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# A THEORETICAL ANALYSIS OF THE PACKING AND POLYMORPHISM OF THE 2-HYDRO NITRONYL NITROXIDE CRYSTAL

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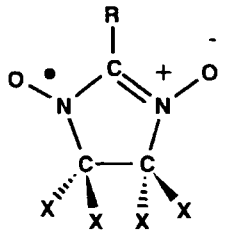
Abstract The packing of the two crystallographics forms the 2-hydro nitronyl nitroxide (HNN) molecule has been studied. Using the ab initio methodology described in the accompanying paper, the packing is rationalized. In both crystals the primary structure are the HNN dimers linked trough C(sp2)-H...O-N contacts. These dimers form planes of molecules, which constitute the secondary structure. The structure and stability of the planes are different in the two crystals. Finally, the planes form stacks, the tertiary and last structure in both crystals. The forces involved in each type of structure have been quantified. The relationship between the two polymorph crystal forms have been analyzed and rationalized.

## INTRODUCTION

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] Therefore, understanding and controlling the factors which govern the packing of these crystals is a key step towards the design of

molecular magnetic crystals. In the previous paper,[2] we have described how the packing of a molecular crystal can be analyzed using the data from ab initio computations. This is the aim of this work is to apply the previous methodology to rationalize 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 HNN radical is the simplest member of the nitronyl nitroxide radicals,[1,3] whose general formula is :




being HNN the member in which R=H. A recent study[4] has allowed to find two crystal phases (thereafter identified as the α-HNN and β-HNN phases), both showing an antiferromagnetic behavior. A thermal analysis of the α-HNN phase 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 begin thermal decomposition. This paper is devoted to rationalize these two packing structures using the analytical the methods described in detail in the accompanying article. These results should also help to understand the packing motifs generated by the five member ring common to other members of the nitronyl nitroxides family.

## METHODOLOGY

The packing of a molecular system is one of the minima found in the total interacting energy of the crystal, that is, is influenced by all the intermolecular interactions present in the crystal. However, this energy can be analyzed looking at its components and at how the dimers and other small aggregates are formed: the crystal is a progressive built up of packing units and the possible minima in these aggregates can be rationalized knowing the properties of the possible intermolecular interactions, and in particular, of the strongest

ones. In the most stable packing structures the molecules aggregate maximizing the number of strongest interactions. The packing motifs generated by the strongest bonds is the primary structure of the crystal (for instance, planes of molecules), while the weaker bonds are responsible for the secondary one. In a crystal, the aggregation process must be done in such a way that the long range order is preserved, a fact that limits the number of packing forms.

From the above discussion it is clear that to rationalize the packing one has to understand the nature of the intermolecular interactions present in it. Any given crystal can present three types of intermolecular interactions: ionic, hydrogen bonds, and van der Waals, being diffuse in some cases the separation between these classes.[5] The ionic interactions are present when the crystal has ions in it, so they are not possible in the HNN case. Hydrogen bond interactions are found whenever a contact of the type X-H···Y is produced between two molecules of the crystal.[6] They have a strong electrostatic character and are expected to be important in the HNN crystal because this molecule has a strong permanent dipole moment of 3.872 Debyes. Finally, van der Waals interactions are the weak short range found between atoms with no dangling bonds and whose lone pair electrons are at a short distance of each other. This situation that can be represented as X:···:Y, where the symbol : represents the lone pair electrons. The van der Waals interactions are expected to be weaker than the hydrogen bond interactions in the HNN molecule. The information from ab initio computations can help us to determine the possible contacts and their strength.

