

Chirality of α -Nitronyl Nitroxide Radicals in the Solid State

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IN DEDICATION TO THE LATE PROFESSOR OLIVIER KAHN FOR HIS PIONEERING CONTRIBUTIONS TO THE FIELD OF MOLECULAR MAGNETISM

The way in which chirality is manifested in the solid state in a variety of phenyl α -nitronyl nitroxides is discussed in the context of the preferred conformations of this family of compounds. The preparation of chiral phenyl α -nitronyl nitroxides apparently guarantees the formation of just one conformational diastereomer in the crystals, even if prediction of which is presently unfeasible: of four chiral radicals with the same stereogenic center all four gross conformers are represented. Circular dichroism spectra give useful information regarding the interplay between molecular conformation and optical activity. A variety of both strong and weak hydrogen bonds are at play, leading to the formation of chains and sheets of molecules. The magnetic exchange interactions between the radicals is always weak and antiferromagnetic, and can be attributed to a small face-to-face overlap of the SOMOs. © 2001 Academic Press

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INTRODUCTION

Perhaps one of the most appealing challenges for contemporary molecular magnetism (1–3) is the combination and synergy of magnetism and other material properties in the framework of organic and coordination chemistries, a quest actively promoted and pursued by Olivier Kahn (4–12). Amongst these combinations, one of the most intriguing is, perhaps, that of magnetism and chirality, which amongst other things can result in magneto-optical effects (13–16). Chirality in magnetic materials has up to now been addressed elegantly in the framework of coordination compounds (17–21), but while many chiral radicals have been reported (22–33), the consequences for their magnetic and other properties have not been pursued in detail. Recently, Olivier Kahn's group reported the structure and magnetic properties of an enantiomerically pure chiral α -nitronyl

nitroxide derived from a triazole moiety (8), the aim being to apply this ligand to complex paramagnetic metal ions and control the supramolecular organization of the resulting coordination compounds. Also, a “chiral molecular-based metamagnet” was synthesized by coordination of manganese(II)hexafluoroacetylacetonate with a triplet organic radical (34). Concurrently, we started a research program targeting chiral phenyl α -nitronyl nitroxide radicals of the type **1** (Fig. 1) for the preparation of molecular magnetic materials that might display magneto-optical effects. The solid state structures and optical and magnetic properties are the subject of this discussion.

CONFORMATIONS OF PHENYL α -NITRONYL NITROXIDES IN THE SOLID STATE

In order to optimize optical activity of these compounds, and thus the relation between the molar extinction coefficient and the molar ellipticity (critical for the observation of the desired effects), both constitutional and conformational stereochemistry must be considered. It will be shown that the latter has an important influence on chiroptical properties of the solids. The phenyl α -nitronyl nitroxide radicals have two principle angles that govern their global conformation: (i) the angle formed by the C4–C5 bond and the plane formed by the NCN unit in the imidazolyl ring, T_{IM} , and (ii) that produced by the twist of the NCN unit of the imidazolyl ring and the plane of the phenyl ring, A_{PIM} . Each of these angles has an associated helicity—defined by the descriptors minus (*M*) or plus (*P*)—which imply four gross conformational diastereoisomers (35), *MM*, *PP*, *MP*, and *PM*, composed of two enantiomeric pairs (Fig. 1). In the solid state, a structural database study showed that the enantiomeric *MP* and *PM* pseudo-eclipsed conformers are favored over the less planar pseudo-anti enantiomers *MM* and *PP* (36). A graphic illustration of this situation is presented in Fig. 2, which is a plot of the calculated probability of the molecules in terms of T_{IM} and A_{PIM} .

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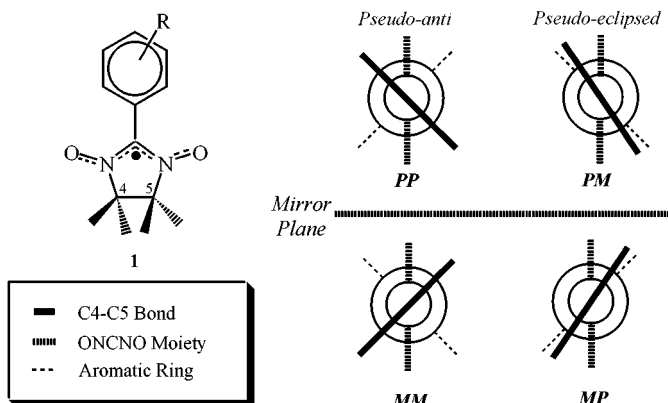


FIG. 1. The phenyl α -nitronyl nitroxide general formula and schematic representations of their four possible gross diastereomeric conformations as viewed from the C4–C5 bond of the imidazolyl ring.

The structural analysis showed that in the vast majority of cases the space groups of the crystals are centrosymmetric, and thus there are equal numbers of the two conformational enantiomers, since there is no chiral influence, although there are important exceptions (37–40). One of these compounds is 2-chlorophenyl α -nitronyl nitroxide **2CINN** (41), which crystallizes in the $P2_12_12_1$ space group, with an angle of $\pm 62^\circ$ between the planes of the ONCNO unit and the phenyl ring. The molecule has a pseudo-anti conformation, with either *MM* or *PP* helicity. Therefore, the compound crystallizes, forming enantiomorphous crystals, each with distinct optical properties. We have studied these properties using circular dichroism spectroscopy.

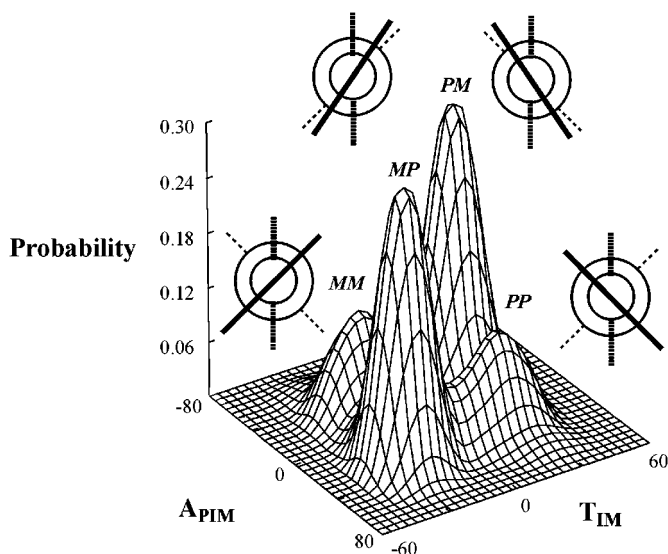


FIG. 2. The distribution of conformers of phenyl α -nitronyl nitroxide radicals in their crystals, as defined by the angles A_{PIM} and T_{IM} .

