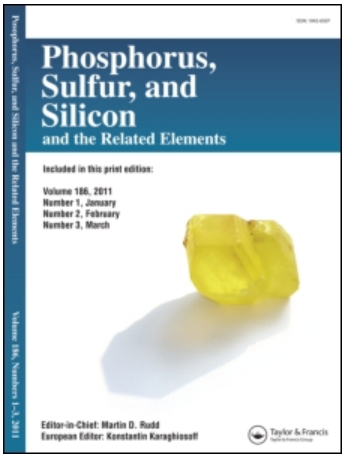

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^{31}P NMR DETERMINATION OF THE ENANTIOMERIC COMPOSITION OF N-PROTECTED 1-AMINOALKYLPHOSPHONATES USING 1-(1-NAPHTHYL)ETHYLAMINE AND EPHEDRINE AS THE CHIRAL AGENTS

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^{31}P NMR DETERMINATION OF THE ENANTIOMERIC COMPOSITION OF N-PROTECTED 1-AMINOALKYLPHOSPHONATES USING 1-(1-NAPHTHYL)ETHYLAMINE AND EPHEDRINE AS THE CHIRAL AGENTS

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Optically active 1-(1-naphthyl)ethylamine as well as ephedrine with N-protected 1-aminoalkylphosphones form in equimolar ratio in $CDCl_3$ diastereoisomeric salts distinguished in ^{31}P NMR spectroscopy. The magnetic nonequivalence of phosphonate groups are in almost all cases large enough ($\Delta\delta$ ^{31}P is up to 0.8 ppm) to determine enantiomeric excess values. Amide cis-trans isomerism were observed in the case of aminophosphonates with urethane type of N-protected group. Two in ^{31}P NMR distinguishable forms of diastereoisomeric systems of N-phthaloyl protected acid with ephedrine exist in $CDCl_3$ solution. The forms exhibit the reversal in the sense of the magnetic nonequivalence.

Key words: Enantiomeric excess (ee), 1-aminoalkylphosphonates, ^{31}P NMR magnetic nonequivalence, 1-(1-naphthyl)ethylamine, ephedrine, diastereoisomeric salts.

INTRODUCTION

Aminophosphonates, analogues of amino acids in which a carboxylic group is replaced by phosphonic group reveal diverse and interesting biological and biochemical properties.[1–2] Biochemical activity is strongly dependent on the enantiomeric composition of the active compound.[3] Therefore, direct and simple methods for the enantiomeric purity determination of the chiral 1-aminophosphonates and their derivatives are still desirable. In our first paper on this subject, we presented a method of the enantiomeric excess determination of the free aminophosphonic acids from the spectra of their Pd(II) complexes.[4] Recently, we proposed the ^{31}P NMR enantiomeric composition determination of 1-hydroxyphosphonic acid esters via their diastereoisomeric phosphonodidepsipeptides[5a,b] and diastereoisomeric salts using optically active amines (esp. NEA).[6] In addition, the

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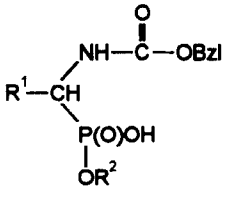
dependence of diastereoisomeric salts magnetic nonequivalence on solvents, concentration and enantiopurity of amine component were studied. Continuing our studies on the optically active amines as the chiral agents we report here their application to the ^{31}P NMR enantiomeric excess determination of N-protected 1-aminophosphonates. Chiral solvating agent (CSA) methods of determination of ee are probably the quickest and simplest to perform in NMR tube, with no problem of kinetic resolution and sample racemization.[7] Diastereoisomeric salt and CSA methods are always grouped together however, interactions between salt components are stronger and exchange processes are slower.[6,7c]

RESULTS AND DISCUSSION

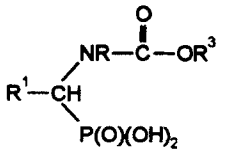
All N-protected 1-aminoalkylphosphonates and optically active amines studied in this work are depicted in Scheme I. The ^{31}P NMR chemical shifts corresponding



1 – 10

No	R^1	R^2
1	Bzl	Bzl
2	Bzl	Et
3	Bzl	Me
4	iBu	Bzl
5	iPr	Bzl
6	Me	Bzl
7	Ph	Bzl
8	Ph	Et
9	Ph	iPr
10	Ph	Me

