Stereoisomerism in Pentaerythritol-Bridged Cyclotriphosphazene Tri-Spiranes: Spiro and Ansa 1,3-Propanediyldioxy Disubstituted Derivatives

Aylin Uslu,*[a] Simon J. Coles,[b] David B. Davies,[c] Robert J. Eaton,[c] Michael B. Hursthouse,[b] Adem Kılıç,[a] and Robert A. Shaw[c]

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Four isomeric products were isolated and purified from the reaction of 1,3-propanediol with the tri-spirane cyclophosphazene-organophosphate compound **1**: viz. the di-monospiro (**2a**), di-monoansa (**2b**) and two monospiro-monoansa derivatives (**2c** and **2d**). It is shown by ^{31}P NMR spectroscopy on addition of a chiral solvating agent (CSA) that both the di-monospiro **2a** and di-monoansa **2b** derivatives are racemates, as expected, whereas no splitting of NMR signals occurred on addition of CSA to solutions of **2c** and **2d**. It is found by X-ray crystallography that the two monospiro-monoansa spirane derivatives, **2c** and **2d**, are *meso* diastereoisomers, which represent a new case of the stereochemistry of bis(disubstituted) cyclophosphazene derivatives of **1**. It is also observed from the ^{31}P NMR spectrum of the reaction mixture, supported by the yields of pure compounds, that formation of a spiro group is about 4.5 times more likely than that of an ansa moiety under the conditions of the reaction.

Introduction

Difunctional reagents with cyclophosphazenes can give rise to four structural types: spiro, ansa, bridged and open chain.[1] For example, the reaction of 1,3-propanediol with cyclotriphosphazene, $N_3P_3Cl_6$, gave spiro, $N_3P_3[O(CH_2)_3O]_xCl_{6-x}$ (x = 1,2,3); ansa, $N_3P_3[O(CH_2)_3O]Cl_4$; spiro-ansa, $N_3P_3[O(CH_2)_3O]_2Cl_2$; open chain, $N_3P_3[O(CH_2)_3OH]Cl_5$ and bridged, $N_3P_3Cl_5[O(CH_2)_3O]N_3P_3Cl_5$ compounds, in which spiro derivatives are by far the major product.[2] It is known that reaction of cyclotriphosphazene with a tetrafunctional alcohol such as pentaerythritol, $C(CH_2OH)_4$, gives a spirane-bridged compound **1**, whose structure (Figure 1) consists of four six-membered rings, each joined by a tetrahedral atom (phosphorus or carbon atom) to the next ring, with each six-membered ring being orthogonal to its neighbours.[3] The stereochemistry of bis(disubstituted) cyclophosphazene derivatives of **1** has recently been elucidated;[4] it was shown that racemates were observed for bis(geminal) derivatives, as well as for non-geminally disubstituted *cis* and *trans* (the latter has two diastereoisomers) derivatives. In the present work, the reaction of the spirane-bridged compound **1** with 1,3-propanediol was investigated and four isomeric disubstituted spiro and ansa derivatives **2a**–**d** were isolated (Figure 1).

Two of the products **2a**–**b** gave rise to chiral compounds corresponding to cases observed previously [bis(disubstitution that is geminal or *cis* non-geminal],[4] whereas the other two derivatives **2c**–**d** have geminal disubstitution in one cyclophosphazene ring and *cis* non-geminal disubstitution in the other cyclophosphazene ring, giving rise to a new case of chirality in such systems, in which both compounds are *meso* diastereoisomers.

Results and Discussion

The spirane-bridged compound **1**, was allowed to react with 1,3-propanediol in a 1:2 mol ratio to give four disubstituted isomers **2a**–**d**, which were separated by column chromatography. Overall, there was a yield of about 25% with compound **2a** (14.9%) being the major product, and with minor yields of **2b** (2.5%) **2c** (4%) and **2d** (3.5%). The products were characterised by elemental analysis, mass spectrometry and ^{31}P NMR spectroscopy. Elemental analysis and mass spectrometry give the same results for the four compounds, as expected for isomers.