CIRCULAR DICHROISM SPECTROSCOPY OF AN ACHIRAL PHENYL α -NITRONYL NITROXIDES IN THE SOLID STATE

The optical activity of matter is most frequently studied using either polarimetry or circular dichroism (CD) spectroscopy (42–45). The latter is particularly informative, since the differential absorption of left and right circularly polarized light is measured at each point in the absorption spectrum, and the optically active transitions can be assigned. Routinely applied to liquids, CD can also be used to study solid chiral materials, most conveniently in the form of KBr discs (46–56).

Since individual crystals of **2CINN** are chiral, they should be optically active. The solid state CD technique demonstrates that this is indeed the case (57). The CD spectra of two ground enantiomorphous crystals in the KBr matrix (Fig. 3) reveal significant Cotton effects at 305, 364, 458, and 590 nm (either all positive or all negative), every one despite the absence of a stereogenic center in the molecule. This result demonstrates the importance of conformation on the solid state optical properties of this family of molecular materials.

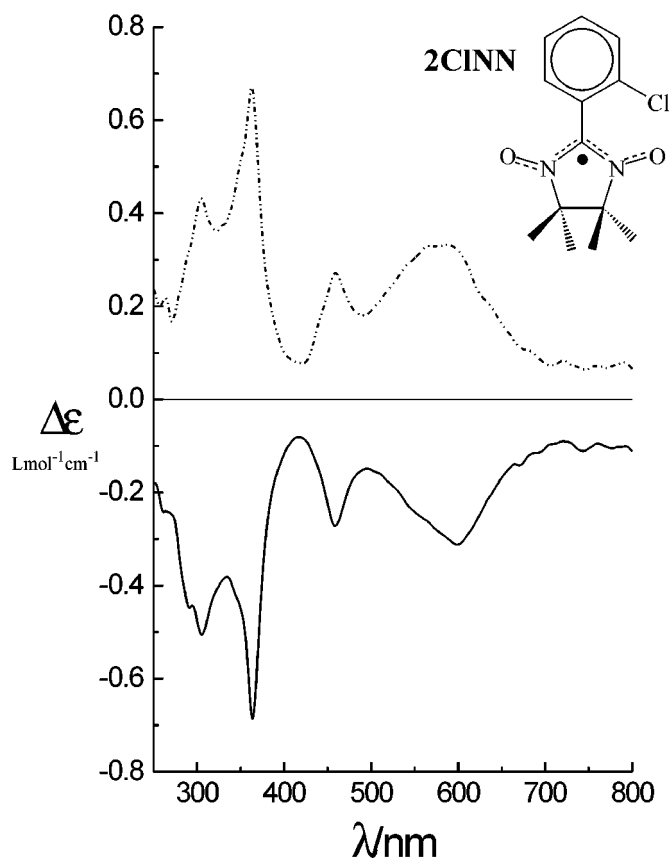


FIG. 3. CD spectra of enantiomorphous crystals of **2CINN** in the KBr matrix.

In principle, magneto-optic studies could be carried out on a material that displays spontaneous resolution of conformational enantiomers, but practically this would mean crystal-picking, which at least in the case of **2CINN** is not feasible since the enantiomeric crystals are not visually distinguishable by their external appearance. One way to ensure that a bulk sample only presents one conformation is to include a stereogenic center in the constituent molecules, and this approach is the one we have employed.

CRYSTAL STRUCTURES OF CHIRAL PHENYL α -NITRONYL NITROXIDES

The incorporation of a stereogenic center in the α -nitronyl nitroxides is synthetically most easily achieved onto the aromatic ring of the phenyl derivatives. We were encouraged that this strategy could lead to conformational preferences as a result of our studies on long-range chiral induction in other aromatic hydrocarbons (58). When a stereogenic center is attached to the phenyl α -nitronyl nitroxide core, a diastereomeric relationship exists between the four conformers in Figs. 1 and 2, and therefore one should be, and up to now is, preferred. This effect has been seen previously in another chiral α -nitronyl nitroxide compound with a stereogenic center close to the radical unit (8).

As a chiral group we chose lactic acid, since it is readily available in enantiomerically pure and racemic modifications, and the presence of the acid functionality was expected to give rise to hydrogen bonding to the NO group of the radical unit (59). This feature has been observed previously in radicals of this and related types (60–63), and hydrogen bonds have been proven to be important for organization of the radicals in the solid state as well as in the propagation of magnetic interactions (64–77).

Specifically, we have studied the following phenyl α -nitronyl nitroxides derived from lactic acid (Fig. 4), (*R*)-**3MLNN**, (*R*)-**2OH5MLNN**, (*R*)- and (*RS*)-**3LNN**, and (*R*)-**4LNN**, whose solid state structural features we shall discuss in turn. The other racemic compounds have yet to form monocrystals suitable for X-ray diffraction. As can be seen, the compounds can be split into two broad groups, those with strong intermolecular bond-forming potential (the acids) and those without (the esters).

