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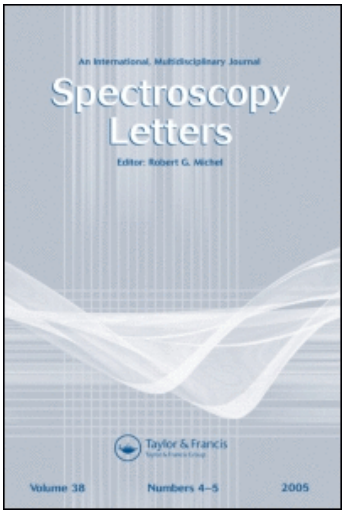

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DIRECT NMR DETERMINATION OF OPTICAL PURITY OF NICOTINIC AND QUINOLINIC CARBOXYLIC ACID COMPOUNDS USING 1, 2-DIPHENYLETHANE-1, 2-DIAMINE AS A CHIRAL SOLVATING AGENT

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ABSTRACT

The use of the chiral solvating agent, (1R,2R)- or (1S,2S)-1,2-diphenylethane-1,2-diamine, in the NMR determination of the optical purity of α-chiral acids has been well documented. The amine forms soluble diastereoisomeric salts with the enantiomers of carboxylic acids, producing differences in chemical shifts between diastereoisomeric salts, thus permitting a direct measure of their enantiomeric composition. However, the acids that were studied principally were the α-chiral acids and, less frequently, β-chiral acids. We used this chiral solvating agent to determine the optical purity of ε-chiral acids of the imidazolinone herbicides imazapyr, imazethapyr, imazamox, imazapic, and imazaquin, in which the carboxylic acid group is attached to an aromatic ring and the chiral center in the imidazolinone ring is five bonds away from

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the acid group.The optical purity of these ε-chiral acids is readily determined in pyridine-d_5 at room temperature with 1,2-diphenylethane-1,2-diamine. In a 2:1 complex of the acid with the chiral solvating agent, the diastereomeric resonances in ^{1}H NMR spectrum are typically non-equivalent by more than 0.05 ppm, thus allowing rapid and direct analysis of optical purity. The effect of stoichiometry, acid enantiomeric purity, concentration, and solvent on the observed non-equivalence is studied. The nature of the diastereomeric salt complex of these imidazolinones with 1,2-diphenylethane-1,2-diamine is also discussed.

Key Words: Imazethapyr (5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid); Imazapic (5-methyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid); Imazapyr (2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid); Imazamox (5-methoxymethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid); Imazaquin (2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinoline carboxylic acid); Enantiomers; Herbicide; Imidazolinones; Chiral solvating agent; 1,2-Diphenylethane-1,2-diamine.

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INTRODUCTION

More effort has been focused recently in the pharmaceutical and agricultural chemicals industries in the field of asymmetric synthesis and chiral separation of enantiomeric compounds since the biological activities of enantiomers can be significantly different. Consequently, direct and fast analytical methods to determine the optical purity and absolute configuration of optically resolved compounds are needed. The application of ^{1}H NMR spectroscopy with chiral solvents for the *in situ* determination of chiral compounds has been well-documented (1). One application of chiral solvating agents is the determination of the optical purity of a chiral acid using a chiral amine or vice versa (1–5). The chiral amine forms soluble diastereoisomeric salts with the enantiomers of acids, producing differences in chemical shifts between diastereoisomeric salts, thus permitting a direct measure of their enantiomeric composition. Most of the methods that are used for the determination of enantiomeric purity of carboxylic acids are applicable only to α-aliphatic or α-aryl carboxylic acids (1,4,5). A few studies were shown for β-carboxylic acids at low temperatures.

We report here the application of a chiral amine as a solvating agent to determine the optical purity of ε-chiral acids of compounds of the imidazolinone class. These imidazolinones contain an acid group that is attached to an aromatic ring

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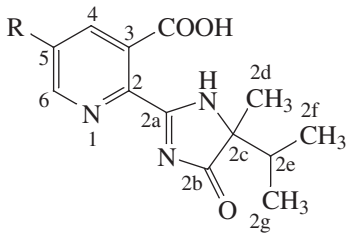
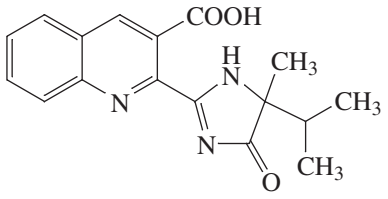
Nicotinic acid compounds



Quinolinic acid compound



R = H; Imazapyr Imazaquin

R = Methyl; Imazapic

R = Ethyl; Imazethapyr

R = Methoxymethyl; Imazamox

Figure 1. Structures of agricultural imidazolinone compounds.

and the chiral center is in the imidazolinone ring, which is five bonds away from the acid group. The imidazolinone class of compounds: imazethapyr (5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid), imazapic (5-methyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid), imazapyr (2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid), imazamox (5-methoxymethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid), imazaquin (2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-3-quinoline carboxylic acid) (Figure 1), are active ingredients in several commercial herbicides that are used widely in agriculture (6–8).