Z-N-Protected 1-Aminoalkylphosphonate Monoesters 1 – 10

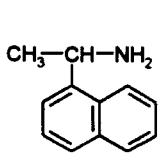


11 – 18

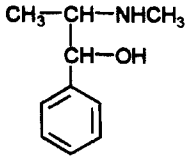
No	R^1	R^3	R	N-Protecting Group
11	iBu	Bzl	H	Z
12	iPr	Bzl	H	Z
13	nPr	Bzl	H	Z
14	iBu	t-Bu	H	Boc
15	iPr	t-Bu	H	Boc
16	iBu	Pht		Pht
17	iPr	Pht		Pht
18	Ph	Pht		Pht

Z = benzyloxycarbonyl group
Boc = t-butoxycarbonyl group
Pht = phthaloyl group

N-Protected-1-Aminoalkylphosphonic Acids 11 – 18



1-(1-naphtyl)ethylamine
NEA



ephedrine
Ephe

Optically active amines

SCHEME I

to the respective phosphonates and their diastereoisomeric salts are collected in Tables I–IV.

We have investigated the diastereoisomeric salts of two optically active amines, extensively employed as resolving agents or chiral solvating agents (CSA), i.e. (1R,2S)(−)ephedrine [**Ephe**] and R(+)-1-(1-naphthyl)ethylamne [**R(+)NEA**] or S(−)-1-(1-naphthyl)-ethylamine [**S(−)NEA**]. As would be expected, similarly to hydroxyphosphonates,[6] phosphorus NMR spectra of diastereoisomeric salts of S(−)-1-phenylethylamine (**S(−)PhEA**] in all cases revealed only single peaks.

^{31}P NMR spectra of Z- and Boc- N-protected acids as well as monoesters (**1**–

TABLE I

δ ^{31}P [ppm] and phosphorus chemical shift differences ($\Delta\delta$ ^{31}P [ppm]) for the main (transoid) form of Z-N-protected 1-aminoalkylphosphonic acid monoesters (**1–10**) and for their diastereoisomeric salts with 2–3 molar excess of the optically active amines. All spectra recorded in $CDCl_3$ one day after preparing samples

No	R^1	R^2	δ ^{31}P	($\Delta\delta$ ^{31}P)	[ppm]
			phosphonates	diastereoisomeric salts	
				R(+)NEA	(1R,2S) (-) Ephe
1	Bzl	Bzl	23.21	19.77 19.52(0.26)	20.53 20.46(0.08)
2	Bzl	Et	22.76	20.54 20.36(0.18)	21.19 21.00(0.19)
3	Bzl	Me	28.04	21.92 21.71(0.21)	22.26 22.08(0.18)
4	i-Bu	Bzl	28.14	21.27 20.894(0.38)	21.95 21.79(0.16)
5	i-Pr	Bzl	27.66	19.77 19.47(0.30)	20.81 20.58(0.23)
6	Me	Bzl	27.43	21.09 20.89(0.20)	21.62 21.49(0.13)
7	Ph	Bzl	21.48	16.32	17.30 17.12(0.18)
8	Ph	Et	20.06	15.80	17.04 16.80(0.24)
(-)8			22.77		16.81
9	Ph	iPr	19.02	14.94	15.69 15.51(0.18)
10	Ph	Me	20.85	17.05	17.95 17.75(0.20)
(+)10			24.67		17.97

TABLE II

δ ^{31}P [ppm] and phosphorus chemical shift differences ($\Delta\delta$ ^{31}P [ppm]) of N-protected 1-aminoalkylphosphonic acids (**11–18**) and for their diastereoisomeric salts with 1.5–2 molar excess of the optically active amines. All spectra recorded in $CDCl_3$ one hour after preparing samples

No		R^1	δ ^{31}P (intensity) acids (in $CDCl_3$)	δ ^{31}P ($\Delta\delta$) [ppm] diastereoisomeric salts with S(-)NEA	[ppm] (1R,2S)(-)Ephedrine
11	Z	i-Bu	26.46(1.9) 25.85(1.0) 23.32 (+ethanol)	17.76	19.18 19.06(0.12)
12	Z	i-Pr	26.25(2.1) 25.43(1.0)	17.59 17.51(0.08)	18.06 18.04(0.02)
13	Z	n-Pr	25.79(2.6) 25.16(1.0)		
14	Boc	i-Bu	26.95(1.0) 26.16(1.4)	20.25 20.10(0.15)	19.69
15	Boc	i-Pr		18.12 17.90(0.22)	18.51 18.37(0.14)
16	Pht	i-Bu	17.89 (+DMSO)		15.18 14.61(0.57)
17	Pht	i-Pr	19.73	15.27 15.05(0.22)	14.93 14.73(0.20)
S(-)17					14.62
18	Pht	Ph	15.35 13.85 (+DMSO)		12.67 12.22(0.45)
S(-)18					11.94