The proton-decoupled ^{31}P NMR spectra of **2a** and **2b** are observed (Figure 2, a and b, respectively) as ABX spin systems resulting from the two phosphazene rings in each compound having the same substitution pattern. However, the two ABX spin systems are quite different as in **2a** the X-part is ca. 26–27 ppm and the AB portion is 8–11 ppm, whereas the X-part of **2b** is ca. 11 ppm and the AB portion is 30–32 ppm. The assignment of signals of **2a** was assisted

[a] Department of Chemistry, Gebze Institute of Technology, Gebze, Kocaeli, Turkey
Fax: +90-262-754-2385
E-mail: aylin@gyte.edu.tr
[b] University of Southampton, Highfield, Southampton SO17 1BG, UK
[c] School of Biological and Chemical Sciences, Birkbeck College (University of London), Malet Street, London WC1E 7HX, UK

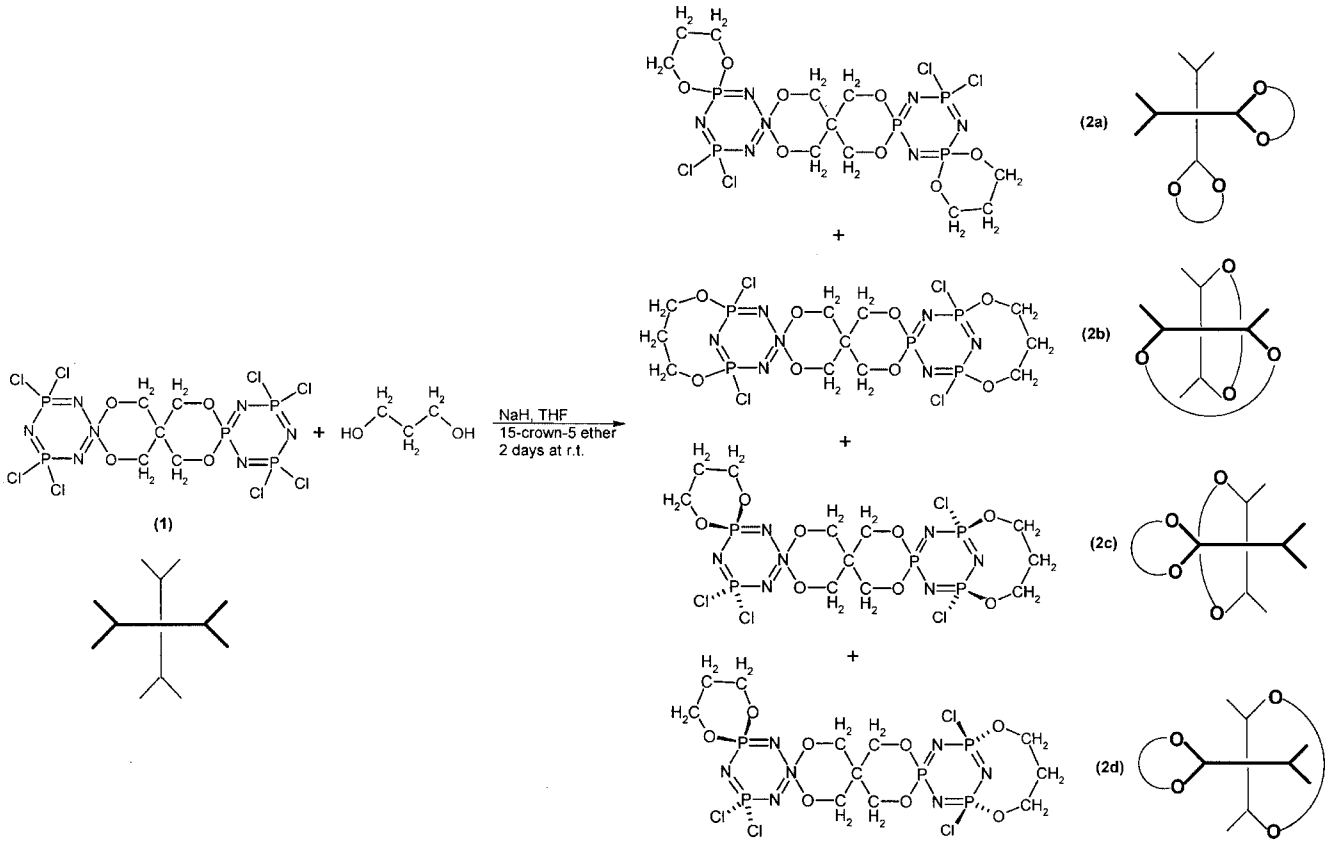


Figure 1. Structures of spirane-bridged unsubstituted, **1**, and disubstituted cyclotriphosphazene derivatives; di-monospiro **2a**, di-monoansa **2b**, and two monospiro-monoansa derivatives (**2c**, *syn*) and (**2d**, *anti*). A diagrammatic representation is also shown for compounds **1** and **2a**–**2d**. For clarity the inner organophosphate rings have been omitted and the outer cyclophosphazene rings, which are orthogonal to each other, are shown in the same projection with the ring to the front in bold type.

by proton-coupled ^{31}P NMR spectra [not shown], which indicates that the 26–27 ppm signal corresponds to a $>PCl_2$ group (no coupling) and the AB portion results from the >P(bridge) and >P(spiro) groups. The ^{31}P NMR spectrum of **2b** at 30–32 ppm is characteristic of a cyclotriphosphazene dioxy-ansa derivative with a relatively small ansa ring[5] and the signal at δ = 11 ppm is given by the >P(bridge) group; the ansa moiety is observed as an AB spin system because **2b** is a chiral diastereoisomer (see below). The ^{31}P NMR spectra are consistent with **2a** being the di-monospiro compound and **2b** being the di-monoansa compound. The ^{31}P NMR spectra of **2c** and **2d** (Figure 2, c and d, respectively) are very similar to each other and