To identify the possible arrangements of the molecules which will generate the packing motifs, one can use the molecular electrostatic (MEP) maps.[7] The one for the HNN molecule[2] shows two strongly attractive region located on each oxygen and repulsive regions over the C-H bonds. Thus, one can expect that the C-H bonds will act as acid groups and the O of the NO groups as basic in the formation of the C-H···O-N hydrogen bond. One can distinguish between two types of carbons according to their hybridization: the methyl carbons are C($sp^3$), while the carbon in between the two NO groups is a C($sp^2$). Using the MP2 method and the 6-311++G(2d,2p) basis set on the adequate model systems we have computed the strength of the C($sp^2$)-H···O-N and C($sp^2$)-H···O-N contacts.[2] They are attractive with a strength of -3.71 and -0.40 kcal/mol, respectively. At the same time, using the same methodology and the adequate model system the N-O···O-N is found to be repulsive by about +1 kcal/mol at the van der Waals distance.[2] In the rest of the paper we will show how this information can be used to understand the packing and polymorphism of the α-HNN and β-HNN crystals.

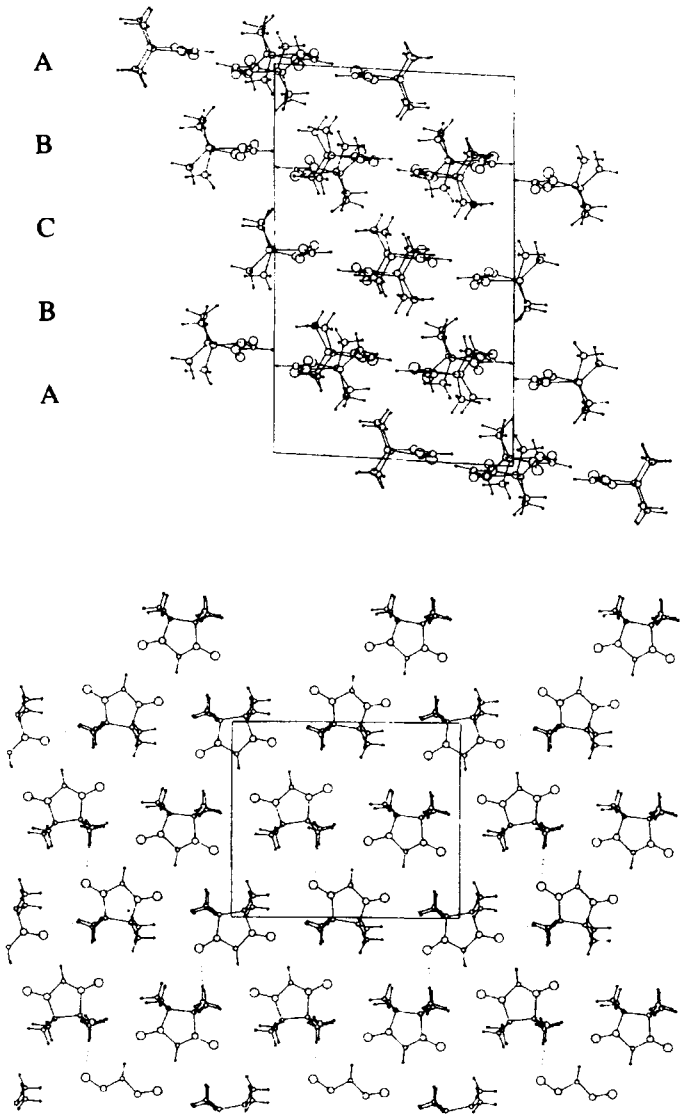



FIGURE 1.- Packing of the α-HNN crystal showing the shortest C-H···O contacts: (a) Extended view along the **b** axis showing the four planes (ABBA) within the unit cell; (b) view of the A plane along the **a** axis.

