (V_{ele}), induction (V_{ind}) and dispersion (V_{dis}). The first one is always repulsive and is proportional to the overlap of the electron distributions. It is only important at short distance and is responsible for the so called repulsive wall which avoids the collapse of one atom atoms into another. The remaining three components are all attractive and have the following form:

$$V_{ele} = -\frac{1}{4\pi\varepsilon_o}\frac{q_i q_j}{r_{ij}} - \frac{2}{3\,k\,T\,(4\pi\varepsilon_o)^2}\frac{\mu_i^2\mu_j^2}{r_{ij}^6}$$

$$V_{ind} = -\frac{1}{(4\pi\varepsilon_o)^2}\frac{(\mu_i^2\alpha_j + \mu_j^2\alpha_i)}{r_{ij}^6}$$

$$V_{dis} = -\frac{3}{4(4\pi\varepsilon_o)^2}\frac{\alpha_i\alpha_j}{r_{ij}^6}\frac{I_i I_j}{(I_i + I_j)}$$

V_{ele} is the dominant term if the molecules have net charge. In the other case is also important and, in general, $V_{ele} > V_{ind} > V_{dis}$. This is specially true for systems with strong dipole moments, as the many nitronyl nitroxides.

One can simplify the analysis centering our attention in the energetically dominant interactions. As the shape of the $E_{ij}(r_{ij})$ intermolecular interactions is a Morse curve, the most important energetic contributions come from interactions located close to the minimum of the curve. The shortest intermolecular contacts to any given atom are small in number and are statistically located in the space along the directions in which the interaction is more stable. This is the base of the statistical analysis of intermolecular interactions. As one increases the distance, the number of contacts increases, but they are located in all the directions of the space. At very large distances, they can be considered as uniformly distributed in the space, thus creating an isotropic Madelung field. This field is the one created by the rest of the crystal in any given atom in its interior and works like the external field in a particle in a box model and stabilizes the energetic levels of the overall system and, in this way, the $E_{ij}(r_{ij})$ interactions. As all intermolecular interactions will feel a similar Madelung field, probably it is not going to change the relative stability of the various minima or the barrier connecting them.

The next step is to understand the nature of each dominant intermolecular interactions present in the crystal. One can classify the intermolecular contacts that a molecule can make in three not always well defined different classes:[6]

1) Ionic interactions: Formed when the atoms i and j are charged. In these interactions the dominant term is the first one in the V_{ele} component. These interactions are long range (they are proportional to $1/r_{ij}$) and isotropic (i.e., the field created by each atom does not depend on the any of the angles). Their strength can be as large as 20 kcal/mol.

2) Hydrogen bonds: A functional definition is one that associates this bonds to the presence of a short X-H···Y interaction, with the X-H group pointing to the lone pairs of the Y atom.[7] The X-H group is called the proton donor or acid group, while the Y atom is the proton acceptor or basic group. It becomes stronger as the atoms X and Y become more electronegative. In these cases the interaction is dominated by the electrostatic component and can be easily visualized as $X^{\delta-}\text{-}H^{\delta+}\cdots Y^{\delta-}$. It is short range (proportional to $1/r_{ij}^{6}$) and directional. It is also very specific: it requires the presence of two complementary groups with potential acid (X-H) and basic (Y) characters. These groups can be easily identified, as we will see later by inspection or, more systematically, analyzing the molecular electrostatic potential (MEP) maps[7] of the molecule or aggregate. The optimum strength normally is between 5 and 0.5 kcal/mol.

3) van der Waals interactions: Linked to the presence of short contacts between the lone pairs of two atoms which have no dangling bond, as the oxygen atom in a carbonyl

group. It can be represented by the X:····:Y symbol and is the weakest of the three types of intermolecular interactions. It just shows up when all except the V_{dis} component become negligible, being its size proportional to the polarizability of the X and Y atoms. It is also short range (proportional to $1/r_{ij}^6$) and not very directional. The optimum values are smaller than 0.5 kcal/mol in general.