consist of five multiplets resulting from the superposition of an A_2X and an ABX spin system; the ABX spin system is similar to that for the spiro derivative **2a**, and the A_2X has similar chemical shifts and coupling constants to those found for the ansa derivative **2b**, but is A_2 rather than AB because compounds **2c** and **2d** are a *meso* diastereoisomers (see below). ^{31}P NMR indicates that both, **2c** and **2d**, are monospiro-monoansa compounds, having slightly different chemical shifts and coupling constants, especially for the spiro-substituted ring. The ^{31}P NMR spectroscopic data for compounds **2a**–**2d** are summarised Table 1.

By analogy with previous work on the stereochemistry of bis(disubstituted) cyclophosphazene derivatives of **1**,[4] it is expected that both compounds **2a** and **2b** are chiral and exist as racemates. The di-monospiro compound **2a** is the case of a bis(geminal) derivative and the di-monoansa compound **2b** has non-geminal disubstitutents that are *cis*.[4] On addition of a chiral solvating agent [CSA, (*S*)-(+)-2,2,2-trifluoro-1-(9′-anthryl)ethanol] it was found that all the ^{31}P NMR signals of compounds **2a** and **2b** exhibit chemical shift changes indicating complexation with the CSA, and that all signals, except the >P(bridge) group of compound **2b**, separate into two lines of equal intensity consistent with compounds **2a** and **2b** existing as racemates. The change in ^{31}P NMR chemical shifts and separation of signals of compounds **2a** and **2b** at a 20:1 mol ratio of CSA:**2a** or **2b** are summarised Table 1. Addition of CSA to compounds **2c** and **2d** also caused changes in chemical shifts of each signal (Table 1), but no separation of signals even at higher mol ratios of 50:1 (**2c**) and 40:1 (**2d**). These results indicate that CSA complexes to compounds **2c** and **2d** in solution, and that both molecules may be *meso*, because CSA does not cause extra splitting of the NMR peaks. Such a caveat needs to be made, in the first instance, because previous NMR work has shown splitting of peaks for *meso* com-