15) showed signals of two forms existing in solution of $CDCl_3$ (see Figure 1a). In contrast, spectra of the aminophosphonates protected by the phthaloyl group (**16–18**), revealed the persistence of only one form. Probably, there exist cis and trans forms of Z- and Boc-group amide bonds, which are stabilized by hydrogen bonds. H-bonded structures are destroyed by a small amounts of ethanol and only one signal shifted to the higher field is observed (see **11** Table II). Consequently, there can exist two forms of diastereoisomeric salts. Both forms of the diastereoisomeric salts with optically active amine sometimes can differ in ^{31}P NMR spectra (see Figure 1b and Table III).

Amide cis-trans isomerism had been the subject of a number of studies, and mainly signals of the transoid form (Z conformer) were noted for analogical amino acid structures.[8]

TABLE III

Changes of the δ ^{31}P ($\Delta\delta$ ^{31}P) for the diastereoisomeric salts of racemic Z-N-1-aminoisopentylphosphonic acid (**11**) with ephedrine depending on the excess of ephedrine (1R,2S)(−)Ephe

molar ratio	δ^{31}P ($\Delta\delta^{31}$P)	
(11) : (1R,2S)(-)Ephe	transoid form	cisoid form
1 : 0	26.51	25.79
1 : 0.4	25.11 25.03(0.08)	24.50
1 : 1	21.73 21.52(0.21)	21.39
1 : 1.8	19.98 19.84(0.14)	19.84
1 : 2.6	19.70 19.57(0.13)	19.48
1 : 4.5	19.26 19.14(0.12)	18.94

TABLE IV

Changes of the δ ^{31}P ($\Delta\delta$ ^{31}P) for the diastereoisomeric salts of racemic N-phthaloyl-1-aminophenylphosphonic acid (**18**) with ephedrine depending on the excess of ephedrine (1R,2S)(−)Ephe

molar ratio	δ^{31}P ($\Delta\delta^{31}$P)
(18) : (1R,2S)(-)Ephe	one hour after preparing salts
1 : 0	15.35
1 : 1	13.14 12.50 (0.64)
1 : 1.3	12.76 12.15 (0.61)
1 : 2.5	11.25 10.91 (0.34)
1 : 3.5	11.02 10.71 (0.31)
1 : 20	11.26 11.08 (0.18)

Enantiomeric Excess Determination of Z-N-1-Aminoalkylphosphonate Monoesters

Two sets of signals have been recorded in the case of monoesters and their diastereoisomeric salts. The spectral data of the main signals are listed in Table I. Additional signals, most probably of cisoid forms with the intensity not higher than 10% of major signals, have been always shifted to the higher field (Figure 1).

Phosphonic group signals of main forms of diastereoisomeric salts have been found to be shifted by *ca.* 5 ppm to higher field of the monoester peaks. The same shift has been observed for the first deprotonation of phosphonate group; it means that in the presence of amine in $CDCl_3$ solution phosphonate group exist in an ionic form.[7,9]

The chemical shift differences of Z-N-1-aminophosphonic monoester diastereoisomeric salts with R(+)NEA as well as (1R,2S)(−)ephedrine are in almost all

