Structural and conformational analysis of 2-triphenylphosphoranylidene succinic acid derivatives by ^{1}H, ^{13}C and ^{31}P one and two dimensional NMR spectroscopy and molecular modelling

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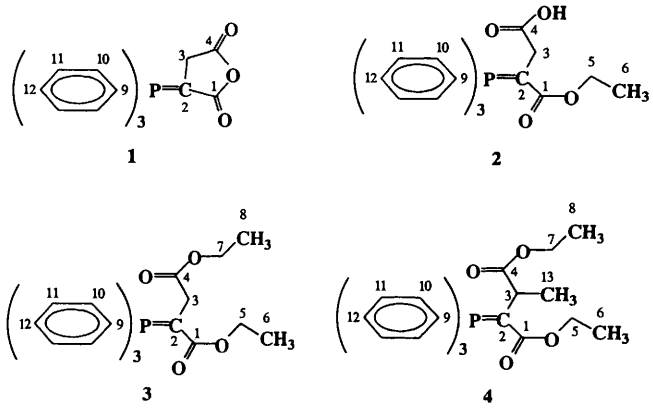
The structure and conformation of 2-triphenylphosphoranylidenesuccinic acid derivatives have been studied by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, in various solvents and at variable temperatures. In 2-triphenylphosphoranylidenesuccinic anhydride (**1**) the conformation is constrained but in the corresponding monoethyl (**2**) and the diethyl (**3**) esters there is an anticlinal relationship between the phosphorus and hydrogens on C-3 and signals of *Z* and *E* isomers were observed with the diethyl ester **3** in solvent-dependent ratios based on ^{1}H, ^{13}C and ^{31}P resonances. Similar results were obtained with the diethyl ester of the 3-methyl derivative **4**. Protonation (deuteronation) of **2** and **3** changes their conformation and P–H couplings. The NMR evidence on conformations of the phosphoranylidenesuccinic acid esters is consistent with T_1 relaxation times and results of molecular modelling.

Introduction

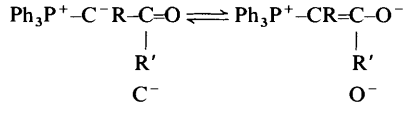
Phosphorus ylides are key reagents in the Wittig reaction which involves intermediates with strong phosphorus–oxygen interactions.[1–3] The bond order at phosphorus depends markedly on the electronic properties of the substituents.

We have used NMR spectroscopy to investigate conformations (and the possibility of phosphorus–oxygen interactions) in a series of 2-triphenylphosphoranylidenesuccinic acid derivatives (**1–4**) which, for simplicity, are shown without charge delocalization in Scheme 1. These ylides



Scheme 1

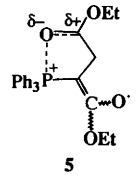
are stabilized by electronic delocalization at the ylidic carbon (C2) which should restrict rotation about the C1–C2 bond axis in the esters **2–4**. The ^{1}H, ^{13}C and ^{17}O NMR chemical shifts[4,5] show that ylides with strongly electron-withdrawing substituents have considerable zwitterionic character and the carbanion- and enolate-like classical (C^- and O^-, respectively) structures dominate (Scheme 2).



Scheme 2

In the succinic acid derivatives **2–4** interactions of carboxy oxygens with the formal phosphonium group could affect the relative stabilities of the *E* and *Z* isomers and also conformations about the C2–C3–C4 bond axes. This interaction is precluded in the anhydride **1** (Scheme 1).

Interaction of a carboxy oxygen with phosphorus could increase the covalency of the latter, as in many nucleophilic reactions of phosphorus(v) compounds where groups add and depart from apical positions.[6] For example in some oxaphospholene derivatives phosphorus is at the centre of a trigonal bipyramid with the phospholene ring in an apical position.[7] By analogy in compounds **2–4** there could be strong interactions between the phosphonium moiety and an oxygen of the β-carboxy group involving either a covalent bond, as in the oxaphospholene derivatives,[7] or the P–C and C–O dipoles as in **5**.



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However, in esters of 2-triphenylphosphoranylidenesuccinic acid the crystal structure has an approximately tetrahedral phosphorus, near trigonal C2, and an overall *Z* configuration and the alkoxy group is *syn* to phosphorus.[8] In the crystal the P–O distance is larger than that corresponding to a covalent bond, but the situation may be different in solution. Both *E* and *Z* isomers have been observed in esters of 2-triphenylphos-

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Table 1 ^{1}H NMR chemical shifts and coupling constants for anhydride (**1**) and monoethyl ester of 2-triphenylphosphoranylidenesuccinic acid (**2**)[a]

		1 $CDCl_3$	**2** $CDCl_3$	**2** CD_3OD	**2** $(CD_3)_2SO$
C3-H_2	*Z*	3.187 s	2.867 d (20)[b]	2.804 br s	2.556 br s
	E			2.725 br s	2.462 br s
C5-H_2			3.815 q (7)	3.953 br s	3.703 br s
C6-H_3			0.739 t (7)	0.966 t (7.2)	0.714 t (7)
C10-H		7.583 ddd	7.619 dd	7.878 dd	7.623 dd
		(14, 7, 1)	(11.5, 8.5)	(12.5, 8)	(12.5, 7.5)
C11-H		7.522 td (7.5, 3)	7.509 td (7.3, 3)	7.760 td (7.5, 3.7)	7.502 td (8, 4)
C12-H		7.632 tq (7, 2)	7.624 t (7)	7.888 t (7)	7.642 t (7)

[a] δ in ppm; coupling constants in Hz are in parentheses. [b] Long-range coupling with ^{31}P.