The radical (*R*)-**3MLNN** (78), which crystallizes in the space group $P2_12_12_1$, has a molecular conformation in which the chiral side-arm is folded back toward the α -nitronyl nitroxide moiety (Fig. 5). This position seems to be favored by the formation of an intramolecular $[Csp_2-H \cdots O]$ hydrogen bond between the C–H at the 2-position of the aromatic ring and the ester oxygen atom ($[H \cdots O]$ distance, 2.53 Å, $[C-H \cdots O]$ angle, 148.8°). Only one of the four possible gross conformational diastereoisomers is observed in the crystals, the pseudo-eclipsed *MP* conformer, in which the angle between the C4–C5 bond

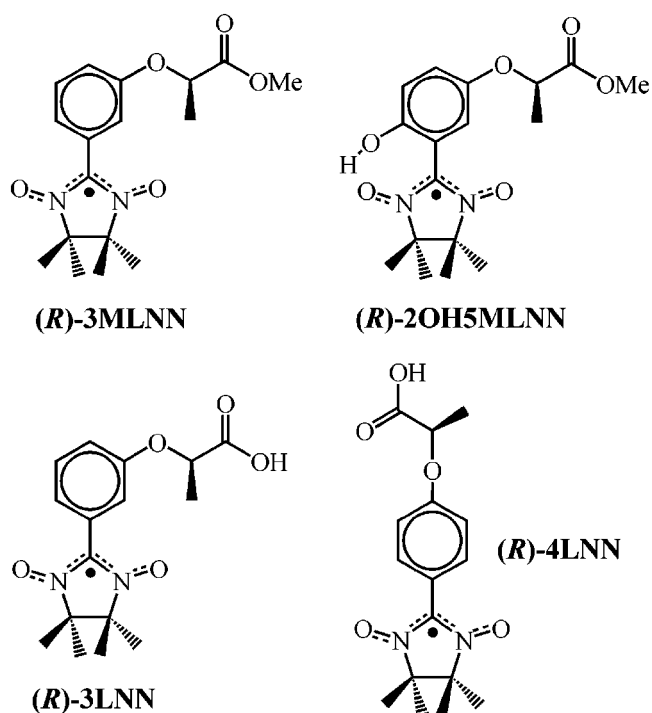


FIG. 4. Molecular formulas of the chiral phenyl α -nitronyl nitroxide radicals studied in this work.

and the N–C–N bond planes in the imidazolyl ring is -21.0° and that between the phenyl ring and NCN planes is $+30.9^\circ$.

The related radical (*R*)-**2OH5MLNN**, in which the chiral group is at the same position of the phenyl ring with respect to the radical unit as (*R*)-**3MLNN**, has a pseudo-anti-*PP* conformation in the solid state (79). Thus, although the chiral group is oriented differently in the two compounds, the angle between the phenyl ring and NCN plane is of the same sign (Fig. 5). In this molecule there is a strong intramolecular hydrogen bond between the OH group and one of the NO groups ($[H \cdots O]$ distance, 1.72 Å, $[O-H \cdots O]$ angle, 169.9°). As in the closely related radicals with an OH group in the 2-position, which both present bulk ferromagnetic behavior (80–82), a large angle is forced between the phenyl ring and NCN planes $+37^\circ$, considerably greater than in (*R*)-**3MLNN**.

The molecules of (*R*)-**3MLNN** and (*R*)-**2OH5MLNN** pack forming various $[C-H \cdots O]$ hydrogen bonds (83–90), of which the $[Csp_3-H \cdots O]$ from the methyl groups attached to the imidazolyl ring and the NO groups are particularly common in this family of radicals (35, 81, 91–97). The former forms a complicated three-dimensional structure in which hydrogen-bonded chains propagate along the crystallographic *a* and *b* directions generating a heavily corrugated sheet (Fig. 6). The crystal packing of the latter also invokes a host of $[Csp_3-H \cdots O]$ hydrogen bonds,

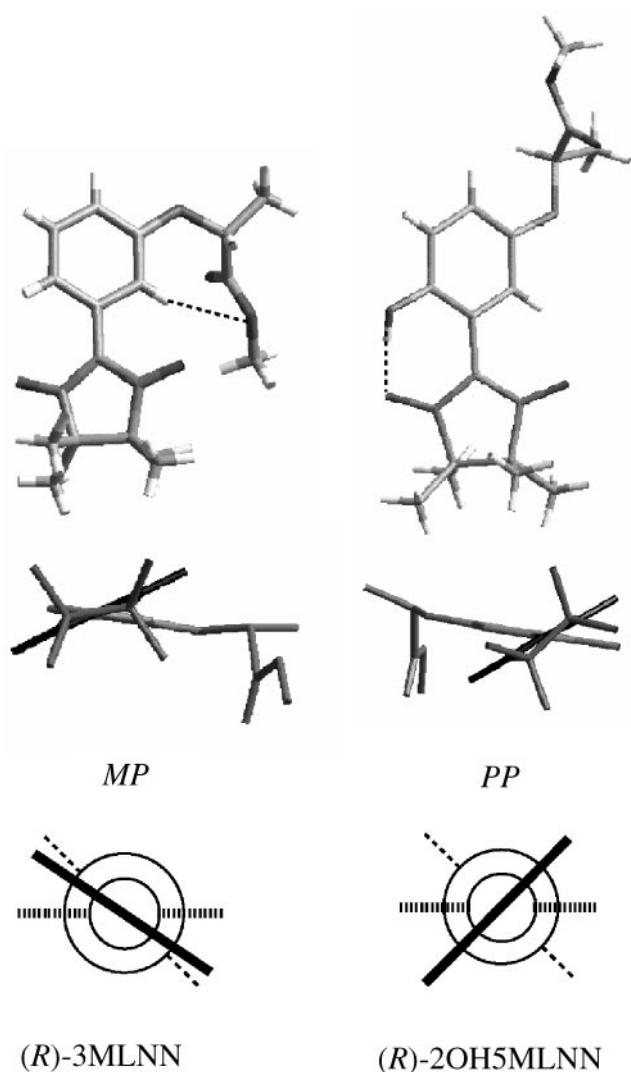


FIG. 5. Conformations adopted by (R) -3MLNN and (R) -2OH5MLNN in their crystals.

resulting in the formation of chains that come together to form sheets. (Fig. 7).

