Circular dichroism studies of crystalline chiral and achiral α-nitronyl nitroxide† radicals in a KBr matrix

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The X-ray crystal structures of a series of four chiral phenyl α-nitronyl nitroxides substituted in the aromatic ring with an (*R*)-lactate moiety are compared, and reveal the presence of all four gross diastereomeric conformations resulting from the twisted conformations of the phenyl and α-nitronyl nitroxide moieties. The use of KBr discs as solid solutions for the study of the circular dichroism (CD) spectra of these radical crystals provides useful information concerning the conformational stereoisomerism displayed by the compounds, both intrinsically chiral and other achiral radicals which crystallise in chiral space groups. The optimum conditions for obtaining the solid state CD spectra have been investigated, and require a short ball-milling of the mixture followed by careful recording of the spectrum. The Cotton effects observed in the CD spectra have been correlated with the observed enantiomeric forms of the pseudo-*anti* and pseudo-eclipsed conformers in the crystals of chiral lactic acid-derived phenyl α-nitronyl nitroxides and an achiral phenyl α-nitronyl nitroxide that crystallises in a chiral space group.

Introduction

Chirality of crystals and solid materials can have a great impact on the properties which they display.[1–9] The study of the optical properties of these materials is greatly aided by the technique of circular dichroism (CD) spectroscopy.[10–12] Our interest in the use of CD in the solid state[13–36] stems from the recent studies we have performed concerning the preparation and characterisation of chiral phenyl α-nitronyl nitroxide radicals of the type **1** (Fig. 1).[37–39] These crystalline molecular materials were targeted in order to explore the possibility of observing magneto-chiral effects[40] in a purely organic medium, given that some of this family of compounds present bulk ferromagnetic order.[41–46] As part of this study, it is essential to understand the effects of constitutional and conformational stereochemistry of the radicals, since an optimum relation between the molar absorption coefficient and the molar ellipticity in a given part of the electromagnetic spectrum is critical for the observation of the desired effects.

In this context, we studied the conformational preferences of this family of compounds in the solid state,[39] in which four possible conformational isomers exist (Fig. 1), defined by the combination of the angles formed between (i) the C4–C5 bond and the plane formed by the NCN unit in the imidazolyl ring, α, and (ii) the NCN unit of the imidazolyl ring and the plane of the phenyl ring, β, each of whose helicity is defined by the classical descriptors minus (*M*) or plus (*P*). Thus, the helicity of the two descriptors of the angles α and β, given in the form αβ, describe the overall conformation of the molecule, which can have four possible states, *MM*, *MP*, *PM* and *PP*. The results of our study were that a preference exists in the solid state for the relatively flat enantiomeric *MP* and *PM* pseudo-eclipsed conformers over the more twisted pseudo-*anti* enantiomers *MM* and *PP*, with equal numbers of each enantiomer because of the absence of asymmetry. In the case that a stereogenic centre is attached to the phenyl α-nitronyl nitroxide core, a
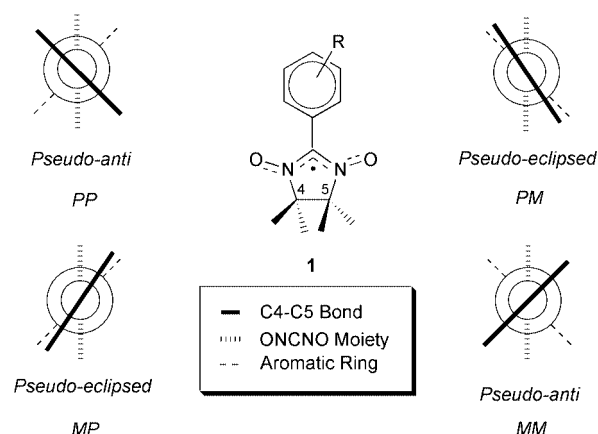
† The IUPAC name for α-nitronyl nitroxide is 4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-1*H*-imidazol-3-ium-1-oxyl.