Table 2 ^{13}C and ^{31}P NMR chemical shifts and coupling constants for 2-triphenylphosphoranylidenesuccinic acid derivatives[a]

		1 $CDCl_2$	**2** $CDCl_3$	**2** $(CD_3)_2SO$[b]	**3** $CDCl_3$	**3** $(CD_3)_2SO$[b]	**4** $(CD_3)_2SO$[b]
P	*Z*	−36.46			−29.01	−28.16	−27.93
	E	−36.46			−29.07	−28.09	−27.86
C1	*Z*	166.89 (17.4)	172.94	174.54	169.55 (12.6)	168.64 (13.0)	
	E			174.66	170.31 (19.4)	169.75 (17.1)	
C2	*Z*	33.46 (136)	39.27 (88)		33.55 (130)	33.95 (166)	
	E				34.72 (136)	32.91 (160)	
C3	*Z*	36.65 (11.3)	35.05	36.45	32.47 (12.7)	32.78 (12.6)	38.25 (11.7)
	E				31.85 (11.8)	31.99 (12.3)	37.45 (11.6)
C4	*Z*	174.17 (19.5)	170.87	168.54	174.50	174.21	
	E				174.68	174.15	
C5	*Z*		60.84	63.92	56.80	56.57	56.14
	E				57.32	57.01	56.74
C6	*Z*		13.74	13.89	13.48	13.89	13.74
	E				14.59	15.06	14.83
C7	*Z*				59.20	59.34	59.29
	E						59.42
C8	*Z*, *E*				13.64	14.00	14.06
C9	*Z*	123.49 (95)	122.97 (90)	118.18 (87)	127.13 (91)	126.54 (81)	127.5 (90)
	E				126.57 (92)	127.25 (81)	126.8 (89)
C10	*Z*	132.89			133.15 (7.2)	133.32 (9.7)	133.19
	E					133.4 (10.4)	133.10
C11	*Z*	129.03 (12.3)			127.8 (10.4)	128.6 (11.3)	128.63
	E				127.92 (9.9)	128.6 (10.9)	128.55
C12	*Z*,*E*	132.8			131.16	131.9	131.83
C13	*Z*						18.36
	E						19.49

[a] δ in ppm; coupling constants with P are given in Hz and are in parentheses. Assignments agree with those for 2-triphenylphosphoranylidene ketones and 2-triphenylphosphoranylidene carboxylic esters.[9] [b] Assignments by ^{13}C–^{1}H correlated spectroscopy.

phoranylidene carboxylic acids by ^{1}H NMR spectroscopy,[9] and they interconvert on warming. Similar results have been observed in carbonyl-stabilized ylides, where electron withdrawal favours formation of *E* and *Z* isomers in solvent-dependent ratios.[10–12]

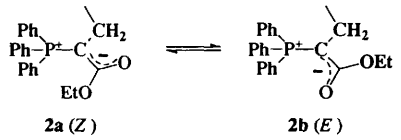
Therefore NMR spectroscopy provides information on *E* and *Z* isomerization about the C1–C2 bond axis and also on the possibility of restricted rotation about the C2–C3–C4 bond axis due to P–O interactions, and substitutent and medium effects on interconversion of isomers or conformers.

Results and discussion

Chemical shifts and couplings

The simplest compound of our series, 2-triphenylphosphoranylidenesuccinic anhydride (**1**), has a simple ^{1}H spectrum in $CDCl_3$ (Table 1). The 3-CH_2 signal at 3.187 ppm appears as a singlet because of weak coupling with ^{31}P, due to a synclinal conformation of the C2–C3 bond in the cyclic anhydride (**1**, Scheme 1). Coupling constants of ^{1}H with ^{31}P are 0–2 Hz for dihedral angles P–C–C–H of 60–90° and increase to 10–40 Hz for angles of 120–180°.[7b,11] The ^{13}C spectrum has signals for C1, C2, C3 and C4 at 166.89, 33.46, 37.00 and 174.17 ppm, respectively, all coupled with phosphorus (Table 2). In these and other NMR spectra we saw no evidence for different signals of the phenyl groups.

The ^{1}H NMR spectrum of the ethyl ester of 2-triphenylphosphoranylidenesuccinic acid (**2**) depends on the solvent. In $CDCl_3$ the signal of C3-H_2 is a sharp doublet at 2.867 ppm (J_{P-H} = 20 Hz) (Table 1), which implies that the two hydrogens of C-3 are equivalent and that in this compound the conformation of P–C2–C3–H is anticlinal, with an average dihedral angle of *ca.* 120° (**2**, Scheme 1).[7b,13] We saw only a single set of signals of the phenyl groups.



2a (*Z*) **2b** (*E*)

At 25 °C the ^{1}H NMR signals of C6-H_3 and C5-H_2 of the monoester **2** $CDCl_3$ are a sharp triplet and quartet, respectively (Table 1), consistent either with existence of one isomer, or with two, rapidly interconverting, *Z*–*E* isomers (**2a** and **2b**). The ^{13}C NMR spectrum fits either conclusion (Table 2). Again there were no differences in the ^{1}H or ^{13}C resonances of the phenyl groups.