The enantiopure (R) -3LNN has a pseudo-anti MM conformation (Fig. 8) in its crystals (space group $P2_1$) while the same enantiomer in the racemic (RS) -3LNN crystals (space group $P2_1/c$) has a pseudo-eclipsed PM arrangement (36). Thus the angle between the phenyl and imidazolyl rings is the same sign for the molecules with the same configuration (R) in the chiral substituent in the two materials. In the racemate, the S enantiomer is related centrosymmetrically with the R enantiomer, and so presents opposite conformation. The chiral sidearm of molecules in both modifications adopts extended conformations in the solid state, unlike the ester derivative, probably as a result of a strong intermolecular hydrogen bond from the acid proton to one of the nitroxide oxygen atoms (see Table 1 for details), resulting in

the formation of molecular chains. These chains pack side-by-side by virtue of the now familiar $[Csp_3-H \cdots O-N]$ hydrogen bonds between the second NO group of the molecule and three hydrogen atoms of the methyl groups in a neighboring radical (Table 1). A corrugated sheet is formed thereby, which is very similar to those formed by the radical 4OHNN (66) from the hydrogen bond topology viewpoint (Fig. 9).

The racemic form of 3LNN forms hydrogen-bonded chains in a similar way to the enantiopure compound with an even stronger hydrogen bond from the carboxylic acid proton and one of the N-O groups (Fig. 10, Table 1). The strength of the intrachain linkage is augmented by the formation of an additional hydrogen bond between the carbonyl oxygen atom and one of the methyl groups adjacent to the N-O group. The chains are joined to one another by weak hydrogen bonds established between the “free” N-O group and the methyl groups of the imidazolyl ring of a nitronyl nitroxide molecule in the neighboring chain as in the chiral compound. Interestingly, homochiral sheets of chains are formed in the c plane. These molecular sheets pile up along the c axis with alternating chirality. There are also

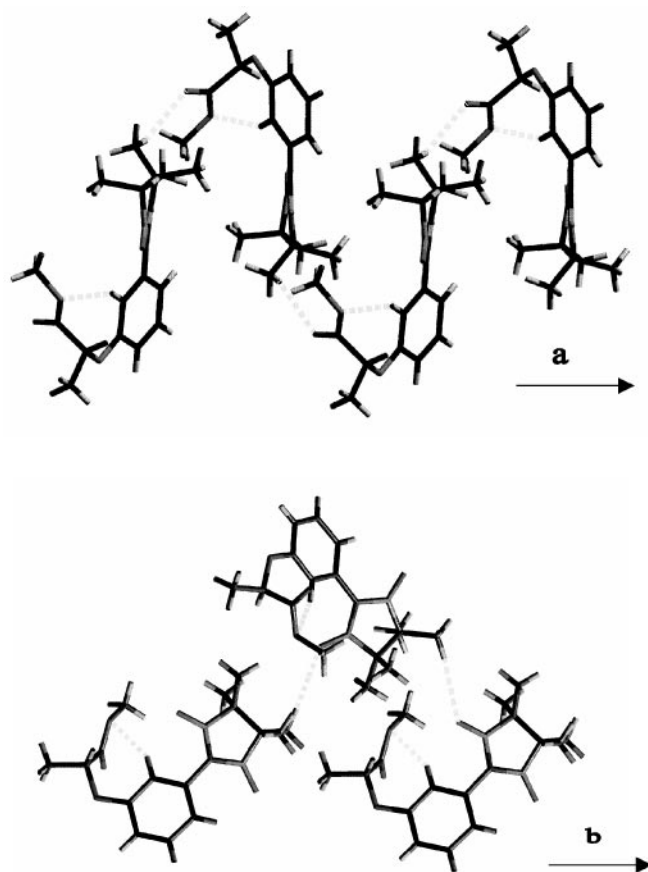


FIG. 6. The hydrogen-bonded chains formed by (R) -3MLNN in its crystals.

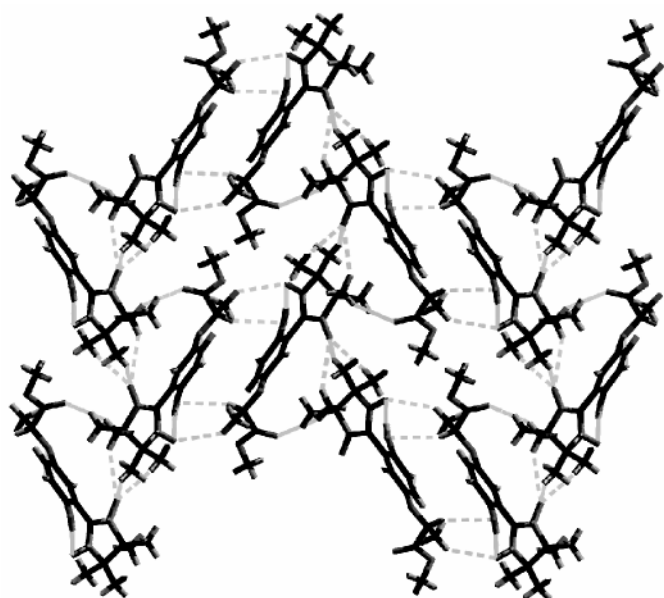


FIG. 7. The hydrogen-bonded sheets formed by (*R*)-2OH5MLNN in its crystals.

weak hydrogen bonds connecting the sheets between the hydrogen atom at the 5-position of the aromatic ring and the oxygen atom of the chiral group directly linked to the phenyl group. The racemate (1.292 g/cm³) is more dense

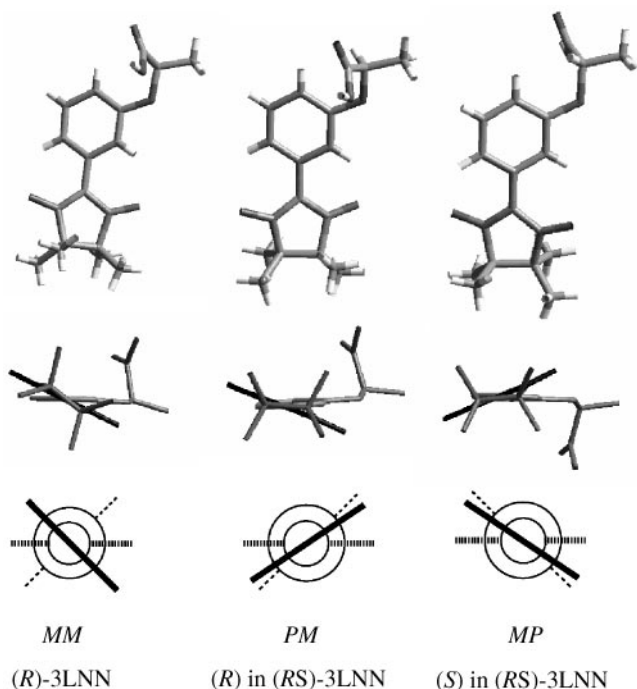


FIG. 8. Conformations adopted by 3LNN in its enantiopure and racemic crystals.