Fig. 1 General formula of phenyl α-nitronyl nitroxides along with schematic representations of their four possible gross diastereomeric conformations as viewed along the long axis of the molecule from the C4–C5 bond of the imidazolyl ring.
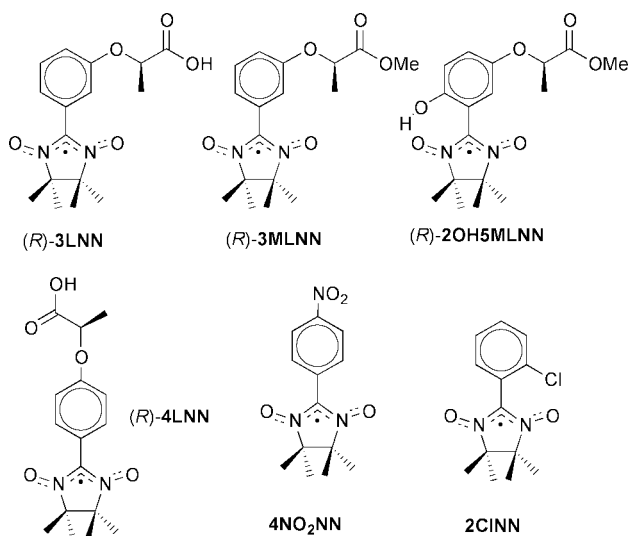
diastereomeric relationship exists between the four conformers, and therefore one should be, and up to now is, preferred as previously seen in another chiral α-nitronyl nitroxide compound with the chiral centre close to the radical unit.[47] Herein we report a study of the solid state CD spectra of a variety of phenyl α-nitronyl nitroxide radicals, both intrinsically chiral and achiral, and correlate the Cotton effects observed with the molecular conformations in the crystals. Specifically, we have studied four chiral phenyl α-nitronyl nitroxides derived from lactic acid, (*R*)-**3LNN**, (*R*)-**3MLNN**, (*R*)-**4LNN**, and (*R*)-**2OH5MLNN**, and the two achiral radicals **4NO₂NN** and **2ClNN**.

Results

Solid state structures of the radicals

Five of the radicals which have been studied in this work, (*R*)-**3LNN**,[39] (*R*)-**4LNN**,[38] (*R*)-**2OH5MLNN**,[48] **2ClNN**,[49] and

DOI: 10.1039/b008379h

the β-phase of **4NO₂NN**[50] have structures which have been solved and reported elsewhere. We have also managed to crystallise and solve the crystal structure of the methyl ester derivative of the acid (*R*)-**3LNN**, (*R*)-**3MLNN**, which is reported here for the first time. This radical crystallises in the space group $P2_12_12_1$, and presents a molecular conformation in which, unlike the other compounds, the chiral side-arm is folded back toward the α-nitronyl nitroxide moiety (Fig. 2). As in the case of the other chiral radicals, only one of the possible gross conformational diastereomers is observed in the solid. The relative disposition of the rings corresponds to the pseudo-eclipsed *MP* conformer, with the angle between the C4–C5 bond and the N–C–N bond planes in the imidazolyl ring being −21.0° and that between the phenyl ring and NCN planes being +30.9°. 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 (*vide infra*). 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. Beyond the molecule, and in contrast to the corresponding acid, there are no strong hydrogen bonds joining the molecules in the crystals of the methyl ester, and it is presumably in part for this reason that the conformation of the chiral group and of the molecule as a whole are distinct in the two compounds. Rather, in (*R*)-**3MLNN** the crystal packing implies intermolecular [C–H⋯O] hydrogen bonds between: (i) the carbonyl group of the ester and a hydrogen atom of one of the methyl groups protecting the radical unit (distance [H⋯O]: 2.75 Å, angle [C–H⋯O]: 143.5°, Fig. 2(a)) resulting in the formation of a chain along the *a* axis; (ii) the NO group of one molecule and a hydrogen atom of one of the methyl groups protecting the radical unit (distance [H⋯O]: 2.70 Å, angle [C–H⋯O]: 173.4°) leading to the formation of a chain along the *b* axis; (iii) the other NO group and a hydrogen atom attached to the 4-position of the aromatic ring (distance [H⋯O]: 2.50 Å, angle [C–H⋯O]: 147.0°).

The acids (*R*)-**3LNN** and (*R*)-**4LNN** also exist as just one of their four possible conformational diastereoisomers in the solid state, solely the pseudo-*anti MM* and pseudo-eclipsed *PM* conformers, respectively.[38,39] The chiral substituents of both radicals adopt extended conformations, giving an overall elongated form to the molecules, as a result of intermolecular [O–H⋯O–N] hydrogen bonds which join the molecules in a chain.