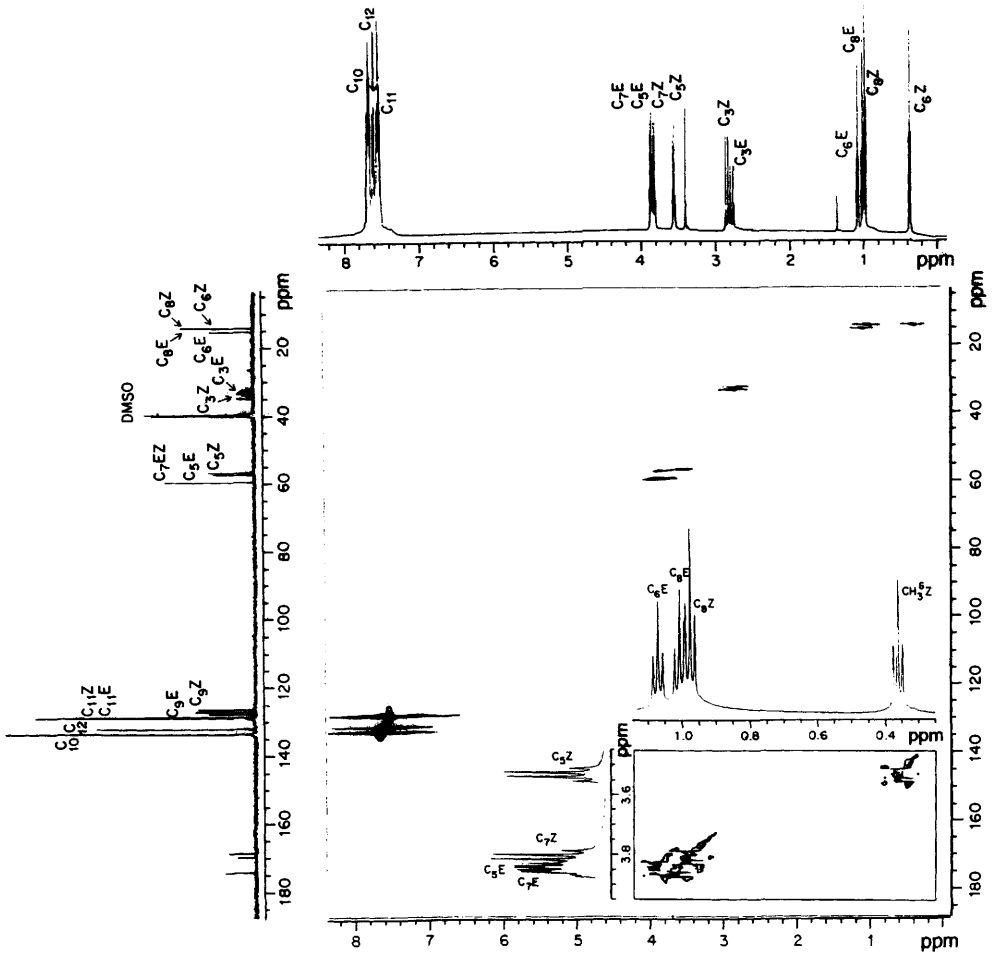


Fig. 1 ^{13}C–^{1}H correlated spectra (HETCOR) for diethyl 2-triphenylphosphoranylidenesuccinate in $(CD_3)_2SO$ at 25 °C. Inset: enlarged portion of a DQF-COSY contour plot of the same compound at 25 °C.

In the more polar solvents, CD_3OD or $(CD_3)_2SO$, the ^{1}H NMR spectrum of **2** has, in the CH_2 region, two broad singlets for C3-H_2 and a broad singlet for C5-H_2 (Table 1), although the C6-H_3 signal is still a sharp triplet. The chemical shift difference between the two singlets of C3-H_2 is due to *E*–*Z* isomerization (**2a**, **b**). In the ^{13}C NMR spectrum of compound **2** in CD_3OD there are two signals with different intensities at 174.54 and 174.66 ppm for C1 which can be assigned to two isomers, but we saw only single signals for C5 and C6 (Table 2).

The ^{1}H NMR spectrum of diethyl 2-triphenylphosphoranylidenesuccinate (**3**) is not very sensitive to a change of solvent from $CDCl_3$ to CD_3OD or $(CD_3)_2SO$. The spectrum has four triplets in the range 0.3–1.2 ppm for groups C6-H_3 and C8-H_3 and four quartets and two doublets in the range 3.5–4.0 ppm for the three CH_2 groups (C5-H_2, C7-H_2 and C3-H_2) corresponding to formation of two equilibrium isomers at 25 °C (Table S1).§ This NMR spectrum resembles those of the methyl esters of 2-triphenylphosphoranylidene carboxylic acids which have signals of the OCH_3 group of the *E* isomer at *ca.* 6.2–6.4 ppm and of the *Z* isomer at 6.6–6.9 ppm in $CDCl_3$, due to slowly equilibriating isomers, and the signals coalesce at higher temperatures.[9] The ethyl esters of these acids have two ^{1}H NMR signals for both the CH_2 and the CH_3 groups.[9b] Assignment of the low-field signals to the *Z* isomer (*ca.* 3.58 ppm for CH_2 and 0.06–0.6 ppm for CH_3) was possible because the CH_3 group, and to some extent the CH_2 group of the ethoxy residue, are diamagnetically shielded by the phenyl groups at phosphorus in this isomer. Our assignments (Table S1) are made on the same basis.

The ^{1}H signal of C3-H_2 of the diethyl ester **3** in CD_3OD has two sharp doublets at 2.861 ppm and 2.783 ppm with the same coupling constant of 17.5 Hz with phosphorus, corresponding to *Z* and *E* isomers. Similar chemical shifts and P–H coupling constants were seen in CD_3OD and $(CD_3)_2SO$. Coupling constants with ^{31}P depend markedly on the dihedral angle of P–C2–C3–H,[6b,12b] so this evidence is consistent with an anticlinal conformation of phosphorus with respect to C3-H_2 (Scheme 1). Observation of two distinct resonances for the groups C5-H_2, C6-H_3, C7-H_2 and C8-H_3, supports the existence of two *E*–*Z* isomers in CD_3OD (Table S1).

Assignments of resonances in Table S1 are also based on homodecoupling experiments. Signal multiplicities change as expected for coupled protons and in some cases we saw a significant decrease in the signal intensity of the corresponding group in the other conformation due to a fast isomerization (Table S2). Two dimensional ^{1}H–^{1}H (DQF-COSY) and ^{13}C–^{1}H (HETCOR) experiments confirmed our assignments (Fig. 1).