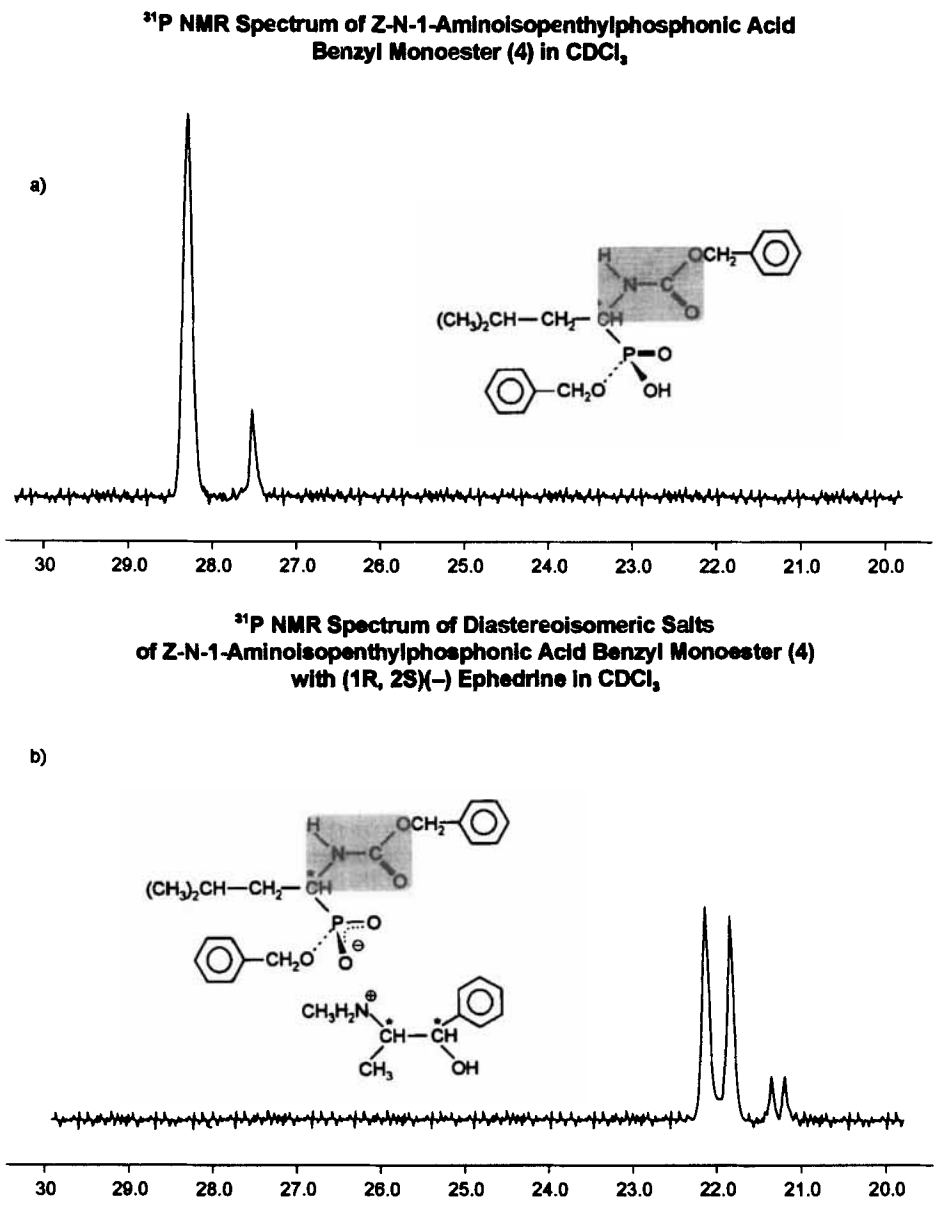


FIGURE 1 ^{31}P NMR spectra of benzyl monoester Z-N-aminoisopentylphosphonic acid (**4**) (a) and their diastereoisomeric salts with ephedrine (b) both recorded in $CDCl_3$ solution. Peaks correspond to trans and cis isomers of N-protected monoester.

cases sufficient to permit accurate integration ($\Delta\delta$ ^{31}P from 0 to 0.38 ppm). The only case in which we were unable to observe nonequivalence with optically active NEA were Z-N-1-aminobenzylphosphonate monoesters (R_1 = Ph; i.e., **7**, **8**, **9** and **10**). As expected, $\Delta\delta$ ^{31}P reaches a maximum value at 1:1 stoichiometry, when salt formation is complete. The plot on the Figure 2 illustrates the changes of the ^{31}P magnetic nonequivalence of **10** depending on the excess of optically active ephed-