It is important to note that, although the stereogenic centre in these radicals is always the same absolute configuration, *all four conformational isomers of the phenyl α-nitronyl nitroxide unit (MM, MP, PM and PP) are represented in the crystal structures* (views of the conformations of the molecules in their
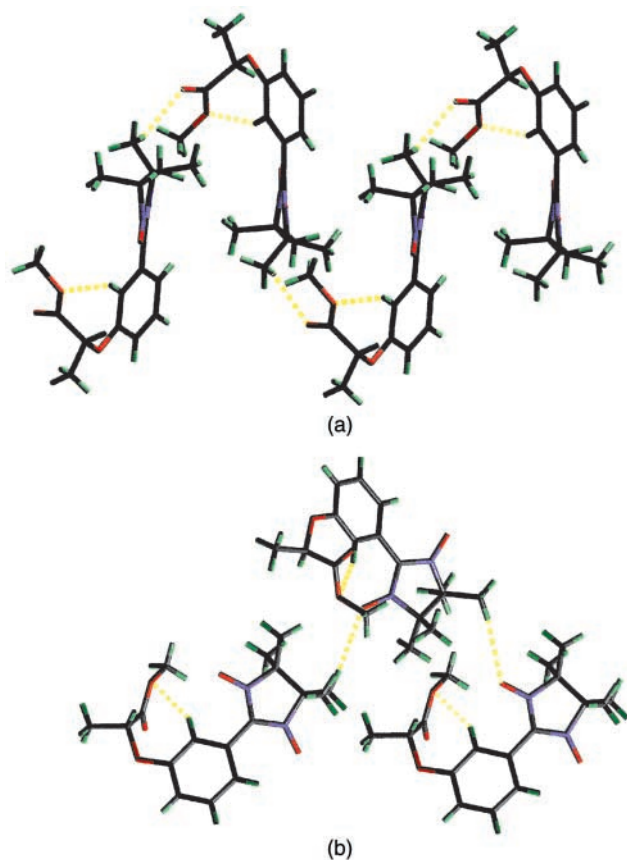

Fig. 2 Representation of the molecules of (*R*)-**3MLNN** in the crystal structure of the compound showing (a) the hydrogen-bonded chain along the *a* axis, and (b) the hydrogen bonded chain along the *b* axis.

crystal structures are shown in Fig. 5, to aid discussion of the CD results).

Recording of solid state circular dichroism spectra

We wished to correlate the structural differences between the radicals with their optical properties using a solid state CD technique, since the spectra of the compounds in solution are a mean of all the molecular conformations adopted in a given solvent and do not necessarily reflect the solid state situation.[51] Four methods have been employed previously for monitoring the chiroptical properties of solid samples: (i) solid solution methods in, for example, KBr;[13] (ii) single crystal measurements;[14] (iii) suspension of powders in a Nujol mull[15] or other liquid medium;[16,17] and (iv) thin film measurements.[18–20] However, somewhat surprisingly, and despite the procedure's potentially wide applicability, it has found relatively limited use, especially in the areas of organic stereochemistry and materials science.[21–29] Toda and Koshima and co-workers[21–29] use Nujol mulls of microcrystalline samples to study enantioselective reactions and stereochemistry of carboxylic acid complexes in the solid state. While this method, which was first reported by Taniguchi and Shimura,[15] is useful in cases where counter-ion exchange is a problem, in our hands it required somewhat tedious sample preparation.‡ An alternative technique is that based on the preparation of discs of the samples in a solid matrix, usually KBr. This method, first detailed for cobalt complexes by Bosnich and Harrowfield[13] and later studied by Kuroda and Saito[14] and others,[30–33] involves the grinding together of the matrix and compound in a ball mill in order to pulverise the
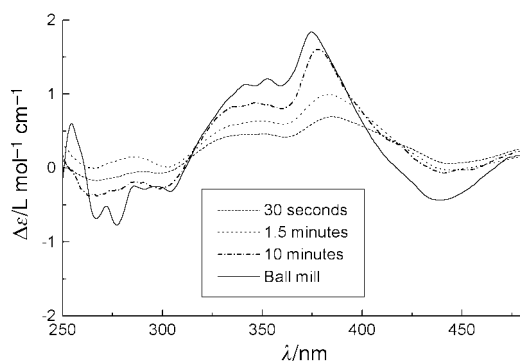
Fig. 3 Solid state CD spectra of discs of (*R*)-**3MLNN** in KBr prepared from mixtures made using various grinding times in an agate mortar and in an agate ball mill for 5 minutes (see the Experimental section for details).

sample, followed by preparation of a thin disc under pressure. The method has also been applied to the study of organic compounds, namely benzamides which form enantiomeric crystals,[34] peptides,[35] and steroidal bile acid inclusion complexes.[36] In these examples, detailed experimental procedures for preparation and recording CD spectra of solid samples are scarce.