The ^{1}H NMR spectra of diethyl ester, **3**, are similar in

§ **Supplementary material available.** Supp. No. 57080 (9 pp). Table S1: ^{1}H NMR chemical shifts for 2-triphenylphosphoranylidenesuccinic diethyl ester (**3**). Table S2: decoupling of ^{1}H NMR signals of 2-triphenylphosphoranylidenesuccinic acid diethyl ester (**3**). Table S3: temperature effects on ^{1}H NMR signals of 2-triphenylphosphoranylidenesuccinic acid diethyl ester (**3**). Table S4: isomer ratio (*Z*/*E*) for diethyl esters of 2-triphenylphosphoranylidenesuccinic acid (**3**) and its 3-methyl derivative (**4**). Table S5: decoupling of ^{1}H NMR signals of 2-triphenylphosphoranylidene-3-methylsuccinic acid diethyl ester (**4**). Table S6: temperature effect on NMR signals of 2-triphenylphosphoranylidene-3-methylsuccinic acid diethyl ester. For details of the Supplementary Publication Scheme see 'Instructions for Authors (1995)', *J. Chem. Soc., Perkin Trans. 2*, 1995, issue 1.

Table 3 ^{1}H NMR chemical shifts for diethyl 2-triphenylphosphoranylidene-3-methylsuccinate (**4**)[a]

		CD_3OD	$(CD_3)_2SO$[b]	$CDCl_3$
C3-H	*Z*	2.361 dq (18.5, 7.0)	2.248 dq (18.0, 7.0)	2.470 dq (18.0, 7.0)
	E	2.249 dq (18.5, 7.0)	2.144 dq (19.0, 7.0)	2.310 dq (18.0, 8.0)
C5-H_2	*Z*	3.527 dq (10.0, 7.0)	3.451 q (7.0)	3.634 q (7.0)
		3.481 dq (10.5, 7.0)		
	E	3.855 dq (7.0, 1.0)	3.835 dq (10.5, 7.0)	3.959 q (7.5)
		3.827 dq (7.0, 1.0)	3.763 dq (10.5, 7.0)	
C6-H_3	*Z*	0.343 t (7.2)	0.306 t (7.2)	0.379 t (7.0)
	E	1.094 t (7.2)	1.041 t (7.0)	1.139 t (6.5)
C7-H_2	*Z*	4.064 q (7.2)	3.991 q (7.0)	4.121 q (7.5)
		4.043 q (7.0)	3.964 q (7.0)	
	E	3.989 dq (8.0, 1.5)	3.909 q (7.0)	4.099 q (7.0)
		3.967 dq (7.0, 1.0)	3.903 q (8.0)	
C8-H_3	*Z*	1.221 t (7.0)	1.186 t (7.5)	1.243 t (8.0)
	E	1.198 t (7.5)	1.150 t (7.5)	
C13-H_3	*Z*	1.213 d (7.5)	1.185 d (7.0)	1.323 d (8.0)
	E	1.106 d (7.0)	1.172 d (6.0)	1.310 d (8.0)
C10-H	*Z*	7.648 ddd (12.2, 7.5, 1.0)	7.643 dd (12.3, 6.0)	7.683 dd (11.0, 8.5)
	E	7.657 ddd (12.0, 8.0, 1.5)		
C11-H	*Z*	7.486 td (7.5, 3.0)	7.564 td (7.5, 2.0)	7.439 td (7.5, 2.0)
	E	7.490 td (7.8, 3.0)		
C12-H	*Z*	7.563 tq (8.5, 1.5)	7.615 t (2.5)	7.525 t (6.5)
	E	7.581 tq (9.0, 2.0)		

[a] δ in ppm, coupling constants (Hz) in parentheses. For second-order spectra approximate chemical shifts and coupling constants were obtained by direct examination. [b] ^{13}C–^1H and ^1H–^1H correlated spectra were recorded [$(CD_3)_2SO$].

CD_3OD and in $(CD_3)_2SO$ (Table S1). In $CDCl_3$, CH_3 and CH_2 signals of *E* and *Z* isomers are still visible, but are considerably broadened due to fast isomerization.

The sharp ^{1}H signals at 25 °C of the *Z* and *E* C7-H_2 and C8-H_3 groups, broaden at 45 °C in $(CD_3)_2SO$, coalesce at *ca.* 75 °C and resharpen at 95 °C as one signal for each group (Table S3). The triplets due to C6-H_3, the quartets due to C5-H_2, and the doublets due to C3-H_2, broaden at 75 °C, but do not coalesce even at 95 °C, where they become very broad. Therefore the *Z* and *E* isomers do not readily interconvert in $(CD_3)_2SO$ (t < 95 °C), although signals of C7-H_2 and C8-H_3 coalesce at a much lower temperature. This isomerization behaviour fits delocalization of the ylidic electrons with an increase in the cationic character of phosphorus and its interaction with carboxy oxygens, and stabilization of dipolar structures by solvation by $(CD_3)_2SO$. In $(CD_3)_2SO$ there are two distinct sharp signals of ^{31}P for *Z* and *E* isomers, but they broaden and partially coalesce in $CDCl_3$. In the ^{13}C NMR spectra different resonances for the two isomers can be identified in $CDCl_3$ and especially in $(CD_3)_2SO$ (Table 2). The behaviour in CD_3OD is similar.

Solvents affect rates of isomerization and isomeric ratios. Polar solvents, *e.g.*, CD_3OD or $(CD_3)_2SO$, cause slow isomerization about the C1–C2 bond, as shown by changes in lineshapes. Hydrogen bonding solvents, *e.g.*, CD_3OD and to a lesser extent $CDCl_3$, favour formation of the *Z* isomer (Table S4), due to a stronger hydrogen bonding of O^- *trans* to Ph_3P (**2b**) which offsets the interaction between O^- and Ph_3P in the *E* isomer. Similar solvent effects on isomerization rates have been seen with alkyl esters of triphenylphosphoranylideneacetic acid.[14] In $(CD_3)_2SO$ increasing temperature increases the amount of the less stable *E* isomer.