They exhibit extremely low mammalian toxicity and high efficiency, resulting in very low application rates and low environmental impact (9). They all inhibit the enzyme acetohydroxyacid synthase (AHAS; EC 4.1.3.18; also called acetolactate synthase or acetolactate pyruvate-lyase (carboxylating)), which is present in plants and bacteria, but not in animals. AHAS catalyzes reactions involving pyruvate and 2-ketobutyrate in the biosynthesis of the branched-chain amino acids leucine, isoleucine, and valine. Since the R and S enantiomers of imidazolinones showed different herbicidal activities (10), an NMR method was developed to determine the optical purity of imidazolinones, in support of the asymmetric synthesis of imidazolinones.

Available lanthanide NMR optical shift reagents (11–13) are not suitable for the direct determination of enantiomeric purity of the acids of these agricultural compounds because they are unstable in the presence of acidic substrates, and

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the lanthanide also causes severe line broadening. Moreover, the carboxylic acid carbonyl group possesses poor σ-binding ability to the lanthanide. Therefore, a derivatization reaction to convert imidazolinone acid to ester or amide would be needed in order to use the lanthanide shift reagents to determine the optical purity of these imidazolinones. Carbonell and Rothchild (14) have already applied the lanthanide shift reagent method to determine the optical purity of the methyl ester of imazapyr. Although a variety of lanthanide shift reagents produce enantiomeric shift differences in protons of the methyl ester of imazapyr, this procedure is not practical for routine optical purity determination of imidazolinones due to severe signal overlap.

Herein is reported a straightforward and direct NMR method to determine the enantiomeric purity of acids of imidazolinones using the chiral solvating agent, (1R,2R)- or (1S,2S)-1,2-diphenylethane-1,2-diamine (DPEDA). This chiral solvating agent has been used to determine the optical purity of a wide range of chiral carboxylic acids (5). However, in these carboxylic acids, only the proton that is on the carbon alpha to the carboxylic acid group showed a significant enantiomeric shift difference. In contrast, imazapyr, for example, has a COOH group five bonds away from the chiral center in the imidazolinone ring. Nevertheless, the methyl group attached to the chiral center showed a significant non-equivalence in shifts of more than 0.05 ppm, which facilitates rapid and direct estimation of the enantiomeric ratio of the imidazolinones. The effect of stoichiometry, acid enantiomeric purity, concentration, and solvent on the observed non-equivalence was studied. The factors that are responsible for the differential shielding are also discussed.

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EXPERIMENTAL

The racemic and enantiomerically enriched imidazolinones herbicides imazethapyr, imazapic, imazapyr, imazamox, and imazaquin were supplied by American Cyanamid Company. Chiral solvating agents were obtained from Fluka: (1R,2R)-(+)-1,2-diphenylethane-1,2-diamine (Fluka, Cat. No. 42745) and (1S,2S)-(−)-1,2-diphenylethane-1,2-diamine (Fluka, Cat. No. 42743).

The preparation of samples for the determination of optical purity of imidazolinones by ^{1}H NMR is very straightforward. Diastereoisomeric salt complexes of the imidazolinones with DPEDA are prepared by adding 0.025-0.05 mmol of (1S,2S)- or (1R,2R)-DPEDA to 0.05-0.1 mmol of imidazolinone in pyridine-d_5 solvent (*ca.* 0.75 mL) and shaking or vortexing until complete dissolution occurs. For a chemical shift reference, either the NMR sample solution is spiked with a chemical shift reference standard, such as tetramethylsilane (TMS), or the residual resonance(s) of the deuteriated pyridine-d_5 solvent is used as an indirect reference.