If the molecule is non ionic, as is the HNN case, the only two possible types of intermolecular interactions are of the hydrogen bond or van der Waals type. Both types of bonds are formed when the adequate complementary groups are close to each other. The second type is weaker and is not going to be the driving force of the packing, except when very weak hydrogen bonds are present. Thus we can center our attention in localizing hydrogen bonds by looking at the potential as acid or basic hydrogen bond groups of the most external atoms of the molecule. In the HNN case, these atoms are all except the $C(sp^3)$ atoms attached to the nitrogens. Once this character has been established, one has to find ways of attaching the acid and basic groups to form dimers, trimers, and higher aggregates. Previous experiences with high order aggregates shows that the most stable aggregate is that which makes the higher number of intermolecular contacts even if the geometry is not the most stable one for the dimer. This trend was long time ago recognized by Etter[6] and is implied in the maximum density packing principle suggested by Kitaigorodsky.[8] The various stable options correspond to the different polymorphs. The barrier to go from one to other polymorph is, like in the case of the covalent bonds, associated to the energy involved in the breaking the intermolecular bonds of one polymorph while the news ones of the other polymorph are being created.

How to define in a systematic and precise way the acid or basic capabilities of a part of a molecule, in particular, of the HNN molecule ?. This can be done with the help of the MEP maps,[7] which not only indicate the nature of the functional group present in the molecule but give some indications about their relative strength. It is not well established at the present moment the issue of the maximum number of contacts one functional group can accept but a rule of thumb commonly accepted is that the maximum number of X-H···Y contacts that can be made to an atom Y is equal to the number of lone pairs on this atom.

The MEP map of a molecule is a representation of the regions where a +1 point charge is attracted or repelled as a function of its position in the space around the molecule.[7] Regions of large accumulation of electron density trend to be attractive, while these regions where the electron density has been depleted have the tendency of being repulsive. A simple way of locating these regions is by inspection of the atomic charges located on each atom. This is not a quantum observable and various methods have been devised to compute this property, not all arriving to the same result for the HNN molecule. Figure 1 shows the

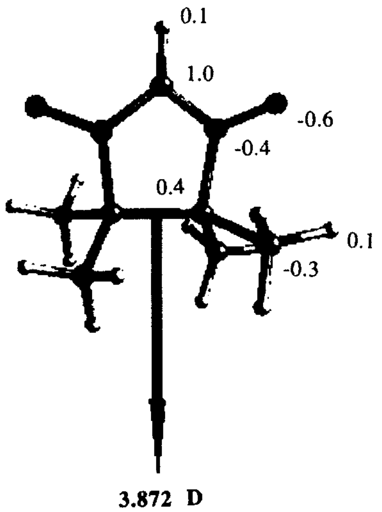


FIGURE 1.- Net charges (in atomic units) located on the atoms according to Bader's Atoms-in-Molecules algorithm. The dipole moment is also shown by an arrow.

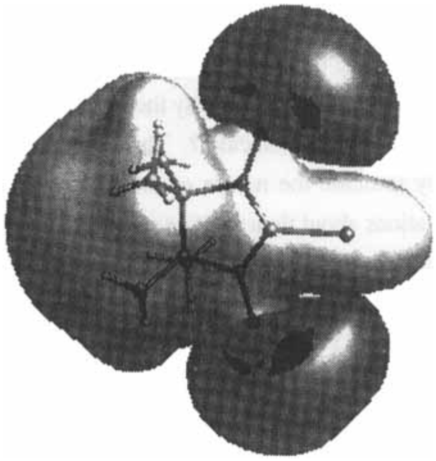


FIGURE 2.- MEP map of the HNN molecule.

values obtained by doing a numerical integration of the atomic region, defined according Bader criteria. Thus, one can expect the C-H groups to be acid groups and the N-O groups to be basic. These conclusions are in total agreement with these obtained analyzing the MEP map (see Figure 2). This map shows the presence of a strong attractive region in the same positions where one would expect to find the lone pairs of the oxygen atoms, and a positive region over the C-H bonds and over the five member ring. Therefore, the C-H bonds are expected to be acid groups in the hydrogen bond and the N-O groups basic groups. Two minimum are found over each oxygen, indicating the possibility of accepting two C-H bonds each.