The diethyl ester of 2-triphenylphosphoranylidene-3-methylsuccinic acid (**4**) has NMR spectra similar to those discussed earlier for **3** and DQF-COSY and HETCOR experiments were used for the assignments. The ^{1}H signal of C3-H is a doublet of quartets for each *E* and *Z* isomer due to coupling with P and C13-H_3 (Table 3). The magnitude of the P–H coupling constants is consistent with an anticlinal orientation of phosphorus and C3-H (Scheme 1) which brings about a *syn* interaction between phosphorus and a β-carboxy oxygen. However, ^{1}H signals of C5-H_2 and C7-H_2 for *E* and *Z* isomers in CD_3OD and $(CD_3)_2SO$ become two quartets, or a doublet of quartets with unequal intensities, corresponding to an ABX_3 system of hydrogens. These results imply that hydrogens in these groups are magnetically non-equivalent and rotations about the C1–O–C5 and C4–O–C7 bonds are restricted. In $CDCl_3$ the signals maintain the same multiplicity, but are much broader, showing that rotation about these two bonds is faster than in the more polar solvents.

Homodecoupling experiments (Table S5) support the signal assignments in Table 3. The temperature effect on the ^{1}H NMR spectrum is similar to that on the unmethylated compound **3** confirming the existence of two isomers and there is coalescence at higher temperatures (Table S6). The resonances of C3-H_2, C7-H_2, C8-H_3 and C13-H_3 coalesce at 65 °C and resharpen at 105 °C. The C5-H_2 and C6-H_3 resonances coalesce at *ca.* 105 °C, and on cooling to 25 °C the spectrum returns to its initial form, showing that there is no overall chemical reaction. The methyl group on C3 may sterically decrease solvation of the *Z* and *E* isomers which should increase rates of their interconversion. This hindrance should especially reduce solvation of the *Z* isomer whose free energy becomes closer to that of the *E* isomer so that their ratio becomes *ca.* one (Table S4).

Effects of deuteronation

Stable phosphonium ylides are protonated (deuteronated) giving the corresponding phosphonium salts with acids (HCl or DCl).[1b] These compounds may exhibit strong P–O interactions if there is a carbonyl group β to phosphorus, as shown for the mono and diesters **2***Z* and **3***Z* in Scheme 3.

Protonation (deuteronation) generates chirality at C2 and hydrogens on C3 become non-equivalent. The ^{1}H NMR spectrum of the monoester **2** in $(CD_3)_2SO$–DCl shows a sharp triplet for C6-H_3 and two doublets of quartets corresponding to an ABX_3 system for the adjacent C5-H_2 group, based on DQF-COSY and HETCOR spectra (Table 4). The non-

Table 4 ^{1}H NMR chemical shifts for 2-triphenylphosphonium-2-deuterio succinic acid derivatives[a]

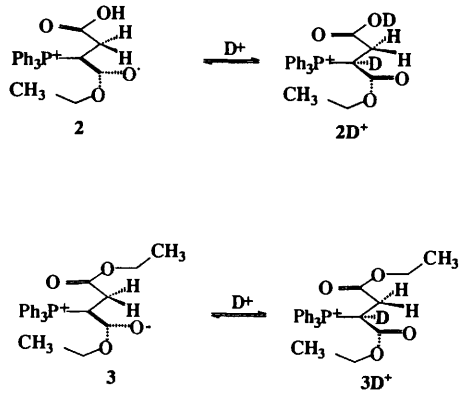
	2[b]	3[c]	4[d] *RR*[e]	4[d] *RS*[e]
C3-H_2[f]	2.567 d (17)	2.888 dd (17.2, 7.5)	3.380 dq (13.0, 7.0)	3.260 dq (12.8, 7.2)
	2.543 d (17)	2.963 dd (17.0, 11.7)		
C5-H_2[f]	3.510 q (6.5)	3.830 dq (10.5, 7.0)	3.626 dq (11.0, 7.0)	3.946 dq (18, 7.2)
	3.533 q (7)	3.869 dq (10.5, 7.0)	3.688 dq (11.0, 7.0)	4.055 dq (12, 7.5)
C6-H_3	0.504 t (7.0)	0.803 t (7.0)	0.899 t (7.0)	0.990 t (7.0)
C7-H_2	—	3.969 q (7.0)	3.940 q (7.0)	4.010 q (7.5)
C8-H_3	—	1.050 t (7.0)	0.929 t (7.0)	1.145 t (7.2)
			1.131 t (7.2)	
C13-H_3	—	—	0.773 d (7.0)	1.554 d (7.0)
C10-H	7.509 dd (12, 8)	7.819 dd (13.0, 8.3)	7.951 dd (13.5, 8.5)	7.905 dd (13, 8)
C11-H	7.784 td (7.5, 3.5)	7.727 td (7.0, 3.5)	7.725 td (7.8, 3.7)	7.762 td (7.5, 3.5)
C12-H	7.927 t (7.0)	7.876 t (7.0)	7.858 t (7.0)	7.858 t (7.0)
C2-H	2.350[g]			

[a] δ in ppm. Coupling constants (Hz) are in parentheses. [b] 0.37 mol dm^{-3} **2** and 3 mol dm^{-3} DCl in $(CD_3)_2SO$. [c] 0.5 mol dm^{-3} **3** and 3 mol dm^{-3} DCl in $(CD_3)_2SO$–D_2O 1:1. Assignments from ^{1}H–^{1}H and ^{13}C–^{1}H correlated spectroscopy. [d] 0.1 mol dm^{-3} **4** and 0.2 mol dm^{-3} DCl in $(CD_3)_2SO$–D_2O 9:1. Assignments from ^{1}H–^{1}H and ^{13}C–^{1}H correlated spectroscopy. [e] Arbitrary assignments of ^{1}H resonances of *RS* and *RR* isomers. [f] The two CH_2 protons where present are magnetically non-equivalent; the group is CH in **4**. [g] Signals are broad ($\nu_{\frac{1}{2}}$ = 20 Hz) due to hydrogen exchange at C_2.