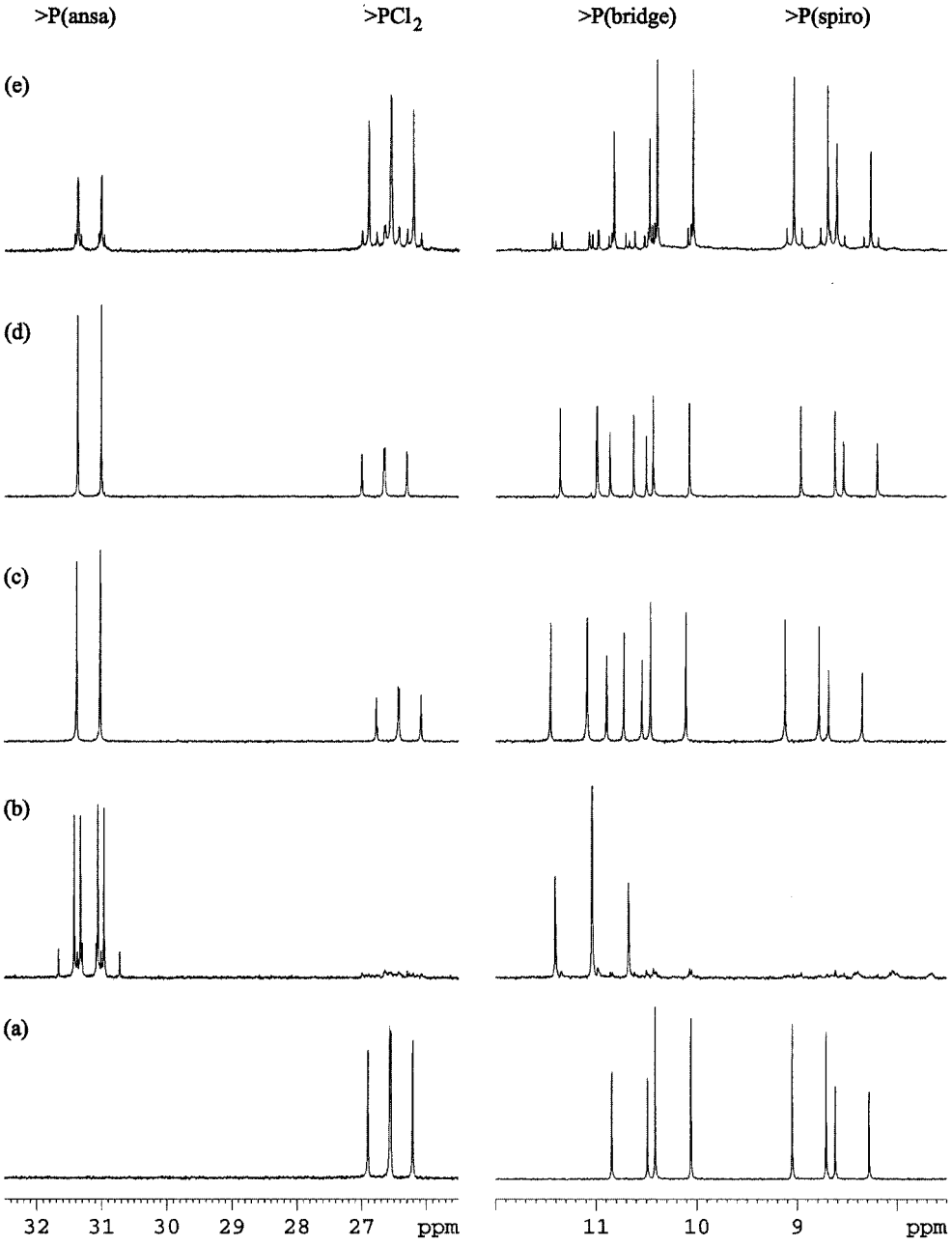


Figure 2. ^{31}P NMR spectra of the reaction mixture and the isolated four isomers of 1,3-propanediyldioxy derivatives of pentaerythritol-bridged cyclotriphosphazenes. (a) **2a**, spiro-spiro, (b) **2b**, ansa-ansa, (c) **2c**, *syn*-spiro-ansa, (d) **2d**, *anti*-spiro-ansa, (e) reaction mixture.