^{1}H NMR spectra were obtained using Bruker AMX-300 and AMX-500 spectrometers. The typical conditions for optical purity determination by ^{1}H NMR are

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as follows: 32K data points, 4-5 KHz sweep width, 3-5 μs pulse width ($\sim$30° nutation angle), and a 10 s relaxation delay. During the processing of the spectrum, an apodization function (e.g. sinebell) may be applied to achieve baseline separation of diastereotopic protons (e.g. the 2d-CH_3 peak of R and S enantiomers). A peak deconvolution procedure (normally performed with the *ldcon* software program) is recommended to obtain accurate integration of the diastereotopic protons.

RESULTS AND DISCUSSION

All imidazolinones containing a free COOH group (Figure 1) were examined. A significant chemical-shift non-equivalence ($\Delta\delta_H$) for 2d-methyl resonance in the diastereoisomeric complexes was observed in pyridine-d_5. Higher values of $\Delta\delta_H$ were always found near 2:1 stoichiometry of imidazolinone:DPEDA. The NMR data are listed in Table 1.

The observed shift non-equivalence of the 2d-methyl singlet is sufficient not only to determine the enantiomeric purity of enantiomerically enriched samples of imidazolinones, but also for assignment of the absolute configuration. The enantiomeric purity of all the imidazolinone compounds was measured accurately by integrating the separate methyl resonances of the diastereomeric salt complexes. Care was taken to ensure that accurate and reliable integrals were obtained by allowing observed signals to relax completely, and by using a line-deconvolution procedure for resonances that were not well separated. This method is, therefore, readily and directly applicable to all imidazolinone herbicides containing a free COOH group.

Parameters Affecting Chemical-Shift Non-equivalence

To maximize the value of the chemical-shift non-equivalence, the variation of $\Delta\delta_H$ with solvents, imidazolinone:DPEDA stoichiometry, imidazolinone concentration, enantiomeric composition, and diastereomeric structures of DPEDA

Table 1. ^{1}H NMR Shift Non-equivalence Observed for Imidazolinones

Imidazolinone	$\Delta\delta_H$ (ppm)
Imazapyr	0.083
Imazapic	0.051
Imazethapyr	0.079
Imazamox	0.091
Imazaquin	0.086

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were studied. Since room temperature spectroscopy is preferred for fast routine NMR analysis, the effect of reduced temperature was not studied in detail. However, an increase in chemical shift separation in $CDCl_3$ solvent was noticed when the temperature was decreased.

Effect of Solvents

The imidazolinones have a very limited solubility in non-polar solvents. For example, although imidazolinones with a pyridine ring (imazapyr, imazapic, imazethapyr, and imazamox) are soluble in $CDCl_3$, imazaquin (with a quinoline ring) is virtually insoluble in $CDCl_3$. The imidazolinones are also only sparingly soluble in C_6D_6. Therefore, pyridine-d_5 was chosen as a suitable solvent for all imidazolinones. Pyridine-d_5 is also better than $CDCl_3$ for all imidazolinones in promoting a large separation of diastereotopic resonances (Figure 2). This reflects the effect of solvation in stabilizing a given conformer in the diastereomeric salt complexes.

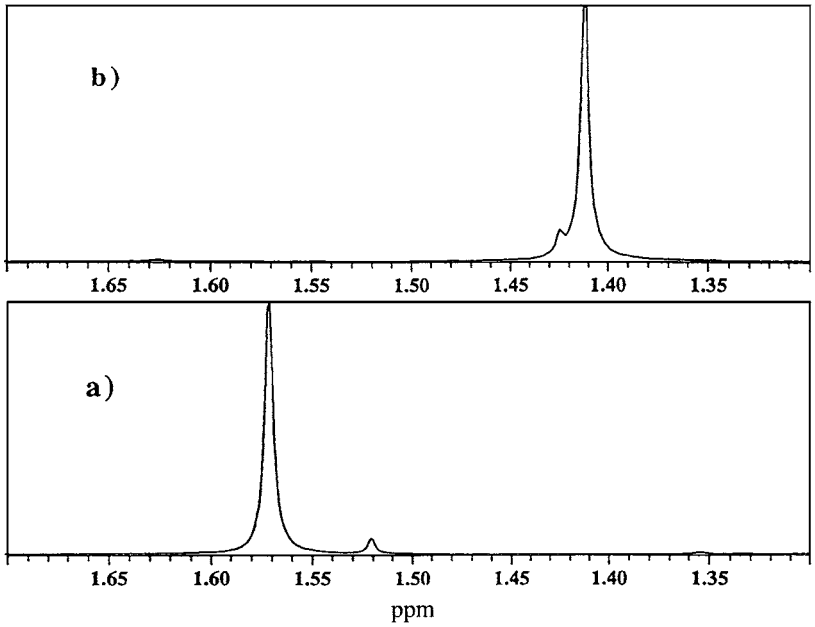

Figure 2. ^{1}H NMR shift non-equivalence for the 2d-methyl resonance of imazapic with (1S,2S)-DPEDA in a) pyridine-d_5 and b) $CDCl_3$ solvents.