Table 5 ^{13}C NMR chemical shifts for 2-triphenylphosphonium-2-deuterio(protio)-succinic acid derivatives[a]

	2[b]	3[c]	4[d] *RR*[e]	4[d] *RS*[e]
C-1	169.25 (14.3)	171.30 (16.5)	171.55 (24.9)	171.49 (16.0)
C-2	34.61 (125)	39.23 (42.0)	*f,g*	*f,g*
C-3	32.56 (10.8)	33.56	37.70	38.02
C-4	175.22	168.05	166.08	166.15
C-5	57.06	65.30	61.30	63.11
C-6	14.34	14.76	13.37	13.28
C-7	—	63.93	62.64	61.87
C-8	—	15.36	13.64	17.75
C-9	126.71 (90.7)	117.67 (86.2)	118.54 (83.3)	117.65 (82.5)
C-10	133.42 (9.8)	135.64 (9.2)	134.26 (15.4)	131.59 (10.1)
C-11	128.65 (11.4)	132.17 (12.6)	130.24 (12.8)	138.92 (11.2)
C-12	132.03	137.47	135.37	135.04
C-13			13.7	13.7

[a] δ in ppm. Coupling constants with ^{31}P (Hz) are in parentheses. [b] 0.37 mol dm^{-3} **2** and 3 mol dm^{-3} DCl in $(CD_3)_2SO$. [c] 0.5 mol dm^{-3} **3** and 3 mol dm^{-3} DCl in $(CD_3)_2SO$–D_2O 1:1. Assignments from ^{13}C–^{1}H correlated spectroscopy. [d] 0.1 mol dm^{-3} **4** and 0.2 mol dm^{-3} DCl in $(CD_3)_2SO$–D_2O 9:1. Assignments from ^{13}C–^{1}H correlated spectroscopy. [e] Arbitrary assignment of ^{1}H resonances. [f] Covered by the solvent signal. [g] Only one ^{31}P signal at −28.049 ppm was seen corresponding to one isomer in $(CD_3)_2SO$.



Scheme 3

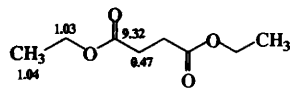
equivalent hydrogens at C3 are coupled with phosphorus, giving an ABX pattern, where X is phosphorus. The coupling constants with phosphorus are *ca.* 7 and 12.2 Hz, implying different dihedral angles for these hydrogens with respect to the P–C bond. The ^{1}H NMR spectrum of the diester, **3**, in $(CD_3)_2SO$–DCl is similar to that of the monoester **2** in the same solvent with non-equivalent hydrogens at C3-H_2 and C5-H_2 (Table 4). The ^{13}C spectra of the mono- and di-esters (**2** and **3**) in $(CD_3)_2SO$–DCl correspond to existence of a single species (Scheme 3, Table 5).

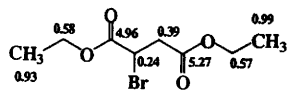
Deuteronation at C2 of the diethyl 2-triphenylphosphoranylidene-3-methylsuccinic diester (**4**) induces diastereoisomerism due to chiralities at C2 and C3. Distinct resonances are observed in the NMR spectrum for almost all hydrogens of this compound (Table 4). Generally the chemical shifts for a given group in the two diastereoisomers (*RR* and *RS*) are similar, except for C13-H_3, showing that this group experiences different environments in the two diastereoisomers. The isomeric ratio is *ca.* 1:1, consistent with *erythro–threo* diastereoisomers having similar free energies of formation. The deuterium atom at C2 is not coupled with the C3-H hydrogen atom, implying that it is rapidly exchanging in an acid–base equilibrium. The ^{13}C chemical shifts from correlated spectroscopy (Table 5) confirm the formation of the diastereoisomers of **4**.

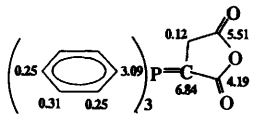
Relaxation times

In small molecules spin–lattice relaxation times (T_1) are controlled largely by the presence of nearly magnetically active nuclei (*e.g.*, ^{1}H) and the overall and local molecular motions,[15] so that lower mobility corresponds to shorter T_1.

Values of ^{13}C T_1 for diethyl succinate and its monobromide and ylides **1**–**4** are shown, and for some compounds ^{13}C signals of both *E* and *Z* isomers were observed. Values for the *E* isomer are given in parentheses. The T_1 value for C2 in **4** was not determined. In diethyl succinate ^{13}C T_1 values of C2, C3, C5 and C6 are lower than those of large alkanes, where T_1 values are *ca.* 8 s (CH_3) or slightly lower (CH_2).[15] These differences are due to steric and dipole–dipole interactions that reduce segmental flexibilities. Introduction of a heavy atom (Br) or residue (Ph_3P) at C2 reduces T_1 values in compounds **2**–**4** and diethyl monobromosuccinate. These T_1 values of the anhydride **1** are higher than those of the diesters **3** and **4** in $(CD_3)_2SO$ probably because it is approximately spherical and can tumble readily. The small differences in T_1 values of the diester **3** in







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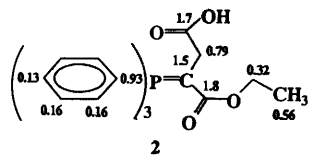

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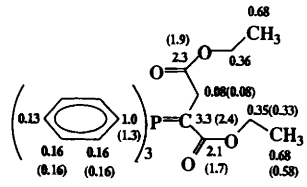

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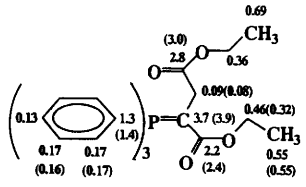
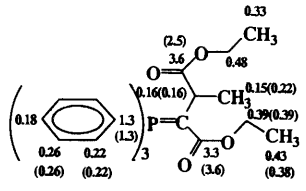


3 ($CDCl_3$)



4

$CDCl_3$ and $(CD_3)_2SO$ can be ascribed to the higher viscosity of the latter.