pounds with remote stereogenic centres on addition of CSA (and Chiral Shift Reagents, CSR).[6] However, in the case of compounds **2c** and **2d** the centres of chirality in the cyclophosphazene ansa moiety are part of the same ring and only two bonds apart and so complexation with CSA will affect both centres at the same time, as is normally found for other analogous systems,[6] i.e. the anomalous ^{31}P NMR effect with CSA is not expected for compounds **2c** and **2d** and so both are expected to be *meso* compounds.

Although NMR spectroscopy has been used to show that both compounds **2c** and **2d** are different monospiro-monoansa derivatives, such data cannot be used to assign an absolute structure and hence compounds **2c** and **2d** were characterised by X-ray crystallography.

The crystal structures of **2c** and **2d** (Figure 3) show that both molecules contain six rings, two phosphazene units bridged by a pentaerythritol molecule in a spirane arrangement, a spiro-$O(CH_2)_3O$ unit in one cyclophosphazene ring and an ansa-$O(CH_2)_3O$ moiety in the *cis*-configuration in the other cyclophosphazene ring.[7]

In both **2c** and **2d** the cyclophosphazene ring is essentially planar for the spiro-containing moiety, whereas for the ansa-substituted moiety the cyclophosphazene ring is non-planar, indicating strain which is relieved by the ring

Table 1. ^{31}P NMR parameters of compounds **2a**–**2d** and the effect of addition of CSA.

Compound[a]		Ansa moiety Chemical shifts /ppm		^2J(P,P)/Hz	Spiro moiety Chemical shifts /ppm			Coupling constants ^2J(P,P) /Hz		
	Struct.	>P(ansa)	>P(bridge)		$>PCl_2$	>P(bridge)	>P(spiro)			
		1,2	3	1,3; 2,3	1	2	3	1,2	1,3	2,3
(i) ^{31}P NMR parameters of spirane compounds										
2a	sp–sp				26.55	10.43	8.69	71.7	68.8	87.1
2b	an–an	31.31; 31.08	11.05	74.3; 72.8 48.6 (1,2)[b]						
2c	sp–an *syn*	31.21; 31.21	11.09	73.5	26.42	10.48	8.77	71.0	68.5	87.9
2d	sp–an *anti*	31.20; 31.20	11.00	73.5	26.65	10.45	8.61	72.5	68.9	86.5
(ii) Effect of addition of CSA on chemical shifts (ppb) and ^2J(P,P) at 20:1 mol ratio										
2a	sp–sp $\Delta\delta$[c]				43 (35)	–75 (8)	–13 (15)	71.6	68.5	86.8
2b	an–an $\Delta\delta$[c]	10; 22 (4); (7)	–76 [d]	73.8; 72.5 48.6 (1,2)[b]						
2c	sp–an *syn*[d]	12	–108	73.2	53	–77	–22	70.9	68.3	87.6
2d	sp–an *anti*[e]	16	–82	73.4	24	–60	–5	72.3	68.6	86.2