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Effect of Stoichiometry

In order to maximize the chemical shift separation of R and S enantiomers, variation of stoichiometry was studied. For example, a standard solution of imazethapyr (0.1 mol/L) was titrated against varying concentrations of (1S,2S)-DPEDA solutions to generate a range of stoichiometric ratios. The observed chemical shift separation for the 2d-CH_3 resonances was recorded in the range 0.1 to 0.8 mole ratio of DPEDA to imazethapyr (Figure 3).

The shape of the titration curve, which has a maximum chemical shift separation *near* 0.5 mole ratio of DPEDA:imidazolinone, implies the predominant formation of a 2:1::imidazolinone:DPEDA complex, as might be expected for a diamine salt of a monoacid. In the diastereomeric complex of (1S,2S)-DPEDA/(R)-imidazolinone, which appeared as the lower field 2d-CH_3 singlet, large chemical shift changes were observed. This implies that the diastereotopic methyl group in the complex of (1S,2S)-DPEDA/(R)-imidazolinone is closer, on average, to the neighboring anisotropic phenyl group of DPEDA in the preferred conformation of the complex.

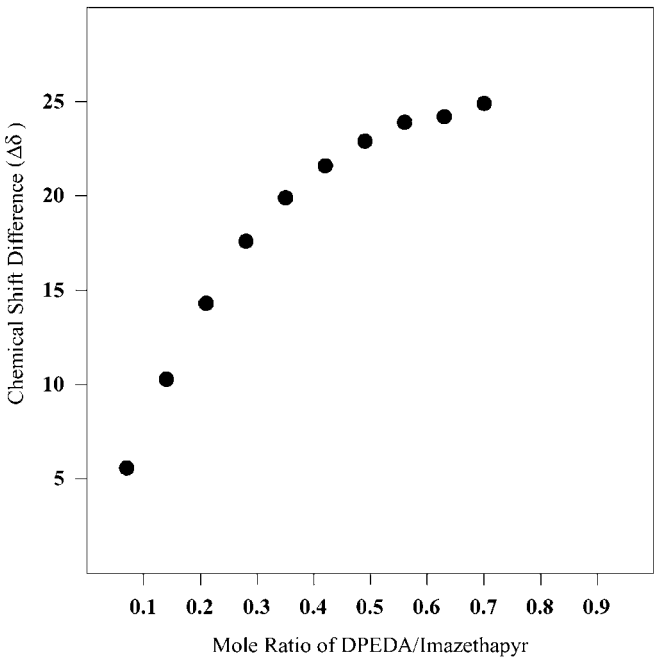

Figure 3. Variation of ^{1}H NMR chemical shift non-equivalence of 2d-methylresonance of imazethapyr with molar ratio of DPEDA:imazethapyr.

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Effect of Concentration

Proton NMR spectra for the complex of (1S,2S)-DPEDA with racemic imazethapyr were recorded in pyridine-d_5 in the concentration range 0.1 mol/L down to 0.025 mol/L. For the 2d-CH_3 resonances, $\triangle\delta_H$ increased quite steeply up to about 0.1 mol/L (Figure 4). Clearly, increasing the concentration of imazethapyr favors the formation of the salt complexes. Since solubility is a limiting factor, a maximum concentration 0.1 mol/L was used for routine analysis. It was noted that the diastereomeric complex of (1S,2S)-DPEDA and (R)-imidazolinone, which appeared as the lower field 2d-CH_3 singlet, exhibited a greater sensitivity in chemical shift to changes in concentration. This differential sensitivity compared to salts of (1S,2S)-DPEDA and (S)-imidazolinone may arise if the association constants for salt formation are different in the two diastereomeric complexes, or if the structures of the complexes are different such that the 2d-CH_3 group in (1S,2S)-DPEDA/(R)-imidazolinone complex is closer to the magnetically anisotropic phenyl group compared to that in (1S,2S)-DPEDA/(S)-imidazolinone complex.