Introduction of the bulky Ph_3P group into succinic esters should slow molecular tumbling and decrease all T_1 values but the relatively low T_1 values at some positions of esters **2**–**4** indicate decreases in conformational mobility. These could be due to electronic delocalization with an increase in C1–C2 bond order and interactions between phosphorus and oxygens of the carboxy residues. This interaction should slow rotation about the P–C2 bond axis and T_1 values in the phenyl groups in the esters **2**–**4** are generally lower than for the anhydride **1**. However, the phenyl groups are equivalent on the NMR timescale so that rotation is not strongly hindered by P–O interactions.

Molecular modelling

Conformations of the *E* and *Z* isomers of the diester, **3**, predicted by using MM2 parameters and with charge localized on oxygen of the β-carboxy group are shown in Fig. 2. The predicted conformation of the *Z* isomer is very similar to that of the crystalline *tert*-butyl ester of 1-methoxycarbonylethyl(triphenyl)phosphorane.[8] The simulations predict that P–C2 and H–C3 dihedral angles are different for the two hydrogens with values of 45 and 162° for *Z* and 32 and 148° for *E*.

Conformations of protonated **3** [$3H^+$(A) and $3H^+$(B)] are shown in Fig. 2 based on MM2 parameters. The predicted dihedral angles between P–C2 and the hydrogens on C3 are 55 and 170°, in reasonable agreement with the different P–H coupling constants observed in DCl–$(CD_3)_2SO$. Estimated P–O distances, Å, for the *Z* (*E*) isomer of **3** are 3.06 (3.25) and 4.10 (3.47) for α- and β-carboxy groups, respectively. As a result there should be strong dipole–dipole interactions involving phosphorus and the carboxy oxygens which slows rotation about the C2–C3–C4 axes.

Conclusions

There are interactions between phosphorus and the β-ester group in mono- and di-ethyl esters of 2-triphenylphosphoranylidenesuccinic acids (**2** and **3**) in CD_3OD, $CDCl_3$ and $(CD_3)_2SO$, and P–H coupling constants show that there is an average anticlinal relationship between phosphorus and C3-H_2 in agreement with the predictions based on MM2 simulations.

We never saw more than one set of NMR signals of the phenyl groups, so if oxyphosphorane derivatives [7a] are present the phenyl groups must equilibriate readily either by pseudorotation, or through acyclic structures.

There is extended conjugation involving the α-carboxy group which increases the C1–C2 bond order and both *Z* and *E* isomers are present. The *Z* isomer with O^- *trans* to the triphenylphosphoranylidene group is favoured relative to the *E* isomer by solvation in polar solvents. In acidic solutions 2-triphenylphosphoranylidenesuccinic acid esters are protonated (deuteronated) at carbon 2 and the conformation about the C2–C3 bond axis changes. Methyl substitution at C3 in **4** gives two equilibriating *erythro*–*threo* diastereoisomers with similar free energies.