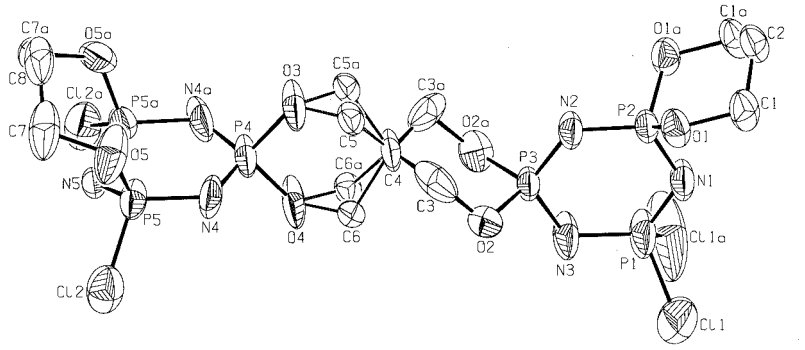
[a] 202.45 MHz ^{31}P NMR measurements in $CDCl_3$ solutions at 298K. CSA is chiral solvating agent, (*S*)-(+)-2,2,2-trifluoro-1-(9′-anthryl) ethanol. [b] AB coupling for ^2J(P,P)/Hz in ansa ring. [c] $\Delta\delta$ is the difference in chemical shift (ppb) of racemic signals at a mol ratio of CSA:**2** of 20:1. [d] No separation of signals observed up to a mol ratio of CSA:**2** of 50:1. [e] No separation of signals observed up to a mol ratio of CSA:**2** of 40:1.

nitrogen atom containing the ansa moiety being significantly out of plane; 0.262 Å **2c** and 0.289 Å **2d**.[8] The difference between the two structures is that in **2c** the ansa- and spiro-propanediyldioxy units are in a *syn* arrangement, whereas in **2d** there is an *anti* arrangement of the ansa- and spiro-propanediyldioxy units. The *syn* and *anti* structures are shown in Figure 1 for **2c** and **2d**, respectively, from which it can be clearly seen that both molecules have a plane of symmetry and so are not chiral, confirming the ^{31}P NMR results. The stereochemistry of bis(disubstituted) cyclophosphazene derivatives of **1** has recently been elucidated[4] and compounds **2c** and **2d** give rise to a new case of stereochemistry of these spirane derivatives.

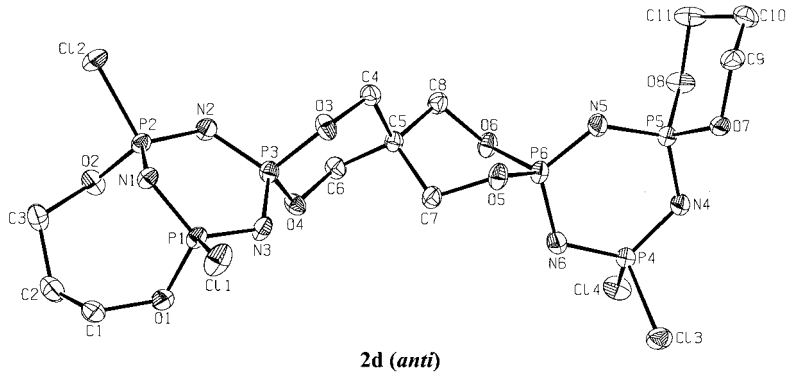
The ^{31}P NMR spectrum of the reaction mixture of compound **2** is shown in Figure 2(e). Using the NMR spectroscopic data in Table 1, it is possible to assign all the ^{31}P NMR signals in the reaction mixture to the four disubstituted compounds **2a**–**2d** (i.e. there is no evidence of the starting material, mono-substituted or higher substituted compounds). Assuming similar relaxation times for ^{31}P NMR signals of phosphorus nuclei with similar substitution patterns, the analysis gives spiro-spiro **2a** (ca. 70%), *syn*-spiro-ansa **2c** = *anti*-spiro-ansa **2d** (ca. 12%) and ansa-ansa **2b** (ca. 6%), which corresponds to the formation of a spiro being about 4.5 times more likely than that of an ansa moiety. This was confirmed by the similar relative distribution of compounds observed as a result of isolation and purification after column chromatography (**2a**, ca. 60%; **2b** ca. 10%; **2c** ca. 16%; **2d** ca.14%), though the results do not match exactly, because there are likely to be small differences in the efficiency of isolation and purification of the four compounds. The preference for spiro over ansa 1,3-propanediyldioxy derivatives of cyclophosphazene is not surprising given that the spiro ring is a six-membered thermodynamically stable chair form, in contrast to the eight-membered strained ansa ring.[8] In fact, it is somewhat surprising that significant quantities of the ansa derivatives are formed. However, in the reactions of cyclophosphazenes with diols in THF solution it has been observed[9–12] that the formation of ansa derivatives is promoted by using the more reactive sodium alkoxides (rather than the less reactive neutral pentaerythritol and tertiary base used previously[3]). It was also expected[11,12] that addition of 15-crown-5 ether (which should make the nucleophilic alkoxide more reactive by reducing ion-pairing) might also assist in the formation of ansa derivatives with 1,3-propanediol in this work. The reaction conditions for the formation of spiro and ansa derivatives of cyclophosphazenes with diols are currently being investigated.