The combination of an acid and basic group always gives an stable contact when isolated in gas phase and the minimum of this contact is at the optimum intermolecular distance for that acid-base combination. The presence of other groups in nearby positions can affect the formation of this bond or even make it impossible. To find the possible orientations in which attractive hydrogen bonds can be made for dimer one just has to overlap the attractive and repulsive regions of the MEP maps (which correspond to electron excess or deficient regions). This procedure can be extended to find the possible stable conformations of aggregates of any size. The process is very similar to that of finding all the topologies to connect bonds of different type following a lock-and-key rule. Notice that for crystals one requires that the structures obtained present long range order. When all of these things are combined, the number of ways the molecules can be associated is very small compared with all the possible combinations of dimers.

APPLICATION TO THE PACKING OF THE 2-HYDRO NITRONYL NITROXIDE RADICAL

The application of the previous ideas can be illustrated for the HNN case, looking at the possible ways of forming planes of long range ordered molecules. Figure 3 shows some possible arrangements of HNN molecules in the plane. Each molecule is represented by a circle with lines attached to it, which represent the acid and basic groups: the acid groups have an arrow at their end, while the basic groups have an inverted arrow at their end. The lines are placed along the same relative orientations in which the groups are located respect to the center of mass of the molecule. Arrangement **a** corresponds to a situation in which the methyl groups are linked to the NO groups. The propagation of this structural motif gives rise to a perfectly ordered plane with long range order. This is not the case or arrangement **b**, similar to the previous one but with the molecules of the second column rotated 120°, in order to make news $C(sp^2)$-H···ON contacts and the methyl···ON also present in **a**. When the packing motif is propagated along one direction gives rise to strips but there is no obvious way to propagate along a second direction in the plane without introducing disorder, that is, no long order is found for arrangement **b**. This is not the case of the other four arrangements, which have been selected among many others because present two dimensional long range order. For arrangement **c** we represent two parallel strips, each with the shape the letter z, and connected by (methyl)$_2$···NO bridges. This is just a possible polymorph of **a**. Arrangements **d**, **e** and **f** are just three possibilities obtained by association of dimers. cases **d** and **f** are obtained from the same dimer modifying the relative orientation, a triangle in the first case and a pentangle in the second. The dimer used in arrangement **d** and **f** is obtained after forming two C(sp^2)-H···ON contacts. The dimer used in arrangement **e** is the result of forming simultaneously one C(sp^2)-H···ON contact and one methyl ···ON contact. This is just a pale reflection of the multiple possibilities open. Obviously, at the three dimensional level the situation is even more complex, so one does not have to be surprised of finding many polymorphs within a small energetic range.

The number of possibilities to deal with can be greatly reduced if one is interested in the most stable polymorphs. This implies that one has to determine the strength of the intermolecular interactions present in the packing. If this is the case, one can select only these arrangements which maximize the number of strong contacts. The aggregate which saturates all the strong bonds is the primary structure of the packing. These aggregates sometimes still have the possibility of forming more intermolecular contacts with other aggregates using its weaker intermolecular bonds. In this case, we have an association of aggregates or secondary structure of the packing. Higher order structures (tertiary and so on) could be formed in some cases via the intermolecular contacts which have not been used up to now. As one goes to higher level structures of the packing, the hydrogen bonds still not used are weaker and their strength can be similar to that for typical van der Waals interactions. So, while hydrogen bonds and ionic interactions are expected to be the main forces controlling the primary structure and probably the secondary, higher orders can be influenced in some cases by the possible van der Waals interactions.