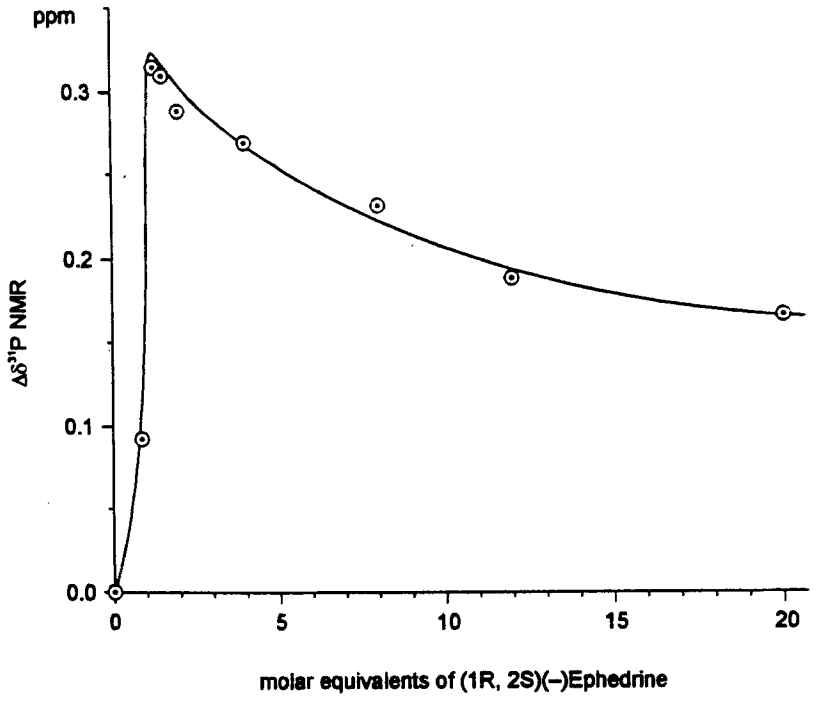


FIGURE 2 Changes of the $\Delta\delta$ ^{31}P NMR value for the diastereoisomeric salts of benzyl monoester of (+/−) Z-N-protected 1-aminobenzylphosphonic acid (**10**) with (1R,2S)(−)ephedrine depending on the excess of (1R,2S)(−)ephedrine.

rine. The same shape of plot (typical for the diastereoisomeric salts, but not for the CSA) we have observed for the similar 1-hydroxyalkylphosphonate salts.[6] Addition of molar excess of optically active amines always caused upfield shifts in the resonances and reduction of $\Delta\delta$ ^{31}P values (see Table III and IV). Such behaviour may be attributed to the increased dissociation of phosphonic group (upfield shift)[9] and the acceleration of the exchange processes between diastereoisomeric ion-pair components (reduction of $\Delta\delta$ ^{31}P values).

^{31}P NMR spectra of R(+)NEA or (1R,2S)(−)Ephe diastereoisomeric salts had shown two separated peaks when the racemate or enantiomerically enriched samples of **8** and **10** were used and a single peak in the case of optically pure compound.

Using different mixtures of preweighted enantiomeric composition of (−)(**8**) and (+)(**8**) or (−)(**10**) and (+)(**10**) we recorded the pairs of signals with the baseline resolution almost in all cases (the values of $\Delta\delta$ ^{31}P varied from 0.15 to 0.30 ppm). Their integration was a measure of diastereoisomeric composition which is related directly to the enantiomeric composition of the original mixture. The agreements with accuracy from 0.1–5% between known preweighted compositions and ^{31}P NMR determined values were obtained.

The main disadvantage of this method is the fact, that the signals of both forms (main-transoid and cisoid) can overlap and the accuracy of determining the enantiomeric excess can be low.

Diastereoisomeric Salts of Z- and Boc-N-protected 1-Aminoalkylphosphonic Acids (**11–15**)

^{31}P NMR data of the acids (**11–15**) and their salts are collected in Tables II and III. Two sets of signals have been recorded in the case of acids and their diastereoisomeric salts. Similarly to the monoesters, additional signals, most probably of cisoid forms, with the intensity near 50% of main signals have been found shifted to higher field. Only in case of Boc-*N*-1-aminoisopentylphosphonic acid (**14**) the upfield shifted form dominates in $CDCl_3$ solution. Also, ^1H NMR spectra showed that the —NH— proton (proton adjacent to the amine group) exists in two different surroundings (for instance amine protons of **11**: 5.60 ppm [J_{HH} = 9.8 Hz] and 6.28 ppm [J_{HH} = 10.2 Hz], coupled with proton from the asymmetric carbon atom). The —NH— proton signals of dominating form were shifted to higher field. It can be evidence on existing of hydrogen bonds stabilizing both transoid and cisoid forms.