A detailed account of the factors which must be controlled in order to record reliably and in a practical manner the CD spectra of a family of crystalline organic materials, namely phenyl α-nitronyl nitroxide radicals, is given in the Experimental section. The preparation of KBr discs of the compounds appealed to us since it is, in principle, a relatively simple technique not needing particularly special sample preparation. Given that literature reports are somewhat contradictory or vague concerning the preparation of the discs for CD measurements, and the difficulty we first experienced in obtaining reliable spectra, we repeated tests on the following variables: (i) grinding time of the KBr–compound mixture (see Fig. 3); (ii) thickness and concentration of the discs; (iii) pressure in disc preparation; (iv) band width of the incident light; (v) rotation of the disc in the machine and averaging of the spectra. We used the radical (*R*)-**3MLNN** as our standard, since its CD spectrum has well-defined and characteristic Cotton effects. An optimum spectrum for the compound is shown in Fig. 3. The optimum conditions during preparation are (i) short ball milling of the sample (although a very thorough grinding of the sample with an agate pestle and mortar gives similar satisfactory results); (ii) a concentration of between 0.2 and 0.4 weight percent of compound in a disc with thickness of between 0.4 and 0.8 mm, pressure of disc pressing having no effect,§ and during the recording of the spectra the band width used was 2 nm, but could be opened up to 10 nm in the case of compounds with broad Cotton effects, which is the case here (see the Experimental section). The widening of the band width reduces noise in the spectrum which results from high absorption at the narrower settings.

The success of the technique requires a random orientation of the crystallites in order to avoid *linear* dichroic effects, which might swamp the circular dichroism, and represents an added difficulty in recording the CD spectra of single crystals or films should they present structural alignment of the chromophoric units.[12,52] Scattering of the light signal is another potential problem, although not as acute as in the recording of absorption spectra, since the scattering of circularly polarised light in a turbid medium is approximately three times less than that

§ Discs were generally pressed to 10 ton pressure to ensure good quality, but pressing under 8, 6, 4 or even 2 ton gave essentially identical spectra, although the latter had a greater tendency to be opaque, giving higher absorbance. There is no evidence that grinding or pressing of the samples described herein produces crystalline phase transitions, but in the general sense it is important to consider this possibility.
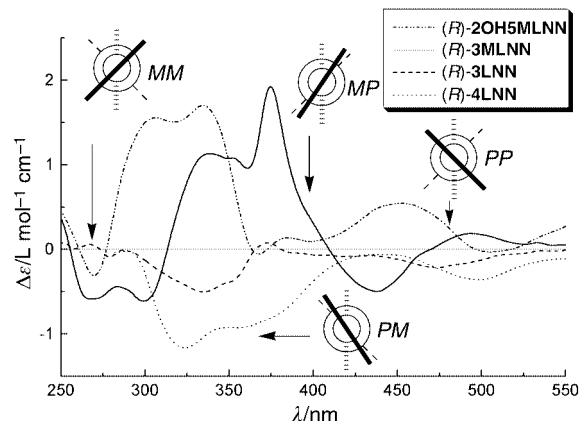
Fig. 4 Solid state CD spectra measured in a KBr matrix of (*R*)-**3LNN**, (*R*)-**3MLNN**, (*R*)-**2OH5MLNN** and (*R*)-**4LNN** along with the gross conformations of the compounds in their crystals.

of linearly polarised light,[53] and in the commercial spectropolarimeters (such as the one used in this study) the difference between absorption of right and left circularly polarised light is recorded. Therefore, provided scattering does not augment the observed absorption too much, the effects are generally small. These arguments explain the observed effects of grinding time on the spectra obtained.

Discussion

Our objective at the outset 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 (*R*)-**3MLNN**, (*R*)-**3LNN**, (*R*)-**2OH5MLNN** and (*R*)-**4LNN** under the optimum conditions described above, and their CD spectra are presented in Fig. 4, along with a schematic representation of their conformations in their crystals. Views of the conformations of the molecules in their crystal structures are shown in Fig. 5.