TABLE 1
Hydrogen Bond Distances and Geometries Found in Crystals of the Carboxylic Acids (*R*)-3LNN, (*R,S*)-3LNN, and (*R*)-4LNN

Radical	H bond	[H ... O] distance (in Å)	[X-H-O] angle (in °)	[X-H-O] distance (in Å)
<i>(R)</i> -3LNN	O-H ... O-N ^a	1.886	156.2	2.657
	^{lm} CH ₃ ... O-N ^b	2.766	150.3	3.632
	^{lm} CH ₃ ... O-N ^b	2.550	147.7	3.400
	^{lm} CH ₃ ... O-N ^b	2.541	150.6	3.410
<i>(R,S)</i> -3LNN	O-H ... O-N ^a	1.650	172.9	2.635
	^{lm} CH ₃ ... O=C ^a	2.543	163.9	3.485
	^{lm} CH ₃ ... O-N	2.697	147.8	3.556
	^{lm} CH ₃ ... O-N	2.482	152.4	3.372
	C-H ... OR ^c	2.585	146.0	3.405
<i>(R)</i> -4LNN	O-H ... O-N ^a	1.627	159.2	2.619
	^{lm} CH ₃ ... O=C ^a	2.671	141.3	3.579
	^{lm} CH ₃ ... O=C ^a	2.741	140.8	3.546
	CH ... O-N ^b	2.331	155.5	3.210
	^{lm} CH ₃ ... OR ^b	2.785	176.6	3.753
	^{lm} CH ₃ ... O=C ^c	2.619	153.0	3.512
	^{lm} CH ₃ ... O=C ^c	2.738	148.2	3.599
	^c CH ₃ ... O-N ^c	2.662	144.4	3.496
	^{lm} CH ₃ ... OR ^c	2.554	141.7	3.369

Note. ^{lm}CH₃ indicates the methyl groups attached to the imidazolyl ring, and ^cCH₃ those attached to the stereogenic center.

^aIndicates intrachain hydrogen bond.

^bIndicates intrasheet hydrogen bond.

^cIndicates intrastack hydrogen bond.

than the enantiopure (1.264 g/cm³) compound, in accord with Wallach's rule (98).

The molecules of (*R*)-4LNN have pseudo-eclipsed *PM* conformations (Fig. 11) in the crystals of the compound that pertain to the space group *P*2₁2₁ (99). The angle between the phenyl and imidazolyl rings is therefore the same as that in the other two carboxylic acids presented here. This radical also forms hydrogen-bonded chains through the carboxylic acid to nitroxide link (Table 1), again augmented by a weak interaction between the carbonyl group and one of the methyl groups of the neighboring radical. The particularly strong hydrogen bond between acid and N-O group leads to a significant difference between the nitrogen-to-oxygen atom bond lengths (1.276 and 1.301 Å). The chains come together through [Csp₂-H ... O] hydrogen bonds from one of the hydrogen atoms at the 3-position of the aromatic ring and the otherwise "free" NO group, thus forming highly corrugated sheets. These sheets stack on top of each other by virtue of various [Csp₃-H ... O-N] hydrogen bonds (Fig. 12) between parallel chains, as well as a [Csp₃-H ... π] interaction between the methyl group attached to the stereogenic center and the benzene ring (shortest distance 2.893 Å).

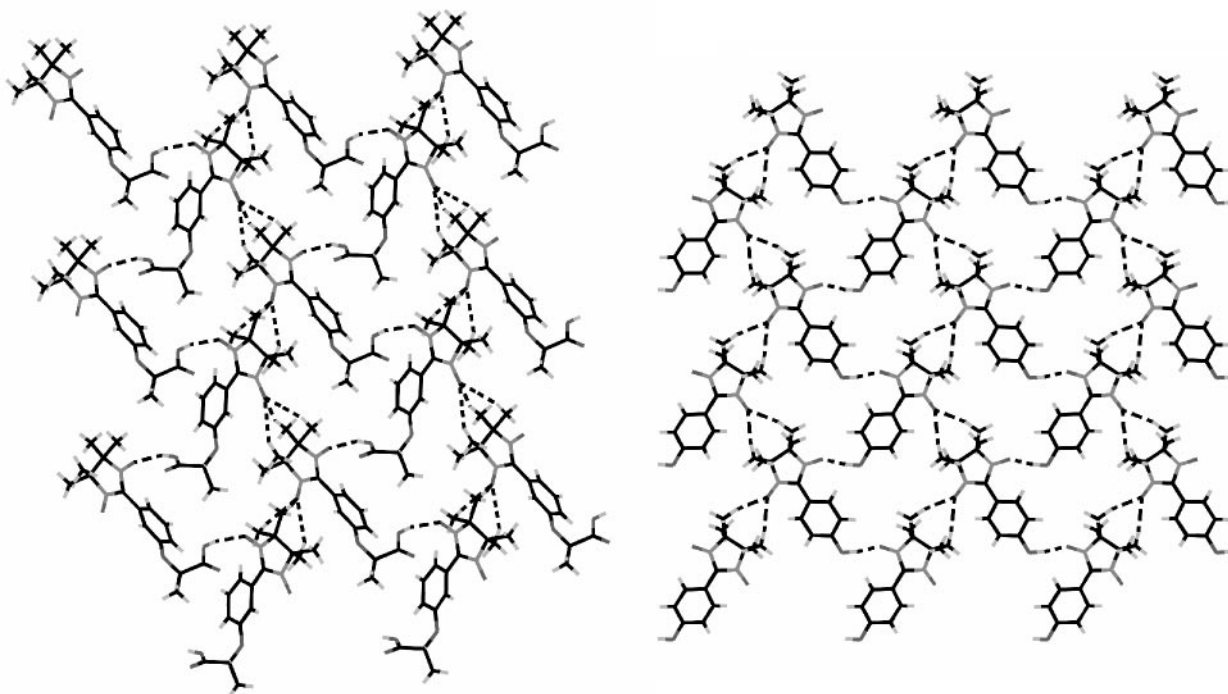


FIG. 9. The hydrogen-bonded chains and sheets formed by (*R*)-3LNN and 4OHNN in their crystals.