Phosphonic group signals of main forms of diastereoisomeric salts have been found to be shifted by *ca.* 9–7 ppm to higher field of the acid peaks. Changes δ ^{31}P and $\Delta\delta$ ^{31}P NMR with an excess of the amine (see Table III) indicate the deprotonation of phosphonate group when molar equivalent of amine was added. The cisoid forms of the diastereoisomeric salt (i.e. **11** with Ephe) showed in ^{31}P NMR only the single peaks.

The chemical shift differences (0–0.22 ppm) of the Boc- and Z-N-1-aminophosphonic acid diastereoisomeric salts with optically active NEA as well as Ephe were not sufficient to accurate measure enantiomeric excess of the phosphonates. The peaks were not often baseline separated and in addition, signals of both forms (main-transoid and cisoid) were often overlapped.

Enantiomeric Excess Determination of N-Phthaloyl-1-Aminoalkylphosphonate Acids

^{31}P NMR spectral data of the acids (**16–18**) and their salts are collected in Tables II and IV, and presented on the Figures 3 and 4. Contrary to the Z- and Boc-N-protected 1-aminoalkylphosphonic acids, only one single peak was recorded in the ^{31}P NMR spectra of N-phthaloyl protected acids. Showing only one stable form in $CDCl_3$ or in DMSO solutions. We recorded single peaks for the diastereoisomeric salts of enantiomerically pure **17** and **18** with molar equivalence of optically active ephedrine. Respectively, pairs of signals we noticed when salts of racemic **16**, **17** and **18** were studied (Table II). The variations in the magnitude of nonequivalence of racemic **18** with the excess of ephedrine are typical for the diastereoisomeric salts and are consistent with those of hydroxyphosphonate salts.[6] The highest value of $\Delta\delta$ ^{31}P NMR was observed for the equimolar ratio amine to phosphonate, the magnetic nonequivalence decreased with an excess of amine from 0.64 to 0.18 ppm (Table IV).

Using different mixtures of preweighted enantiomeric composition of (−)(**17**) and racemic (**17**) or (−)(**18**) and racemic (**18**) we recorded the pairs of well separated signals after adding equimolar of optically active ephedrine to $CDCl_3$ solution. The agreements with accuracy from 0.1–2.5% between known preweighted compositions and ^{31}P NMR determined values were obtained.

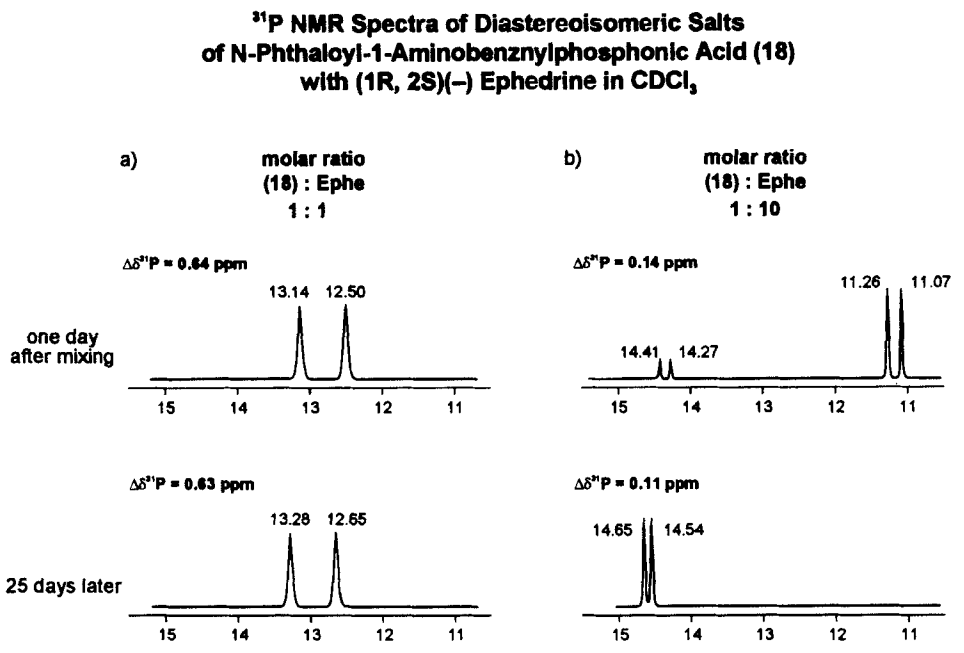


FIGURE 3 Changes of the ^{31}P NMR spectra for the diastereoisomeric salts of (+/−)N-phthaloyl-1-aminobenzylphosphonic acid (**18**) with (1R,2S)(−)ephedrine $CDCl_3$ in the period of 25 days for equimolar stoichiometry (a) and for 10 molar excess of (1R,2S)(−)ephedrine.