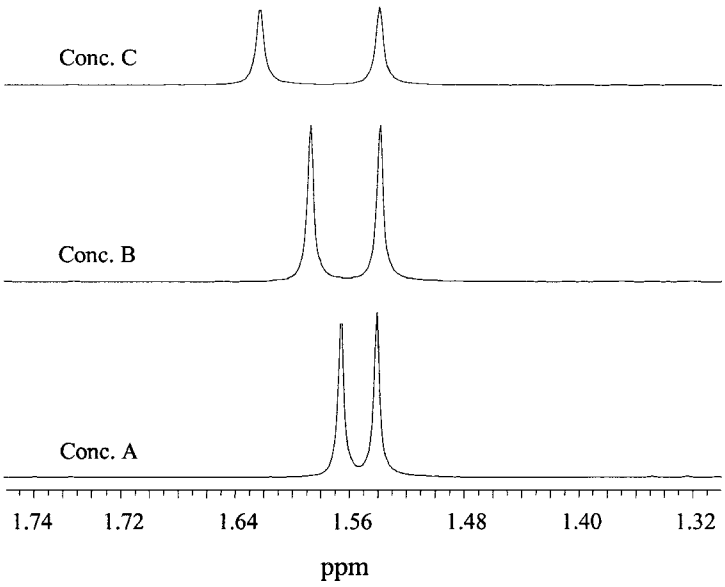

Figure 4. Variation of ^{1}H NMR chemical shift non-equivalence of 2d-methyl resonance with concentration for the diastereoisomeric complexes of racemic imazethapyr and (1S,2S)-DPEDA at 2:1 stoichiometry. Conc. A = 0.022 mol/L; Conc. B = 0.049 mol/L; Conc. C = 0.112 mol/L.

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Effect of Enantiomeric Composition

For the complexes of imazaquin with (1S,2S)-DPEDA in pyridine-d_5 and at room temperature, the variation of the chemical shift separation $\Delta\delta_H$ for the 2d-CH_3 was studied as a function of the enantiomeric purity of the imazaquin. The chemical shift difference between the anisochronous 2d-CH_3 resonances is sufficient to permit direct integration, and the method is intrinsically sensitive. Baseline resolution of the enantiomers was observed for R:S ratios ranging from 15:85 to 99:1 (Figure 5).

Using this method, one can detect the residual enantiomer at levels less than 1%. The detection limit of this method is set by the signal to noise limit of the NMR spectrometer used. The observation of the sense of chemical shift non-equivalence for a range of known enantiomeric composition may be used to correlate absolute configuration of the imidazolinone with chemical shift. The sense of the shift non-equivalence is the same for all the imidazolinones that were examined with (1S,2S)-DPEDA. This information may then be used to assign the absolute configuration of the imidazolinones.

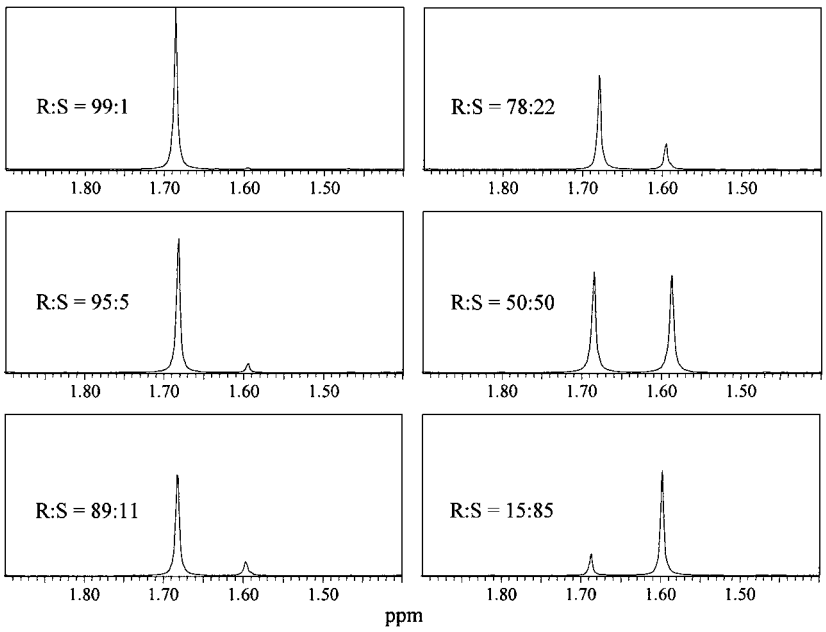

Figure 5. ^{1}H NMR shift non-equivalence for the 2d-methyl resonance of imazaquin of varying enantiomeric composition in the presence of (1S,2S)-DPEDA.