The chromophores associated with each Cotton effect were assigned precisely with the electronic transitions of (*R*)-**3LNN** in its crystal using *ab initio* molecular orbital calculations in previous work, in which the calculated CD spectrum reproduced the experimental spectrum remarkably well.[39] This work implied that the Cotton effect located at approximately 470 nm is associated with n→π* transitions of the nitronyl nitroxide moiety. This optically active transition lies between the visible absorption band associated with the n→π* transition of this group, located at 600 nm in the UV–visible spectrum, and a UV absorption, located between 340 and 380 nm. This latter absorption band has a Cotton effect associated directly to it, a negative one at approximately 340 nm, and is assigned to the π→π* transitions of the ONCNO moiety from a common ground state to excited states which have two orbital contributions (for this reason two Cotton effects are observed in some of the CD spectra in Fig. 4). Importantly for this work, changing the sign of the angles formed between the 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 feature of the CD spectra which is most easily interpreted in terms of a correlation with the crystal structures of the compounds are the Cotton effects centred at between 300 and 400 nm, which have a sign and magnitude dependent upon the twist angle (*β*) between the planes of the NCN unit of the imidazolyl ring and that of the phenyl ring. The *β* angles are +36.9° for (*R*)-**2OH5MLNN**, +30.9° for (*R*)-**3MLNN**, −25° for (*R*)-**3LNN**, and −29° for (*R*)-**4LNN**. According to the calculations described above, for positive *β* angles between the planes, *i.e. P* helicity, a positive sign is observed in the Cotton effects. The shift to higher energy in the position of these
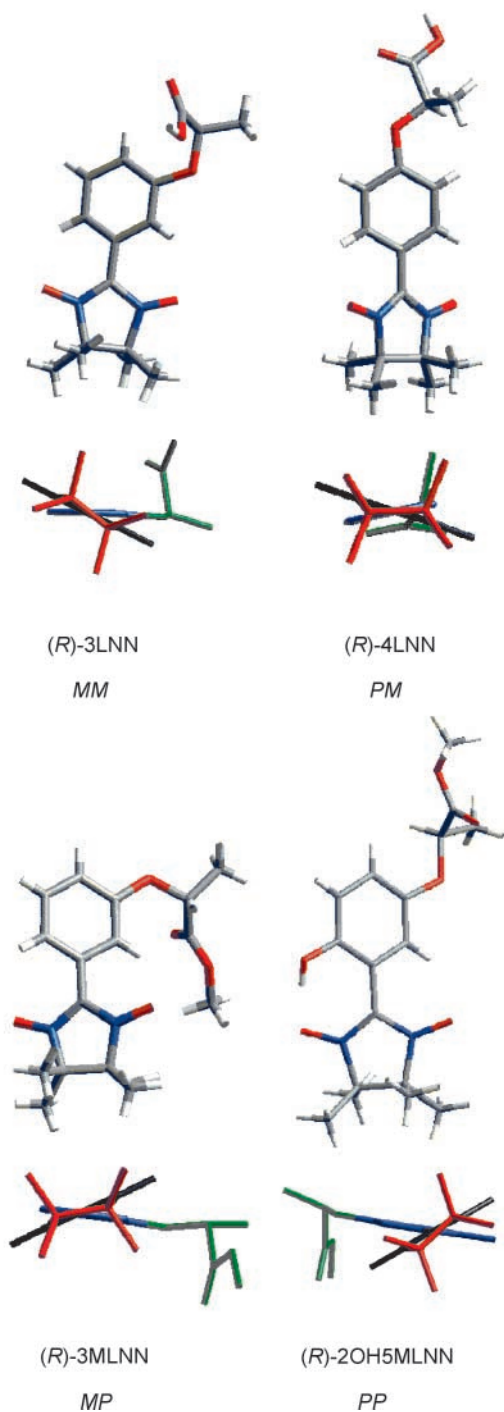
(R)-3LNN (R)-4LNN
MM PM

(R)-3MLNN (R)-2OH5MLNN
MP PP

Fig. 5 Views of the molecules of (R)-**3LNN**, (R)-**3MLNN**, (R)-**2OH5MLNN** and (R)-**4LNN** in their crystal structures in the classical colours, and end-on views with the chiral lactate groups in green, the aromatic ring in blue, the ONCNO moiety in black, and the CMe$_2$CMe$_2$ unit in red.

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.

The calculations carried out for (R)-**3LNN** also indicated[39] that the sign of the Cotton effect of the same radical at approximately 490 nm (associated with n→π* transitions of the ONCNO unit) depends on the torsion angle a in the imidazolyl unit. However, in (R)-**3LNN** and (R)-**3MLNN** this torsion angle has the same negative sign (−18.5 and −21.0°, respectively), as it does in the opposite sense in (R)-**4LNN** and (R)-**2OH5MLNN** (+28 and +26°, respectively), yet the Cotton effects are very different. Those displayed by (R)-**3MLNN** (negative at 438 nm and positive at 495 nm) are not explained by the aforementioned calculations, and their origin is as yet
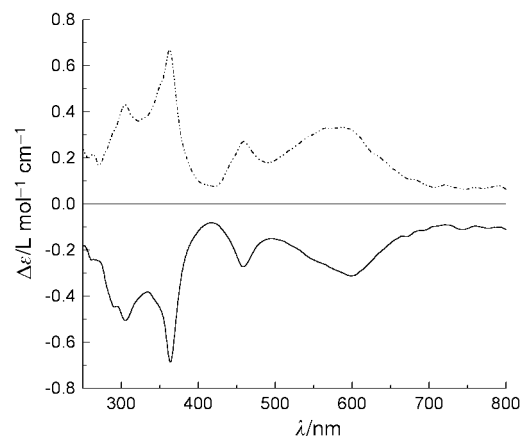

Fig. 6 The solid state CD spectra of enantiomorphic crystals of **2ClNN**.

unclear. However, it should be noted that the strong hydrogen bond present in the structure of (R)-**3LNN** causes a large difference between the lengths of the two N–O bonds, and therefore presumably influences the position of this transition.