To our surprise, additional, downfield shifted single peaks (pairs of peaks for the racemic phosphonates) occurred on the spectra when we used molar excess of the amine component. The process is illustrated on the Figures 3 and 4. The same scale is used in each figure, to facilitate comparisons.

For the diastereoisomeric salts of (**18**) and enantiomerically pure Ephe with molar ratio 1:1 we have recorded almost the same spectra in the period of one month from preparing the salt (Figure 3a). Spectra of the salts with ten molar excess of ephedrine had been systematically changing. Intensity of the upfield shifted peaks decreased, while the intensity of the peaks in downfield increased. After 25 days almost only peaks in downfield were recorded. Again, the larger magnitude of magnetic nonequivalence (0.64 ppm) in case of equimolar ratio implies that the exchange processes of ions are slow and diastereoisomeric ion-pairs are well solvent separated. After adding excess amine two forms exist in solution. On the basis of chemical shifts comparison signals shifted to downfield would be assigned to the ion-pairs. Most probably, more stable, the solvent separated ion-pairs (peaks shifted downfield) are created from the larger aggregates of ions (upfield shifted peaks). The small value of $\Delta\delta$ ^{31}P NMR in the case of 10 molar excess indicates a rapid exchange of an amine component.

The same process we observed for salts of racemic and enantiomerically pure (**17**). Spectrum on Figure 4c was recorded one hour after mixing S(−)**17** with 3 equivalents of (1R,2S)(−)Ephe, peak at 13.36 ppm corresponds to one form of diastereoisomeric salt. After two weeks, the form at lower field dominates (17.68