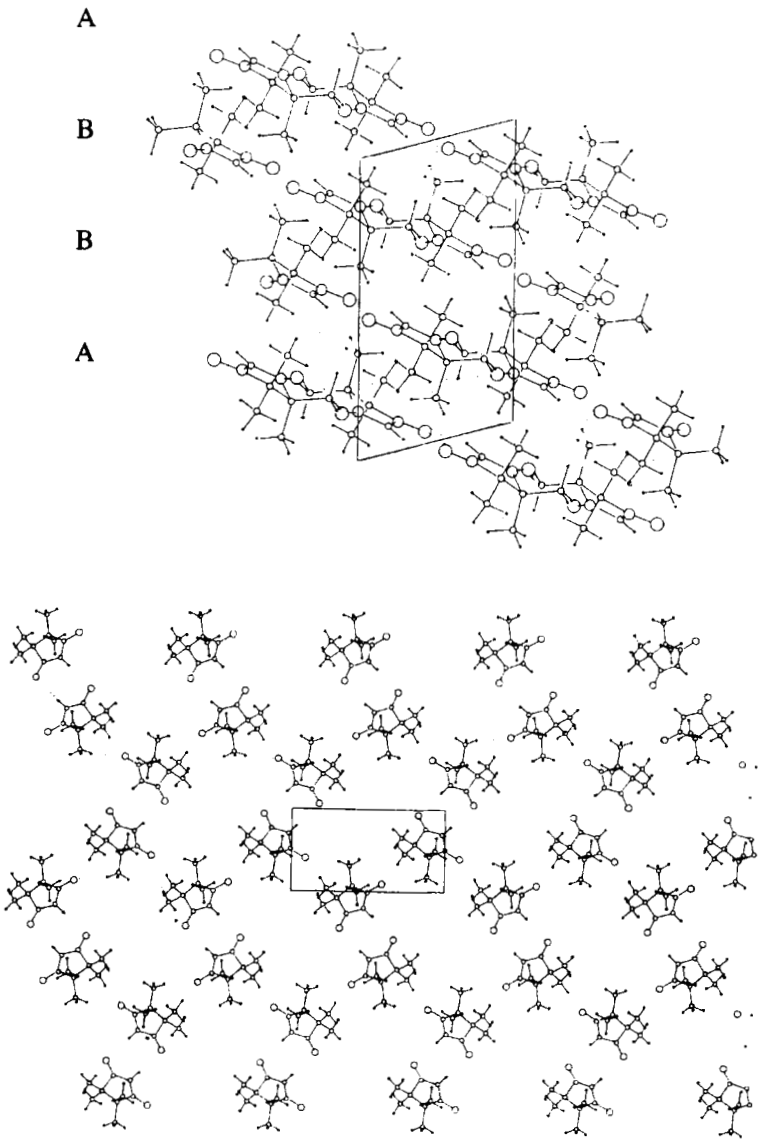



FIGURE 2.- Packing of the β-HNN crystal showing the shortest C-H···O contacts: (a) Extended view along the **b** axis showing the five planes (ABCBA) within the unit cell; (b) view of the A plane along the **a** axis.

## RESULTS AND DISCUSSION

### The packing of the α and β phases of the HNN crystal

The α-HNN crystal contains four molecules per unit cell arranged in such a way that the crystal belongs to the $P2_1/n$ spatial group.[4] The unit cell has the following crystallographic parameters: a = 11.879 Å, b = 11.611 Å, c = 6.332 Å and β = 104.48°. The β-HNN crystal has sixteen molecules per unit cell packed in such a way that the space group is the $P2_1$ one.[4] The crystallographic parameters of the second crystal are: a = 19.991 Å, b = 14.091 Å, c = 12.144 Å and β = 92.92°.

For an in depth understanding of the packing of these systems is better to have a more exhaustive picture of their packing. We can plot, in an extended way, the shortest contacts between the molecules of the crystal (i.e., those contacts whose distance is around the sum of the van der Waals radii of the two atoms making the contact). Figure 1 shows a view of the structure of the α-HNN crystal in which the intermolecular C-H···O contacts smaller than 3.5 Å have been indicated by broken lines, while Figure 2 shows, indicating also the C-H···O contacts, a view of the structure of the β-HNN crystal. In both cases the packing is characterized by the superposition of planes, each resulting from the aggregation of HNN dimers. The formation of planes is not surprising because is the most stable way of ordering dipole moments and the HNN molecule has a strong dipole moment originated by his two NO groups. At a first look, the previous structural consideration could indicate that the planes constitute the primary structure of the crystal, while the stacking of these planes the secondary one.