All the chiral radicals described here present only one of their gross conformational diastereomers in their crystals. Therefore we can conclude that the incorporation of a stereogenic center in the radicals, even be it remote from

the sources of conformational chirality, induces the crystallization of one conformer. However, although the stereogenic center in the enantiopure radicals ((*R*)-3MLNN, (*R*)-3LNN, (*R*)-2OH5MLNN, and (*R*)-4LNN) is of the same absolute configuration, all four conformations (*MM*, *MP*, *PM*, and *PP*) of the phenyl α -nitronyl nitroxide unit are present in the crystal structures. Thus, while one diastereomeric conformation alone is apparently guaranteed by inclusion of the stereogenic center, *a priori* we cannot say which one it will be. This situation is surely a consequence of the different conformations of the chiral groups in the compounds. In the acids the angle between phenyl and imidazolyl ring is the same, presumably because the stereogenic center is brought into approximately the same geometrical position in the three cases. The fact that the imidazolyl ring presents different conformations could be a result of the hydrogen bonds formed between the methyl groups attached to it and the NO groups in other molecules, which have greatly differing conformations and connectivity.

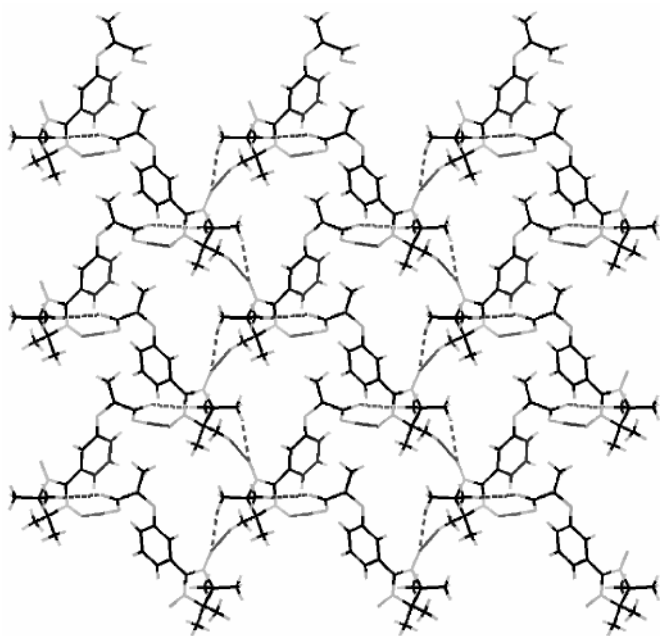


FIG. 10. The hydrogen-bonded sheets formed by (*RS*)-3LNN.

CIRCULAR DICHROISM SPECTRA OF CHIRAL PHENYL α -NITRONYL NITROXIDES

One of our objectives during this work was to correlate the CD spectra of the radicals with their molecular conformation in the solid state. To this end, we recorded the solid state spectra of the four chiral radicals in the KBr matrix.

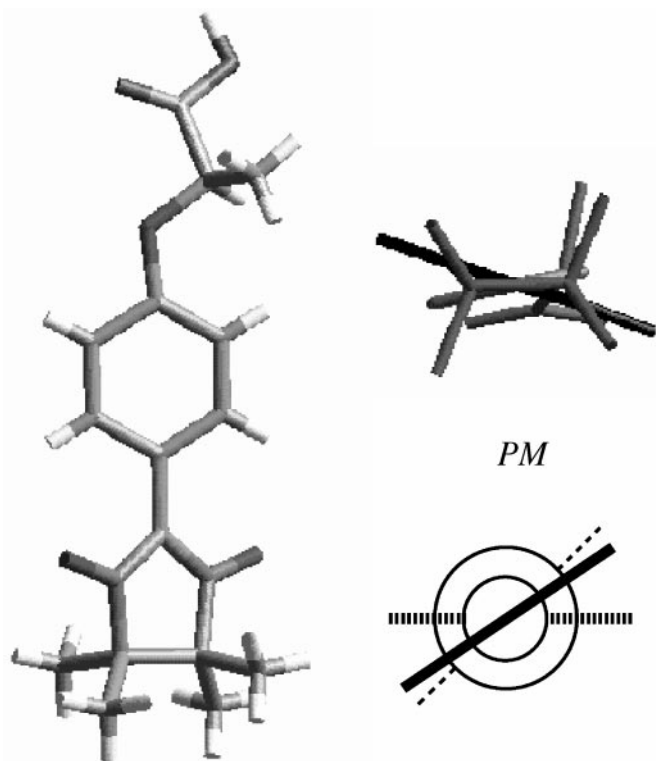


FIG. 11. The conformation of (*R*)-4LNN in its crystals.

Their CD spectra are presented in Fig. 13, along with a schematic representation of their conformations in their crystals.

Each Cotton effect was assigned precisely with the chromophores responsible for the electronic transitions of (*R*)-3LNN in its crystal by means of *ab initio* molecular orbital calculations, in which the calculated CD spectrum reproduced the experimental spectrum remarkably well (36). This work implied that $n \rightarrow \pi^*$ transitions of the α -nitronyl nitroxide moiety are responsible for the negative Cotton effect located at approximately 470 nm. The UV absorption band has a negative Cotton effect associated directly to it, between 340 and 380 nm, which is assigned to $\pi \rightarrow \pi^*$ transitions of the ONCNO moiety. Importantly for this work, changing the sign of the angles formed between the

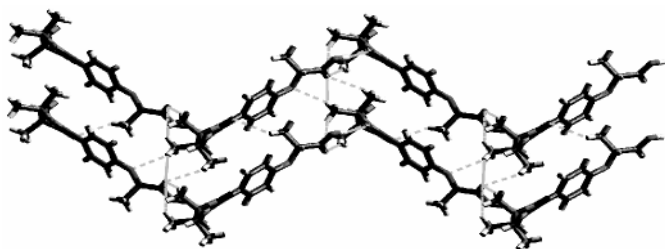


FIG. 12. The weak hydrogen bonds responsible for the stacking of sheets of (*R*)-4LNN.