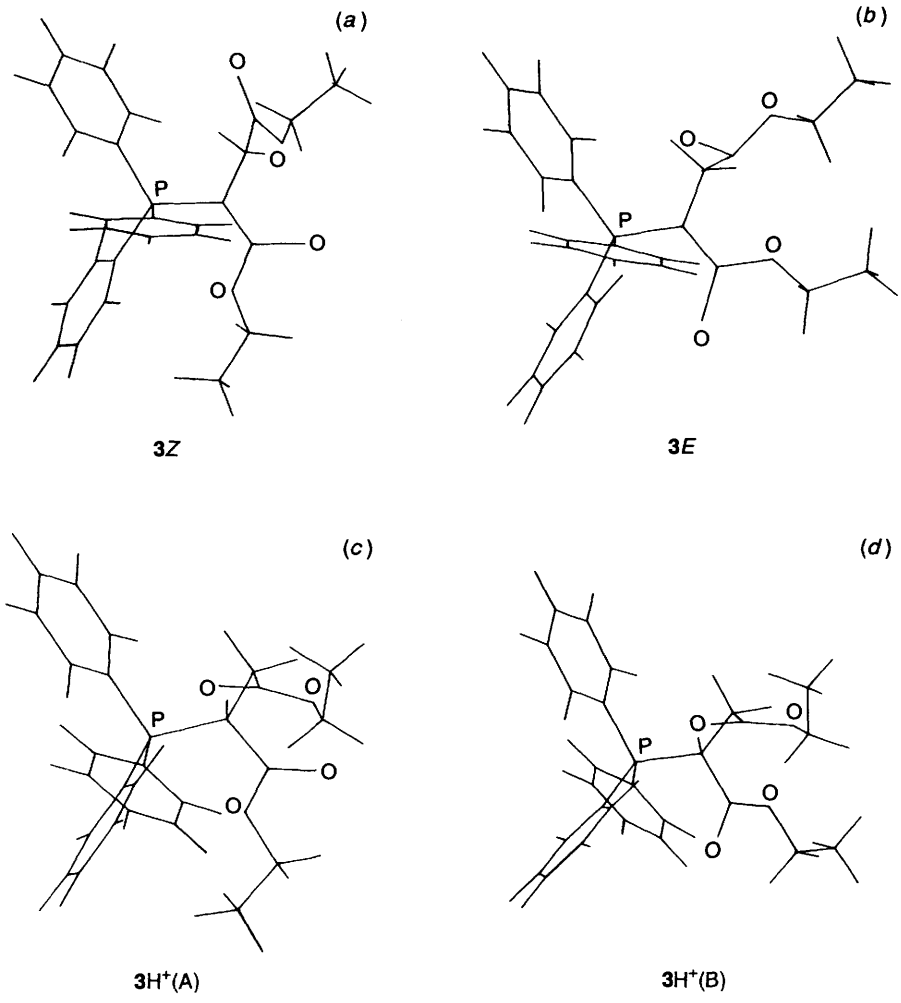


Fig. 2 Stick model of **3** and $3H^+$ obtained by molecular mechanics minimizations with MM2 parameters. The phosphorus and oxygens are labelled showing the P · · · O proximities.

Experimental

Materials

2-Triphenylphosphoranylidenesuccinic anhydride (**1**) was a commercial sample (Aldrich). The monoethyl ester of 2-triphenylphosphoranylidenesuccinic acid (**2**) was obtained by refluxing the anhydride **1** (4 mmol) in absolute EtOH (40 cm^3), evaporation of EtOH *in vacuo* and recrystallization from EtOAc.

The diethyl ester of 2-triphenylphosphoranylidenesuccinic acid (**3**) was obtained by refluxing ethyl triphenylphosphoranylidene acetate (90.8 mmol) and ethyl bromoacetate (46 mmol) in 150 cm^3 EtOAc for 4 h. After filtration of the bromide salt of ethyl triphenylphosphonium acetate, the solvent was evaporated off to give an oil which crystallized in light petroleum and was recrystallized from EtOAc–hexane 1:1 to give 14.1 g of crystals, mp 105–107 °C (71% yield) (Found: C, 72.35; H, 6.35. Calc. for $C_{26}H_{27}O_4P$: C, 71.88; H, 6.26%).

The diethyl ester of 2-triphenylphosphoranylidene-3-methylsuccinic acid (**4**) was obtained by methylating the lithium salt of diethyl ester **3** (4.6 mmol) with MeI (23 mmol) in anhydrous THF (30 cm^3) at room temperature for 18 h. The lithium salt was obtained from **3** and lithium diisopropylamide in anhydrous THF (10 cm^3). After removal of the ammonium iodide by filtration, and evaporation *in vacuo* of THF, the product was dissolved in $CHCl_3$ and was washed with saturated NaCl to neutral pH. The dried solution ($MgSO_4$) was evaporated and the residue was treated with EtOAc, and the resulting crystals were filtered off and recrystallized (EtOAc). Ethyl diester **4** 1.52 g (74%), mp 169–171 °C (Found: C, 72.1; H, 6.52. Calc. for $C_{27}H_{29}O_4P$: C, 72.3; H, 6.52%).

NMR spectra

^1H NMR spectra were recorded on a 500 MHz spectrometer at 25 °C, in 16K memory points and a spectral width of 3000–4000 Hz with a relaxation delay of 1.5 s. The concentrations in $CDCl_3$, CD_3OD and $(CD_3)_2SO$ (Aldrich) were 0.05 mol dm^{-3}. Chemical shifts were reported relative to the solvent ^1H signals [$CHCl_3$ 7.240; CHD_2OD 4.780 and $(CD_3)_2SO$ 2.490 ppm]. For the deuteronation experiments DCl in D_2O (5.3 mol dm^{-3}) was added to DMSO.

The ^{13}C NMR spectra were recorded on the same instrument with the same solutions, with broad-band decoupling, spectral width of 12 000 Hz, 16K memory points and delay of 2 s. Chemical shifts were reported relative to the solvent ^{13}C signals [$CHCl_3$ 77.0; CHD_2OD 49.0 and $(CD_3)_2SO$ 39.5 ppm].

The ^{31}P NMR spectra were recorded on a 300 MHz spectrometer with 0.05 mol dm^{-3} solutions in $CDCl_3$ and CD_3OD with $[(CH_3)_2N]_3P$ (23.4 ppm) as an external standard, with proton broad-band decoupling. Data acquisition was made by using 16K memory points for a width of 2000 Hz and a delay of 3 s.

T_1 measurements

Relaxation times T_1 were measured at 125.76 MHz at 25 °C by using an inversion recovery method. Proton broad-band

decoupling was on parallel with the 90° pulse and acquisition time, but off during the relaxation delay to avoid excessive sample heating. The 90° pulse was determined for each system and a mean value was used corresponding reasonably well to all carbon atoms in a molecule. The relaxation and the longest variable delay was three to four times greater than the longest T_1. The T_1 values were calculated by using a non-linear fit of three parameters (the Levy equation) for fast inverse recovery FT experiments.[16] Concentrations were the same for all the solutes and the error in the T_1 values is *ca.* 20%.

Correlated spectra

All measurements were made on a 500 MHz spectrometer at 25 °C. The ^1H–^1H correlated spectra (DQF-COSY) were recorded in the phase-sensitive mode[17] with the 90° pulse determined before each experiment. For the heteronuclear ^{13}C–^1H shift correlation (HETCOR)[18] the 90° pulse for ^{13}C and the 90° pulse for ^1H when observing the ^{13}C signals were determined under the same experimental conditions. An example of a ^{13}C–^1H correlated spectra is given in Fig. 1.

Molecular modelling

Structures were simulated on a CAChe Tektronix computer. The parameters are: relaxation factor = 1; convergence to 4×10^{-3} kJ mol^{-1}, and energy terms include: bond angles and stretch, dihedral angles and improper torsions, intramolecular van der Waals, electrostatic and hydrogen-bonding interactions.

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