Within each crystal all the planes included in the unit cell are identical but differ by their relative position, sometimes by an inversion center, sometimes by a relative displacement along some symmetry element. Consequently, within the unit cell of the α-HNN crystal we can distinguish crystallographically two types of planes, identified as A and B, ordered in a sequence ABBA, with the B planes closer to the inversion center located in the center of the cell. Within the unit cell of the β-HNN crystal there are five planes, ordered in a sequence ABCBA, with the C plane passing through the inversion center located in the middle of the unit cell.

The internal structure of the planes in the α-HNN and β-HNN crystals is different although the dimers which constitute the planes have a similar structure. In both crystals the dimers are made by means of two $C(sp^2)$-H···O-N contacts (see Figures 1 and 2). However, the geometries of the two types of dimers, although similar, is slightly different: The $C(sp^2)$-H···O angle is 162° in the α-HNN crystal to be compared with the 156° value for the β-HNN crystal; The shortest H···O distance is 2.416 Å in the α-HNN crystal and 2.256 Å in the β-HNN crystal, while the H···H distances are 2.688 and 3.085 Å in the α-

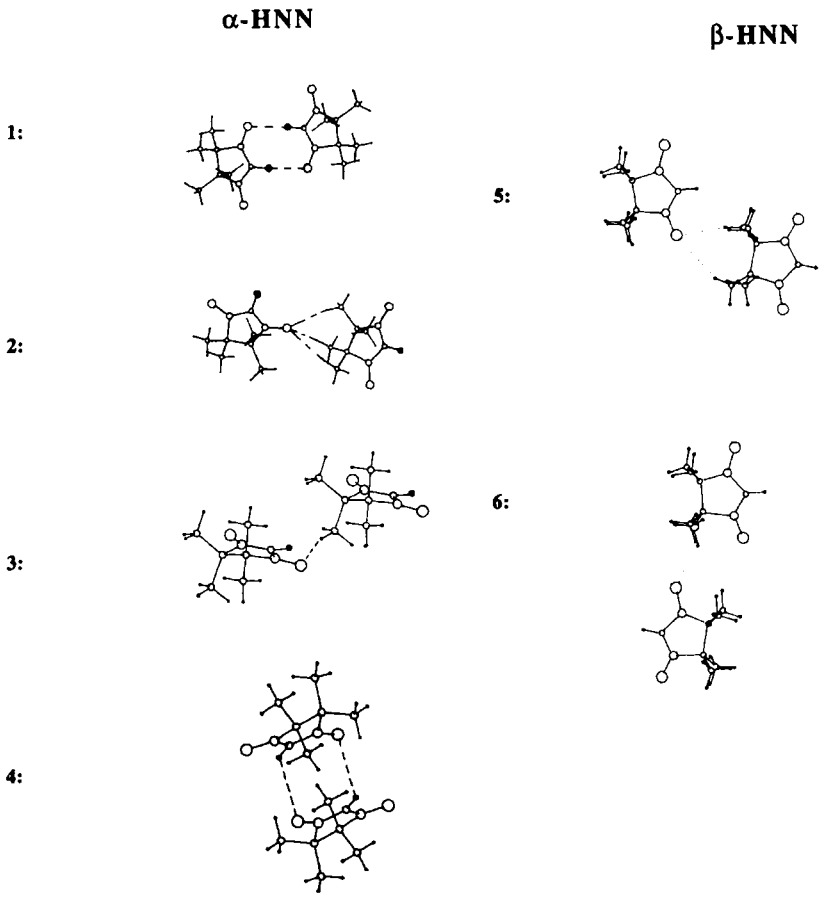



FIGURE 3.- Types of arrangements found in the α-HNN and β-HNN crystals.