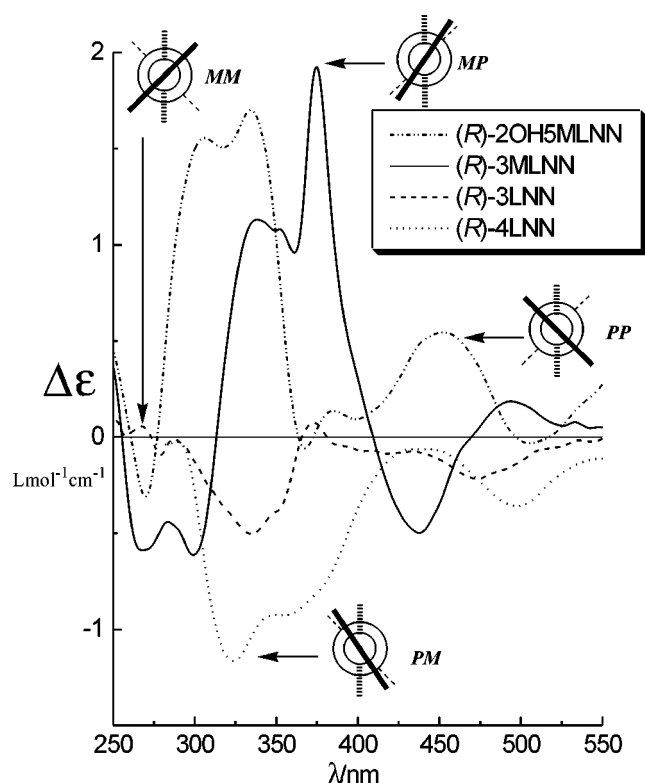


FIG. 13. The CD spectra of the four different conformational diastereomers of the chiral phenyl α -nitronyl nitroxides recorded in the KBr matrix.

planes of the NCN unit of the imidazolyl ring and that of the phenyl ring and the torsion angle in the imidazolyl ring in the calculation changed the sign of these Cotton effects.

The attribute of the CD spectra that apparently correlates with the crystal structures of the compounds is the Cotton effects centered at between 300 and 400 nm, whose sign and scale depend upon the twist angle between the imidazolyl and phenyl rings. The A_{PIM} angles are $+36.9^\circ$ for (*R*)-2OH5MLNN, $+30.9^\circ$ for (*R*)-3MLNN, -25° for (*R*)-3LNN, and -29° for (*R*)-4LNN. The calculations described above indicate that positive A_{PIM} angles, i.e., *P* helicity, produce *positive* Cotton effects. The shift to higher energy in the position of these Cotton effects for (*R*)-2OH5MLNN is presumably a result of the high torsion angle between the rings, and consequent lowering of conjugation in the molecule.

Somewhat unexpectedly, the Cotton effects observed for the ester (*R*)-3MLNN are much higher than for the corresponding acid (*R*)-3LNN, despite the fact that the angles between the planes of the rings are quite similar. The feasible causes of the significant differences between the spectra are: (a) the conformation assumed by the chiral group and its alteration of the chiroptical properties of the phenyl α -nitronyl nitroxide unit; (b) the alteration of the intensity of

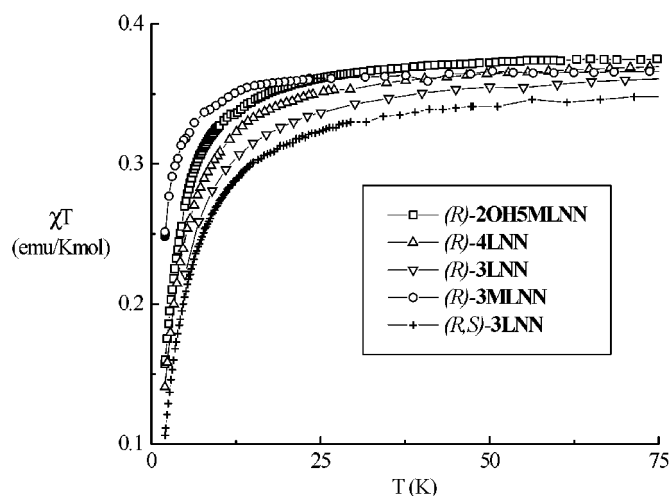


FIG. 14. Magnetic susceptibilities of the chiral radicals represented as χT versus T .

the Cotton effect as a consequence of strong intermolecular hydrogen bonds in *(R)*-3LNN; and (c) other crystal field effects resulting from the different packing of the molecules in the solids. Owing to the remoteness of the chiral group from the active chromophore, option (a) seems unlikely. The radical *(R)*-4LNN also has strong hydrogen bonds between the radicals in its crystals, and yet presents a relatively intense Cotton effect; therefore option (b) seems equally unsuitable. Therefore, packing effects, which were not taken into account in the calculation of the CD spectra owing to the problems associated with such a task, seem to be at the root of the differences.

MAGNETIC PROPERTIES OF CHIRAL PHENYL α -NITRONYL NITROXIDES

The observation of magneto-optical effects is likely to be highest in materials that order spontaneously. Several such molecular materials have been described in the phenyl α -

TABLE 2

Structural and Magnetic Classification of the Chiral Compounds and the Magnetic Interactions in Them as Determined by Fitting of the Magnetic Susceptibility Data to Zero (dimer) and One-Dimensional Models

Compound	Structural type	Magnetic structure	J (K)
<i>(R)</i> -3MLNN	3-D	Chain	-0.7
<i>(R)</i> -2OH5MLNN	Chain	Chain	-1.9
<i>(R)</i> -3LNN	Chain	Chain	-2.2
<i>(RS)</i> -3LNN	Chain	Dimer	-2.3
<i>(R)</i> -4LNN	Chain	Chain	-2.0