As mentioned above, defining the intermolecular interactions responsible of the primary and secondary structures of the packing implies a knowledge of the relative strength of the possible intermolecular interactions the molecular aggregates can make. This information can be obtained from various sources: MEP analysis, statistical analysis of crystals, ab initio computations. The MEP maps, can give us a first preliminary idea about relative strengths and type of bonds of the possible hydrogen bonds, but if reliable predictions are wished one has to obtain more accurate values. The statistical analysis of the

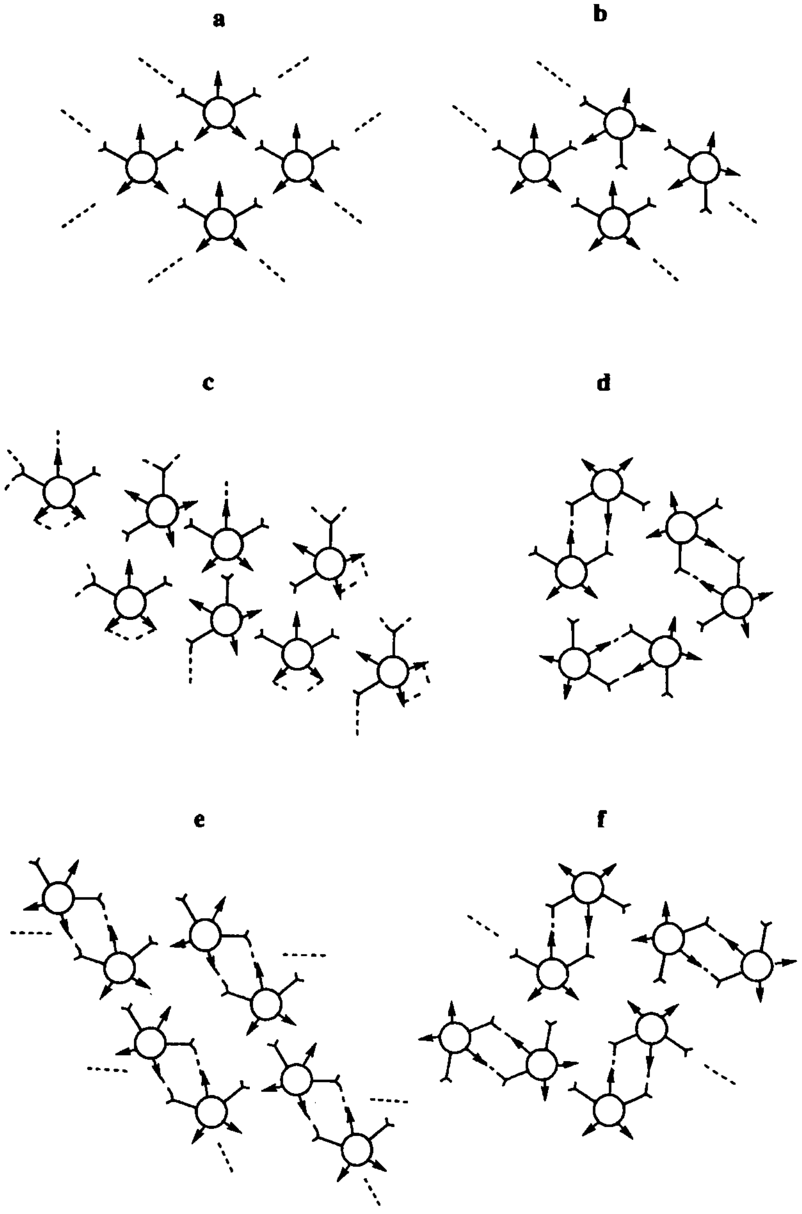


FIGURE 3.- Possible arrangements of HNN molecules to form planes.

intermolecular interactions over a large range of molecules of the same family gives the probability distribution of finding atoms around a given intermolecular contact point. One can then do a connection between the probability of finding short distances and the strength of the interaction. One can also define the anisotropy of each intermolecular contact by looking at the angular probability distribution. The results, although reliable in general, can be misleading in some cases, as short interactions in a similar family of compounds can be due to the presence of strong attractive interactions close to the one of interest, therefore modifying the distribution one would obtain in another environment.