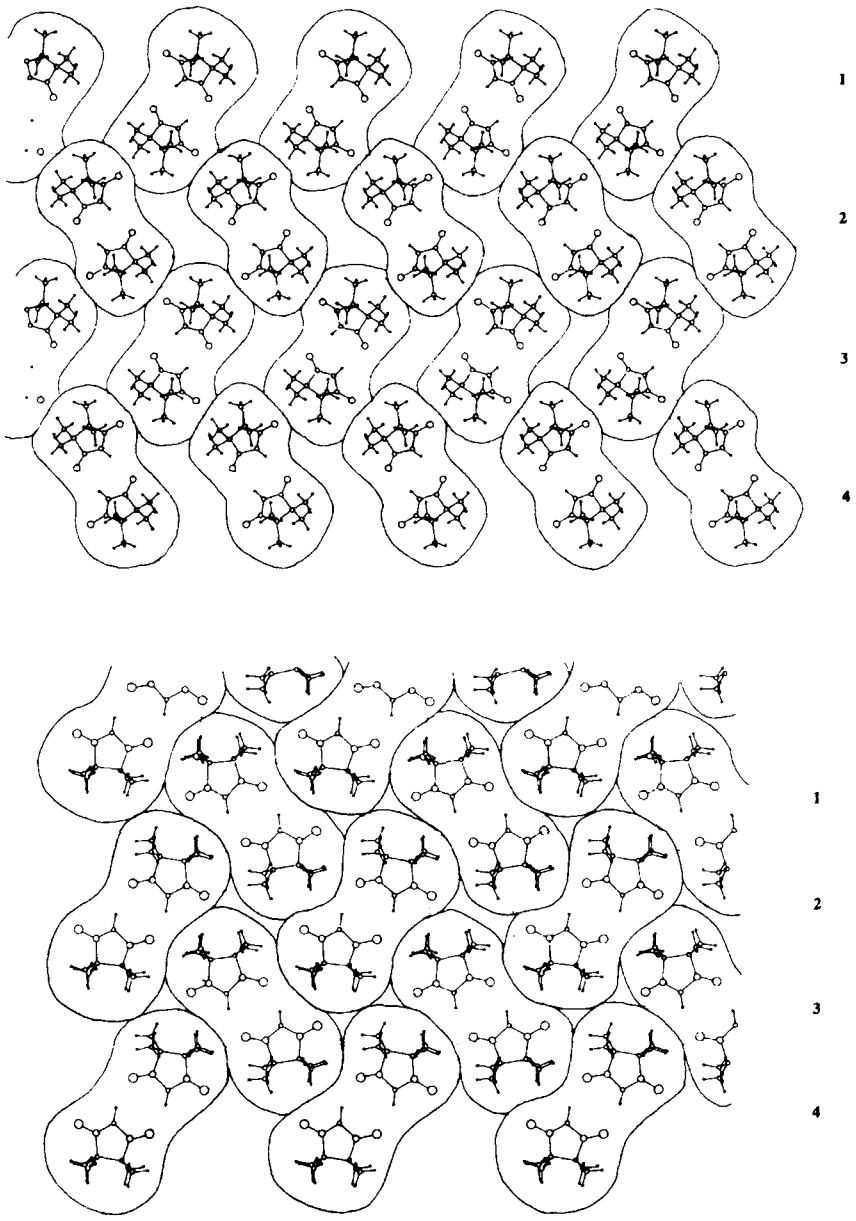



FIGURE 4.- Schematic representation of the planes of the α-HNN and β-HNN crystals (upper and lower part of the Figure, respectively).

HNN and β-HNN crystals, respectively; Finally, the dimers are not strictly coplanar in the α-HNN crystal while they are coplanar in the β-HNN crystal. Ab initio computations[8] have showed that the planar conformation of the dimer is the most stable one but that slight displacements from the planarity are not expensive energetically and the dimer can relax its planarity if in this way it maximizes the number of contacts with the surrounding molecules or the strength of the contacts. The optimum H···O distances in gas phase[8] are both 2.154 Å while the angle is 133.1°. This result can be taken as reference to understand the geometrical distortions induced by the surrounding molecules in the dimer geometry .