A rather surprising result of the CD spectra is that the intensities of the Cotton effects observed in the solid state for the ester derivative (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 possible origins of the great differences between the two spectra are: (i) the conformation adopted by the chiral group and its modification of the chiroptical properties of the phenyl α-nitronyl nitroxide core; (ii) the variation of the intensity of the Cotton effect as a result of strong intermolecular hydrogen bonds in (R)-**3LNN**; (iii) 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 (i) 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 (ii) seems equally unsuitable.

The use of CD of ground single crystals is not limited to the study of intrinsically chiral molecules, but can be applied to achiral molecules which crystallise in chiral crystallographic space groups, and therefore display conformational chirality. This possibility is particularly appealing in the case of studies of conformational stereochemistry, such as this one, since the optical activity of chiral conformations can be studied in the absence of stereogenic centres. Within the family of α-nitronyl nitroxides, several compounds are known which crystallise in chiral space groups. We studied the radical 2-chlorophenyl α-nitronyl nitroxide,[49] which crystallises in the $P2_12_12_1$ space group, with an angle of + or −62° between the planes of the ONCNO unit and the phenyl ring. The molecule has a pseudo-*anti* conformation, with either *MM* or *PP* helicity according to the crystal which is picked.¶ This fact is graphically demonstrated in the solid state CD spectra of the two conformational enantiomers (Fig. 6).

Striking in the spectra of this achiral compound is the intensity of the CD signal despite the absence of a stereogenic centre in the molecule, which does not form stable atropisomers in solution. As to the assignment of the handedness of each crystal, given that the sign and magnitude of the Cotton effect between 300 and 400 nm are correlated with the twist angle between the planes of the NCN unit of the imidazolyl ring and that of the phenyl ring, the enantiomorph which displays a

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¶ The crystals of the enantiomorphs are indistinguishable by optical microscopy, and therefore they had to be picked by trial and error. In fact, the first five crystals picked were the (+) (dextrorotatory) enantiomer.

negative Cotton effect in this area should correspond to the molecule with M helicity between the two rings. Confirmation of this hypothesis would require definite solution of the crystal structure of one of the two enantiomers (which as a result of the lack of heavy atoms is not feasible in this case). A remarkable feature of the spectra is the intensity of the Cotton effect centred at 580 nm, which coincides with the absorption band in the UV–visible spectrum and is not so prominent in the spectra of the chiral derivatives which form a part of this work. A possible source of the augmentation of this Cotton effect, which probably arises from the n→π* transitions of the ONCNO unit, is the proximity of the chlorine atom to the radical unit thereby enhancing the optical activity of the compound as a result of the more twisted environment.

It is important to note that *no* Cotton effects are observed from molecules which pack in non-centrosymmetric space groups which are not chiral, among them the first organic bulk ferromagnet, the β-phase of the 4-nitrophenyl α-nitronyl nitroxide (**4NO₂NN**),[54] whose crystals belong to the orthorhombic space group *Fdd*2. Here the cell has a plane of symmetry, and molecules are present with M and P helicity. Clearly, no signal is observed either for achiral molecules which crystallise in centrosymmetric space groups, or by racemic modifications of compounds which crystallise as such, of which (*RS*)-**3LNN** is an example.[39]

Concluding remarks

The presence of a stereogenic centre appended to the phenyl α-nitronyl nitroxide radicals leads to the preferential crystallisation 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 crystallisation 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 KBr disc method of recording CD spectra of solids is a valuable tool in this study, and is potentially a general one for the determination of optical activity of organic solids, and in the structural correlation of this property, and could conceivably lead to the determination of molecular conformations of molecules in amorphous solids. However, great care must be taken in the method's development to ensure the absence of artefacts. In the case of the phenyl α-nitronyl nitroxide radicals which were the subject of this study, the sign of the Cotton effects observed in the UV part of the spectrum can be correlated with molecular conformation in the solids, although their magnitude cannot. Nevertheless, important information has been provided concerning the influence of crystal structures on Cotton effects resulting from the chromophores in these molecules, both intrinsically chiral and achiral.[55]