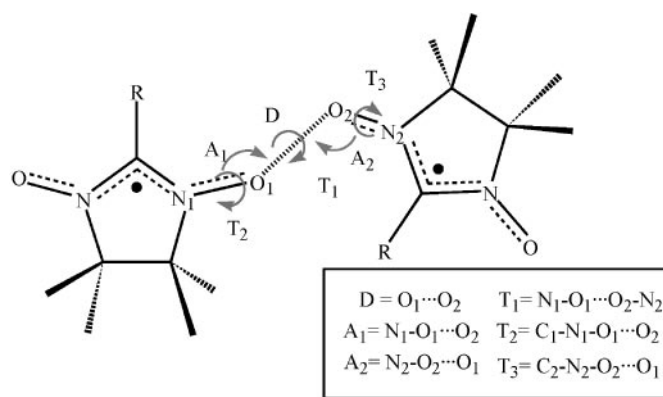


FIG. 15. The distance, two angles, and three torsion angles necessary for a precise description for the relative disposition of two ONCNO moieties.

nitronyl nitroxide clan (80–82, 95, 100–105). The magnetic susceptibility measurements on the chiral compounds discussed here show the presence of unvaryingly very weak antiferromagnetic interactions. The results of fitting the magnetic susceptibility data (Fig. 14) to a one-dimensional chain model and the classification of the materials are collected in Table 2. The principal observation of note is that the interactions in the carboxylic acids are stronger than in the corresponding esters.

In order to describe rigorously the relative orientations of the SOMOs of the radicals (106, 107), whose interactions are responsible for the observed magnetic behavior, six parameters are necessary (Fig. 15): the distance between the two nearest oxygen atoms (D), two angles (A_1 and A_2), and three torsion angles (T_1 , T_2 , and T_3). These closest distances and angles are presented in Table 3, and the closest contacts are presented graphically in Fig. 16. There are no obvious correlations, in accordance with previous assertions (106, 107), apart from the qualitative one between the distance between the oxygen atoms and the magnitude of the magnetic interaction. These interactions are weak in all cases, chiefly on account of the relatively large distances between the SOMOs. In all cases the planes of the ONCNO groups are approximately parallel, as can be appreciated in Fig. 16, and the highest overlap is seen in crystals of

TABLE 3
Distance and Angles between the N–O Groups in the Chiral Radicals

Compound	D (Å)	A_1 (°)	A_2 (°)	T_1 (°)	T_2 (°)	T_3 (°)
<i>(R)</i> -3MLNN	5.72	114.0	63.9	39.1	-111.0	-92.4
<i>(R)</i> -2OH5MLNN	5.04	98.5	123.2	-72.5	-139.2	78.2
<i>(R)</i> -3LNN	4.80	95.4	122.6	87.0	-87.4	133.4
<i>(RS)</i> -3LNN	4.90	100.3	78.6	34.9	-96.2	-97.8
<i>(R)</i> -4LNN	4.07	92.4	134.9	-162.5	89.4	-106.5

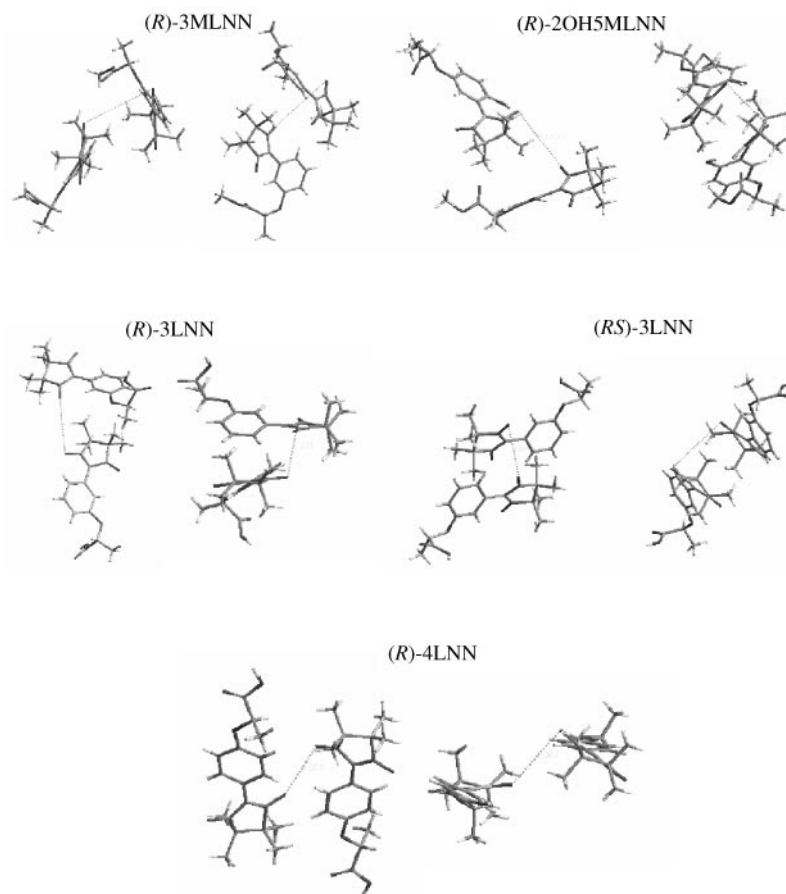


FIG. 16. Selected views of the relative disposition of nearest-neighbor ONCNO moieties in crystals of the chiral phenyl α -nitronyl nitroxide radicals.

(*RS*)-3LNN, which present one of the larger antiferromagnetic interactions in these chiral compounds.

CONCLUSIONS

The incorporation of a stereogenic center to the phenyl α -nitronyl nitroxide radicals leads to the preferential crystallization of one of the four possible gross conformational isomers. In the case of the (*R*)-lactate group, in the four chiral compounds presented here the crystallization of all four gross diastereomeric conformations is observed owing to subtle differences in the conformation of the chiral side-chain in the resultant crystal packing. The diastereomers give rise to drastically different CD spectra, a result that emphasises the importance of the molecular conformations when it comes to designing materials that might show magneto-optical effects. All the materials discussed here display weak antiferromagnetic interactions between the unpaired electrons whose magnitude can be rationalized by taking into account the orientation and overlap of the SOMOs. Given the absence of magnetic ordering in the purely organic chiral compounds, we are currently pursuing

alternative routes to magnetically ordered chiral molecular materials.

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