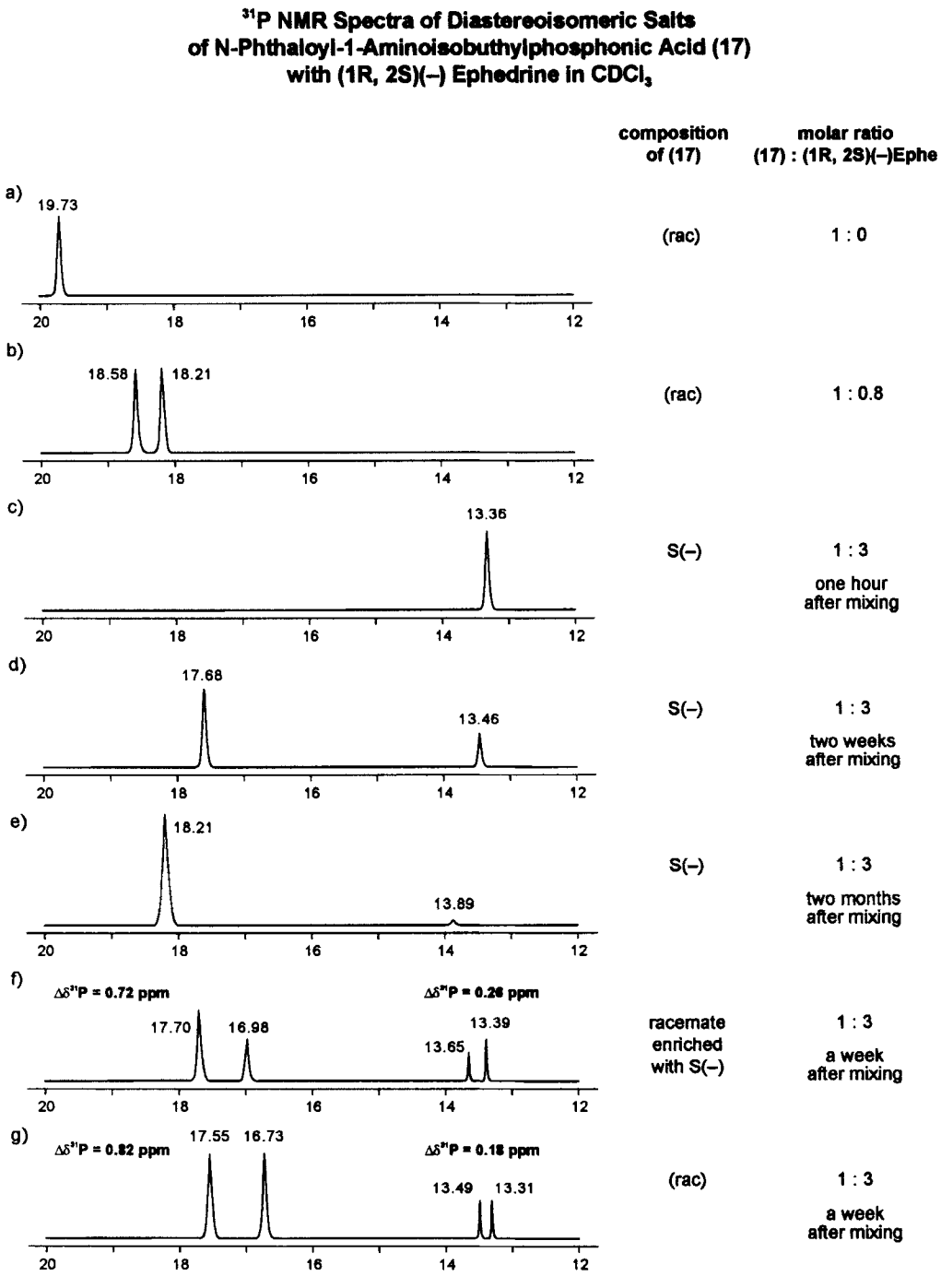


FIGURE 4 ^{31}P NMR spectra the diastereoisomeric salts of N-phthaloyl protected 1-aminoisobuthylphosphonic acid (**17**) with (1R,2S)(−)ephedrine in $CDCl_3$. Variations in time of the chemical shifts, intensity of the peaks and changes of the $\Delta\delta$ ^{31}P NMR value with the composition of (**17**) and the molar ratio of (1R,2S)(−)ephedrine to (**17**).

ppm), two months later only small traces of upfield shifted form were recorded in solution (Figures 4d and 4e).

Accordingly, in the case of equimolar ratio amine to phosphonic acid, the ion-pairs are solvent separated and exchange processes tend to be slow. So that the magnitude of $\Delta\delta$ ^{31}P NMR of ion-pair are high (*ca.* 0.37–0.8 ppm, slow exchange process, Figure 4b,f,g) and the peaks are situated in the low field (protonated form of phosphonate group).

In the presence of an excess of amine phosphonic acids exist in ionic form (upfield shifted form), creating aggregates of ions with rapidly exchanging amine molecules. However, separated ion-pairs in $CDCl_3$ (i.e. amine-phosphonate pairs, probably, in a particular low energy conformation) must be more stable than the larger ion aggregates.

It is necessary to point out that the sense of magnetic nonequivalence of both form is opposite (see Figure 4f). We observed such phenomena for salts of **17** and **18** with (1R,2S)(−)Ephe. This findings do corroborate the suppositions of Pirkle that the composition and size of the salt aggregates, which are found in nonpolar solvents, may change the sense of magnetic nonequivalence of diastereoisomeric salts.[10]

CONCLUSIONS

We herein report the use of optically active 1-(1-naphthyl)ethylamine and ephedrine as the convenient chiral agents for the enantiomeric purity determinations. In a typical experiment, the N-protected 1-aminophosphonate (0.05–0.1 mmol) and equimolar quantity of optically active amine are dissolved in $CDCl_3$ and their ^{31}P NMR (proton decoupled) spectra are recorded. The advantages of the method are that it is quick and simple to perform, amine need not be enantiomerically pure (however, highly enantiomerically enriched amine is preferred to improve $\Delta\delta$ value).[6,7] The concentrations of components can be used in a wide range, $\Delta\delta$ ^{31}P is not affected by dilution of samples. The methods may be improved by the choice of other amines and solvents as well as cosolvents.

EXPERIMENTAL

1-Aminophosphonates were obtained by previously reported procedures **1**–**10**[11] and **11**–**13**, **16**–**18**[12] and **14**–**15**.[13] The proton decoupled ^{31}P NMR spectra of the phosphonates and their salts (0.05–0.1 mmol ml^{-1}) in $CDCl_3$ (or DMSO) were recorded on a FT-NMR spectrometer Bruker AC-200 or Varian-Gemini 200 at 81.0 MHz. An 85% H_3PO_4 solution was used as an external reference. Typical conditions: spectra width 4000 Hz, number of scans 5–20 and digital resolution 0.3 Hz per data points.

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