Experimental

Materials

The radicals (*R*)-2-[3-(1-carboxyethoxy)phenyl]-4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-1*H*-imidazol-3-ium-1-oxyl ((*R*)-**3LNN**),[39] (*R*)-2-{3-[1-(methoxycarbonyl)ethoxy]phenyl}-4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-1*H*-imidazol-3-ium-1-oxyl ((*R*)-**3MLNN**),[39] (*R*)-2-[4-(1-carboxyethoxy)phenyl]-4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-1*H*-imidazol-3-ium-1-oxyl ((*R*)-**4LNN**),[38] (*R*)-2-{3-[1-(methoxycarbonyl)ethoxy]-6-hydroxyphenyl}-4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-1*H*-imidazol-3-ium-1-oxyl ((*R*)-**2OH5MLNN**)[48] and 2-(2-chlorophenyl)-4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-1*H* imidazol-3-ium-1-oxyl (**2ClNN**)[49] were prepared as described elsewhere.

X-Ray diffraction analysis of (*R*)-3MLNN

The radical was crystallised from mixtures of acetone and hexane by slow evaporation. Crystal data: molecular formula $C_{17}H_{23}N_2O_5$, formula weight 335.37, orthorhombic space group $P2_12_12_1$ (No. 19); $a = 1055.9(2)$, $b = 1189.4(2)$, $c = 1401.6(9)$ pm; $\alpha = \beta = \gamma = 90°$; $V = 1.7603(12)$ nm³, $Z = 4$, $\rho_{calcd.} = 1.266$ g cm⁻³, wavelength MoKα ($\lambda = 71.073$ pm), $T = 218(2)$ K, $\mu = 0.094$ mm⁻¹, $F(000) = 716$, reflections collected = 2644, reflections with $I > 2\sigma(I) = 1839$, solved by direct methods using SHELXS-86 (Sheldrick, 1990) and refined with anisotropic displacement parameters by using SHELXL-93 (Sheldrick, 1993) to give final R indices ($I > 2\sigma(I)$) $R_1 = 0.0319$, $wR_2 = 0.0722$. Diffractometer Bruker P4, scan type ω. The data have been deposited with the Cambridge Crystallographic Data Centre.‖

Preparation of KBr discs

The discs were prepared by mixing approximately 200 mg of dry KBr (Aldrich, 98%, heated *in vacuo* at 100 °C for 5 hours and cooled *in vacuo*) and between 0.2 and 1.0 mg of the sample in question (at higher concentrations the absorption of the samples becomes too intense) in an agate mortar and pestle. In the case of samples subjected to ball milling a Retsch MM2 apparatus was employed with agate containers and balls. Milling was performed for 5 minutes at 80 oscillations per minute.** Approximately 150 mg of the mixtures were pressed at 10 ton in a standard press over a period of 10 minutes, and were subsequently weighed and their thicknesses measured with a micrometer, the value being between 0.4 and 0.6 mm. When withdrawn from the press the discs were generally transparent. On occasions where the discs had a slightly opaque appearance this feature did not apparently affect the CD spectra, which were identical to those of the clear discs (although absorbance was higher).

Since the grinding time is a factor in sample preparation, we recorded the CD spectra of a sample containing 0.4 mg of sample and 200 mg of KBr (*i.e.* a sample concentration of approximately 0.2% by weight) ground for 0.5, 1.5 and 10 minutes, and also in a ball mill for five minutes. Approximately 180 mg of this mixture was taken for the preparation of the disc. The resulting average (*vide infra*) CD spectra are shown in Fig. 3. Simple grinding of the mixture in an agate pestle and mortar for 10 minutes gave perfectly reproducible results, which are optimum for this method. Mixing for less time produces spectra wherein the Cotton effects are less well defined, of lower intensity, and displaced from their actual positions, as might be expected as a result of scattering of the light.

The limits of the thickness of the discs were determined. At the lower limit, when the discs are thinner than 0.4 mm then noise from the background becomes a serious problem at the concentration used (0.1% by weight of the compound in KBr), and can lead to large errors in the spectra, as well as being extremely difficult to handle. At the other extreme, discs with thickness greater than 1.0 mm result in spectra with decreased apparent intensity of the Cotton effects, presumably as a result of scattering, and a good compromise thickness is 0.8 mm. The limits of concentration are largely fixed by the sensitivity of the spectropolarimeter and the optical activity of the compounds. In this case, the lower limit is approximately 0.1% by weight,

‖ CCDC reference number 151137. See http://www.rsc.org/suppdata/p2/ b0/b008379h/ for crystallographic files in .cif format.