One can also resort to ab initio computations in which, using the appropriate model systems and methodology, one can compute the strength and anisotropy of any intermolecular interaction. The accumulated experience in the computation of hydrogen bonds and van der Waals interactions[9,10] shows that accurate results are obtained if correlated methods are used (at least second order and sometimes fourth order Moller Plesset (MP2 and MP4, respectively)[11] in conjunction with adequate basis sets[12-13] (that is large and well balanced basis sets as to properly describe all the physical forces). Then, one has to correct the basis set superposition error (BSSE)[9,10] of the computed interaction energy using the counterpoise method.[14] Using this methodology one can decrease the errors to less than 10% of the experimental interaction energy for hydrogen bonds[15,16] and van der Waals interactions.[12,13]

How to carry out ab initio computations and use the information obtained in them to understand the packing of the crystals ?. The first and obvious way would be computing the interaction energy of each pair of molecules and of other higher aggregates, to quantify the energies and the optimum structure of the dimers and other aggregates. This can also give information about the kinetics of polymorphism, through the barriers which separate the various minima for each aggregate. However, even for molecules of the size of the HNN this computation is too expensive for the present generation of computers and software, if accurate results are wanted. Therefore, one can to resort to a more practical approach based on identifying the possible contacts that the molecule of interest can make in the crystal, and then compute the energy of these contacts using ab initio methods and the appropriate model system. We show how this process can be carried out in the following paragraphs.

The possible intermolecular interactions to compute at the ab initio level can be selected using the information from the MEP maps to localize complementary parts of hydrogen bond contacts. For the HNN molecule, good candidates for hydrogen bond contacts from the MEP map are the $C(sp^2)$-H···O and the $C(sp^3)$-H···O interactions, while the lone pairs of the oxygen atoms or the π network of the N-O bonds are good candidates for van der Waals interactions. These two are two orientations of N-O···O-N interactions.

Alternatively, one can select the intermolecular interactions to compute after analyzing the shortest contacts within the crystal or from statistical distributions of contacts carried out for a similar family of crystals. The shortest contacts are the most relevant energetically, for the reasons described above, and are good candidates for being the most attractive ones. Obviously, both approaches can be used in a complementary way.

Once the interactions of interest have been selected, one can compute their strength and directional properties using a dimer which presents the same interaction in an environment as close as possible to the one find in the crystal for the same contact. This means, to use the same substituents in the α and, maybe, in the β positions. In some cases it could be important to include the Madelung field created by the other molecules of the crystal, even in an approximate way, although more studies are under way to define the relative importance of this field.

Good models to describe the $C(sp^2)$-H···O and the $C(sp^3)$-H···O interactions in the HNN molecules are the ones represented in Model I and Model II, respectively, with $r = 2.416$ Å and $\theta = 142.1°$ in Model I and $r = 2.637$ Å and $\theta = 128.7°$ in Model II. The geometry of each fragment is selected in such a way that mimics that of the HNN units in the α-HNN crystal. We have substituted the $C(sp^3)$ groups attached to the N atoms by H atoms located at 1.1 Å to lower the computational cost as the effect of these groups on the O atoms is negligible. For the same reasons the $C(sp^3)$ atom attached to the C in the methyl group has been substituted by a H at the same distance it has in methane. The relative orientation of the two monomers have deliberately been chosen to reproduce the geometry of the two intermolecular contacts in the crystals. One can optimize the geometry to find the most favorable geometry when the monomers are isolated, to compare such a value with the crystal geometry and in this way understand the importance of the other groups present in the vicinity or other environmental effects.