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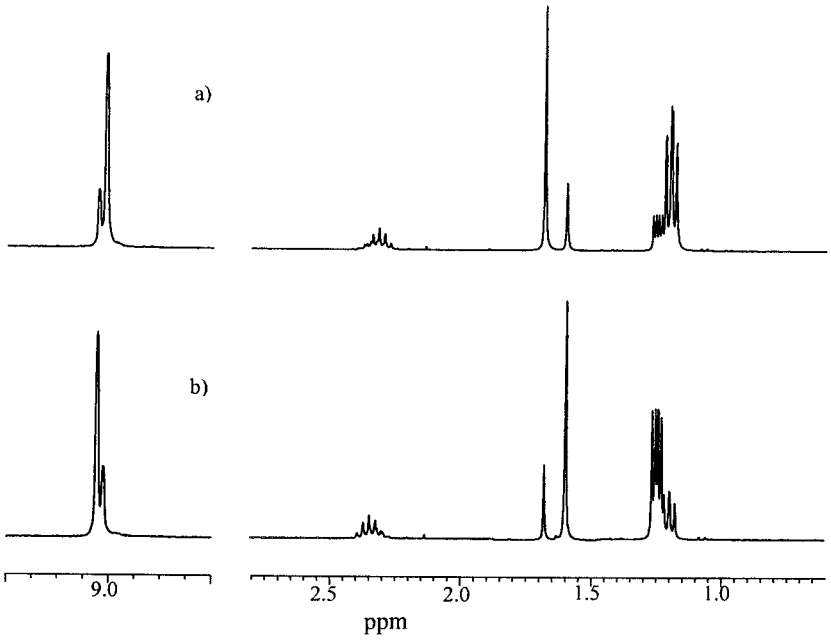

Figure 6. ^{1}H NMR spectra of imazaquin with different chiral solvating agents, a) (1S,2S)-DPEDA and b)(1R,2R)-DPEDA.

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Effect of Structure of DPEDA

Both (1R,2R)-DPEDA and (1S,2S)-DPEDA gave the same degree of chemical shift non-equivalence in complexes with imazaquin. As expected, the chemical shifts for the resonances of R and S isomers were reversed in the complex with (1S,2S)-DPEDA as compared to the complex with (1R,2R)-DPEDA (Figure 6). The 2d-CH_3 resonance of the salt of the (R)-imidazolinone with (1S,2S)-DPEDA always occurs downfield compared to that of (S)-imidazolinone with (1S,2S)-DPEDA. This observation may also be used to assign the absolute configuration of the imidazolinones.

CONCLUSION

An intrinsically sensitive NMR method was developed for the fast, direct and routine measurement of the enantiomeric composition of imidazolinone herbicides containing a free carboxylic acid group, using 1,2-diphenylethane-1,2-diamine as a chiral solvating agent. Experimental conditions such as choice of deuteriated

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solvent, stoichiometry, and concentration were optimized in order to maximize the observed ^{1}H NMR chemical shift non-equivalence in the diastereoisomeric salts. This method avoids the need for derivatization reactions such as esterification and amidation, and also can be used to determine the absolute configuration of imidazolinones.

It is difficult to disentangle the effects of solvation of different solvents, different degrees of association of these two structures of imidazolinone and DPEDA in their complexes, and stabilization by different conformations of the complex. Definitely, solvent is important in terms of association and stabilizing a particular conformation of the complex. Concentration is also important to give the maximum peak separation. The same change in the chemical shift at different enantiomeric compositions of imidazolinone and with either (1R,2R)-DPEDA or (1S,2S)-DPEDA indicates that it is the complex's structure that influences the non-equivalence more than the association constant (in a given solvent). That is why with (1S,2S)-DPEDA, only the R-imidazolinone shows change, while the S-imidazolinone remains the same, indicating only in R-imidazolinone is the 2d-CH_3 group oriented towards the magnetically shielded environment of the two phenyl rings of DPEDA. Moreover, the same chemical shift separation at different enantiomeric composition indicates that the association constant may be large or nearly the same for R- and S-imidazolinone complexes with DPEDA. All imidazolinones exhibited consistently the same sense of non-equivalence in various conditions of concentration and enantiomeric composition. Therefore, DPEDA can be used to correlate absolute configuration within in this series of herbicidal imidazolinones.

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