** When longer milling times or faster motions are employed the samples (at least partially) decompose, probably as a result of the heat generated in the process, which produces very fine particles that are presumably more rapidly decomposed by light and/or atmospheric oxygen. Ball milling for just five minutes gave, on one occasion, the spectra displayed in Fig. 3, which is a minor improvement over the spectra prepared under less forcing conditions. On other occasions, decomposition of the radicals was detected in the solid state CD spectrum (as well as in the IR spectrum of the compound), as witnessed by a change in the ratio between the Cotton effects centred at 380 and 345 nm.
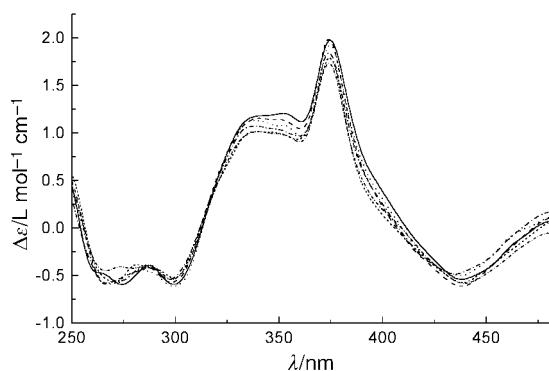
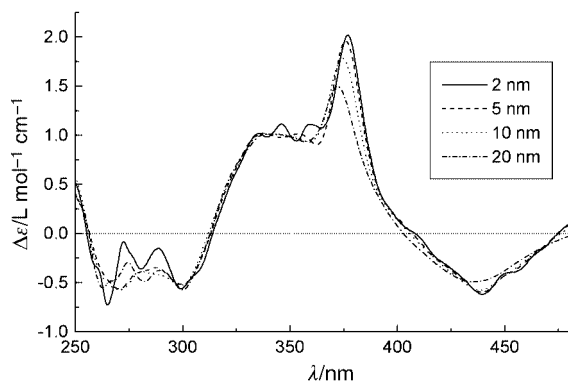**Fig. 7** Effect of disc rotation on the solid state CD spectra of (*R*)-**3MLNN** in KBr.

Fig. 8 Solid state CD spectra of (*R*)-**3MLNN** in KBr measured using different band widths.

and the upper limit, at which absorption distorts the CD signals, is approximately 0.5% by weight.

One of the unavoidable aspects in the preparation of solid discs is the use of pressure to ensure transparency and thereby circumvent scattering effects. However, this treatment can have drastic effects on crystals, such as the conversion of one polymorph into another, and is a potential drawback to the method. At least in the case of the phenyl α-nitronyl nitroxide radicals presented here, this factor proved not to be a problem. Pellets of the same mixture of (*R*)-**3MLNN** in KBr were pressed under pressures of 2, 4, 8, and 10 ton for 10 minutes. The CD spectra did not show any significant difference between them. The discs are more transparent and give better spectra when they are prepared at higher pressures. All the spectra presented herein were pressed at 10 ton.

Recording of CD spectra

The solid state circular dichroism spectra of the KBr discs were recorded on a JASCO-715 spectrometer fitted with a sample holder (borrowed from a VARIAN Cary 5 absorption spectrophotometer) by means of adhesive tape so that the disc was normal to the light beam. The position of the sample in the light beam could be checked by putting the wavelength in a visible part of the spectrum and adjusting the sample holder and disc accordingly. For each spectrum, the disc was rotated at 20° intervals and at least six spectra were averaged using the J700 software associated with the spectropolarimeter. This process is essential given the inevitable slight inhomogeneities in the disc, as has been noted previously by others.[33,35] A representative example is shown in Fig. 7. The value of $\Delta\varepsilon$ given in the spectra is calculated by using the concentration as the molarity of the sample in KBr in mol L^{-1} (after correction for the density of the disc) and using the measured thickness of the disc (using a micrometer) as the path length. The use of absorption for calibration is not recommended, because the absolute value is unreliable because of light scattering.

When recording CD spectra of solutions, the band width of the incident circularly polarised light, which can be adjusted in the spectrometer, is best set at 1 nm. In the case of dilute, perfectly homogeneous thin and transparent discs the same conditions can be employed. However, to avoid disc fragility (as a result of the necessary thinness of the disc) and to generate spectra with minimal noise (which can become important at high absorbances), the band width normally used was 2 nm, but can be opened up to 10 nm (Fig. 8). This experimental condition does not affect the spectra in the case of the radicals reported herein, since the Cotton effects are relatively broad. However, when the band width is widened to 20 nm a significant loss of intensity in the Cotton effect is observed, and therefore this condition should not be employed.

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