Using Models I and II, one can compute the interaction energy, using the MP2 method and the 6-311++G(2d,2p) basis set. The BSSE-corrected interaction energy for the $C(sp^2)$-H···O interaction becomes -3.71 kcal/mol, while that for the $C(sp^3)$-H···O interaction is just -0.40 kcal/mol. That is, we have a strong and a weak hydrogen bond.

In relation to the N-O...O-N interactions, we did a simple computation for the case in which the two NO groups are pointing to each other colinearly. The model system was two H_2NO planar molecules in which the NO groups are facing each other with the C_{2v} axis of each monomer lying one on top of the other. The interaction energy computed using the MP2 method and the 6-31+G(2d,2p) basis set is repulsive at all distances, being at the van der Waals distance about +1 kcal/mol. After correcting the BSSE this energy becomes even a bit more repulsive. Therefore, the NO groups will try to avoid each other as much as

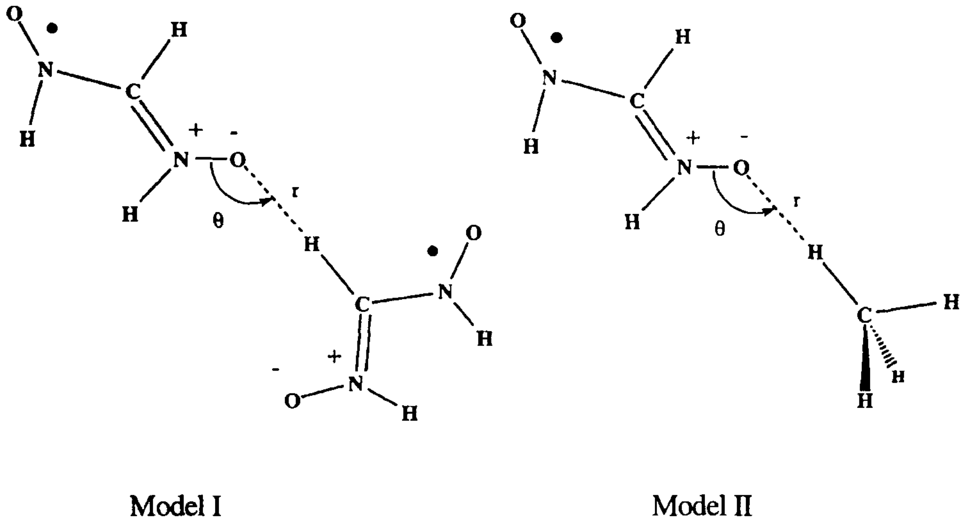


FIGURE 4.- Possible model systems employed to compute the interaction energy of the C(sp^2)-H···O and the C(sp^3)-H···O interactions present in the HNN crystals.

possible if isolated. To increase the size of the magnetic interactions between the HNN molecules one has to make a network of attractive contacts around the NO groups to compensate this trend and approach the unpaired electrons sitting preferentially in these groups.

With the previous ab initio data, one can analyze the structures proposed in Figure 3 and select the most stable ones looking at the number of contacts of each class within the structures. One can, alternatively, do the same analysis on the experimental X-ray structure of the crystal to understand why the crystal packs the way it does it once all the intermolecular interactions are combined and, in this way, understand the packing. What can be concluded up to know from our study is that the primary driving forces of the packing are the C(sp^2)-H···O interactions (-3.71 kcal/mol). On the other hand, the N-O···O-N interaction are repulsive (+1 kcal/mol at the van der Waals distance), while the C(sp^3)-H···O interactions are weakly attractive and can be considered as responsible for the secondary structure. To illustrate the use of the previous ideas in a practical way, in the accompanying article we will show how using these ideas and data is possible to rationalize the packing and polymorphism of the two packing forms of the HNN crystals.

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