The HNN dimer has still two NO groups and eight methyl groups which can be used to make intermolecular contacts with other dimers via hydrogen bonds or van der Waals interactions. Using these contacts, the dimers can make links with their neighboring dimers to form the above mentioned planes. A close look at Figures 1 reveals that in the α-HNN crystal all the interdimer contacts are of the $C(sp^3)$-H···O-N type, with each dimer making 12 contacts, 6 as acid and 6 as base. The interdimer contacts in the β-HNN crystal are also of the $C(sp^3)$-H···O-N type, but the number is larger (24 in total, eighteen of whom are shown in Figure 2). As the two dimers make two $C(sp^2)$-H···O-N intradimer contacts at about the same geometry, one can expect that the planes in the β-HNN crystal are more stable. The formation of planes maximizes the number of contacts and is the most stable conformation for systems with strong dipole moments, as the HNN. Once the planes are formed, the methyl groups still have $C(sp^3)$-H bonds which are unused and can be used to form $C(sp^3)$-H···O-N interplane contacts (one has to keep in mind that each oxygen has two lone pairs and only one has been used in the in-the-plane contacts.

Table I lists the shortest intermolecular distances within the planes and between the planes for the two crystals. The numbers indicate that the contacts are similar in the two crystals, with small variations. On the other hand, the various types of geometrical arrangements that the dimers can make in the α-HNN and β-HNN crystals are shown in Figure 3. Arrangements 1, 2, 5 and 6 correspond to in-the-plane conformations, while 3 and 4 correspond to between-planes conformations, found in the α-HNN and β-HNN crystals. Obviously, arrangement 1 is also found in the β-HNN crystal but is not duplicated in the list.

One can compute the energy associated to each of these geometrical arrangements using the ab initio data for the model $C(sp^2)$-H···O-N and $C(sp^3)$-H···O-N contacts, after multiplying this number by the number of contacts which each arrangement makes. Thus arrangement 1, which makes two $C(sp^2)$-H···O-N contacts, and its interaction energy should be 2x(-3.71) = -7.42 kcal/mol. We tested the validity of this result by computing the interaction energy of the optimized dimer in gas phase and we obtained a value of -7.20 kcal/mol. The difference between this number and the previous one reflect the importance

TABLE I. Shortest intermolecular distances within the α-HNN and β-HNN crystals.

| Class | Contact type | distance[a] α-HNN | distance[a] β-HNN |
|---|---|---|---|
| Intraplane | $C(sp^2)$-H···O | 2.416 | 2.193 |
| | $C(sp^3)$-H···O | 2.554 | 2.431 |
| | $C(sp^2)$-H···H-$C(sp^2)$ | 2.689 | 3.085 |
| | $C(sp^3)$-H···H-$C(sp^3)$ | 2.790[c] | 2.741 |
| | N-O···O-N | 4.271 | 3.642 |
| Interplane | $C(sp^3)$-H···O | 2.535 | 2.637 |
| | $C(sp^2)$-H···H-$C(sp^3)$ | 2.660 | 2.781 |
| | $C(sp^3)$-H···H-$C(sp^3)$ | 2.548 | 2.491 |
| | N-O···O-N | 3.798 | 4.226 |

[a] in Å

[b] per dimer

[c] the next contact is at a distance >3.20 Å

of the polarization effects that one bond induces in the other. However, the geometry of the dimers in the crystal is not the same that the gas phase optimum geometry and, consequently, the interaction energy of each dimers of the α-HNN and β-HNN crystals is -5.53 and -5.44 kcal/mol, respectively. The energy of arrangement 2 can be computed as three times that for a $C(sp^3)$-H···O-N contact, that is, 3 x (-0.40) = - 1.2 kcal/mol, while that for arrangement 3, in which only one $C(sp^3)$-H···O-N contact is made, is -0.40 kcal/mol. Arrangement 4 corresponds to an inter-plane interaction and was computed using a model system similar to Model I but oriented to mimic the geometry of this arrangement in the crystal (that is, the H···O distance was 3.331 Å and the C-H...O angle 85.3°). The BSSE-corrected interaction energy computed using the MP2 method and the 6-311++G(2d,2p) basis set is -1.38 kcal/mol, that is, -0.69 kcal/mol per each long range $C(sp^2)$-H···O-N contact. Arrangement 5 shows two $C(sp^3)$-H···O-N contacts against the same NO groups with an estimated total interaction energy of -0.80 kcal/mol, the same. Finally, arrangement 6, which presents also the same number of $C(sp^3)$-H···O-N contacts,

but connected in a different way, has an estimated interaction energy of -0.80 kcal/mol. Probably the polarization effects will make the energy of the last two arrangements slightly different but not significantly, as was seen above.

How can one characterize the packing of the two crystals at the light of the previous results ?. These values indicate that there are strong and weak hydrogen bonds. The strong $C(sp^2)$-H···O-N contacts are used to form HNN dimers, by large, the most stable geometrical arrangement. Therefore, the HNN molecules will have a strong energetic preference to form dimers and this is the main motif of the primary structure. When the dimers are formed, no new strong $C(sp^2)$-H···O-N contacts can be made as no free $C(sp^2)$-H bonds are left. In the crystals studied here the dimers make contacts among themselves according to one of the types indicated in arrangements 2-6. Arrangement 4 is not a minimum energy structure of the dimer and, if left alone, the two molecules will become coplanar as in arrangement 1. So, arrangement 4 will only be find once the planes are formed. Among arrangements 2, 5 and 6, the first is the most stable one. By making use of it, the crystal will grow one of the planes (making planes always maximizes the number of these contacts) to form the packing motif typical of the α-phase. Using a combination of 5 and 6, the planes of the β-phase are obtained. As the number of contacts to be made is larger and requires a more ordered structure, entropically the growth of the β-phase planes is more difficult, although energetically is more favorable. So, we have justified the secondary structure of the two crystals, the molecular planes. As the NO groups repel each other in the plane, no short NO···ON distances are found in these crystals. Once the planes are formed, there are still some unused intermolecular interactions. The first type is located in the methyl groups, which can still make contacts against the NO groups involved in the $C(sp^2)$-H···O-N contacts, arrangement 3, as only one intermolecular interaction is made there. Otherwise, using arrangement 4, the planes can be attached to each other. The result is the formation of ordered stacks of planes, piled up in such a way that they maximize the interplane interaction energy. This is the tertiary structure of the crystal.

Polymorphic transformations between the α and β phases.

The previous analysis fully rationalizes the structure of the α-HNN and β-HNN crystals and gives clues on the effect that the five member ring can induce in the packing of other similar molecules of the nitronyl nitroxide family. Now we can have a look at the polymorphic α -β transformations.

We can understand the essence of the process looking at Figure 4, where the packing in one of the planes has been schematized using the dimers as packing units. In the α-phase each plane is constituted by rows of dimers, parallel to each other, but pointing in different directions, in such a way that the dimers of one row are nearly perpendicular to

these of the adjacent rows. The n row is liked with the n-1 and n+1 rows by means of arrangement 2 contacts. Each dimer makes two of these contacts to two different dimers of the adjacent row. Each molecule of the HNN dimer is liked to only one molecule of the dimer to which is linked. On the other hand, in the β-phase the contact between the dimers are made in such a way that the dimers in the nth row makes hydrogen bond contacts with these of the n-1 and n+1 rows and, at the same time, "touch" the dimers in the n+2 and n-2 rows, thus allowing the formation of stable $C(sp^3)$-H···H-$C(sp^3)$ van der Waals contacts. Consequently, the dimers in the β-phase are more tightly packed. It is possible to go from the α to the β phase by a collective displacement of the dimers of the n-1 and n+1 rows in the opposite direction towards the center of the dimers of the nth row. The shift is structurally reversible and one can in principle go from the β to the α phase by reversing the it. However, as was mentioned before, the β-phase is much more stable and the barrier to leave the potential well associated to this phase can be much more important than the one needed to enter in it, making irreversible the b to a pathway for thermodynamic or kinetic reasons. Finally, due to the change of structure in the planes, the stacking has to adapt its structure, but this should be no problem as a large number of methyl groups is always available perpendicular to the planes.

In summary, we have seen that one can explain the known properties of the packing of the HNN crystal by a careful use of the MEP maps and the strength of the intermolecular interactions, both data obtained from ab initio computations. The extension to larger systems has been already tested. The results are also satisfactory and will be presented elsewhere.

## ACKNOWLEDGMENTS

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