Experimental Section

Materials: Hexachlorocyclotriphosphazene (Shin Nisso Kako Co Ltd.) was purified by fractional crystallisation from hexane. The following chemicals were obtained from Merck: Pentaerythritol (> 98%), 1,3-propanediol (> 98%), silica gel 60, tetrahydrofuran (≥ 99.0%), dichloromethane (≥ 99.0%), ethyl acetate (≥ 99.0%), *n*-hexane (>96%), sodium hydride (> 60%), 15-crown-5 ether (> 98%). The deuteriated solvent ($CDCl_3$) for NMR spectroscopy was obtained from Apollo Scientific and the chiral solvating agent (CSA), (*S*)-(+)-2,2,2-trifluoro-1-(9′-anthryl)ethanol, from Aldrich Chem. Co.



2c (*syn*)



2d (*anti*)

Figure 3. X-ray crystal structures of the two monospiro-monoansa derivatives **2c** and **2d**.

Methods: Elemental analyses were obtained with a Carlo–Erba 1106 Instrument. Mass spectra were recorded with a VG Zab Spec GC-MS spectrometer using the fast atom bombardment (FAB) method (35 kV) with MNBA as the matrix; ^{35}Cl values were used for calculated masses. Analytical thin layer chromatography (TLC) was performed on Merck Silica gel plates (Merck, Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 230–400 mesh; for 3 g. crude mixture, 100g. silica gel was used in a column of 3 cm in diameter and 60 cm in length). ^{31}P NMR spectra were recorded in $CDCl_3$ solutions with a Bruker DRX 500 MHz spectrometer using 85% H_3PO_4 as an external reference for ^{31}P. In order to assign the signals of some compounds both proton-coupled and proton-decoupled ^{31}P NMR spectra were recorded. Experiments involving the chiral solvating agent (CSA) were performed by addition of small aliquots of a concentrated solution of CSA in the solvent used for NMR spectroscopy and the proton-decoupled ^{31}P NMR spectrum recorded at each addition.

X-ray Crystallography: X-ray structure determination and crystallographic data were collected by means of combined phi and omega scans with a Bruker–NoniusKappaCCD area detector situated at the window of a rotating anode (λ, Mo-K_α = 0.71073 Å). The structures were solved by direct methods, SHELXS-97 and refined by using SHELXL-97.[13] Hydrogen atoms were included in the refinement, but thermal parameters and geometry were constrained to ride on the atom to which they are bonded. The data were corrected for absorption effects using SORTAV.[14] The structure of **2c** exhibits crystallographic disorder about the mirror axis in the space group. In addition a disordered solvent molecule was also present, but was too disordered to resolve and was therefore removed from the model using the SQUEEZE[15] procedure from within the PLATON[16] suite of programs (Table 2).

Table 2. X-ray data for compounds **2c** and **2d**.

	2c	**2d**
Empirical formula	$C_{11}H_{20}Cl_4N_6O_8P_6$	$C_{11}H_{20}Cl_4N_6O_8P_6$
Formula mass	691.95	691.95
Crystal system	orthorhombic	monoclinic
Space group	*Pnma*	$P2_1/c$
a [Å]	12.1255(3)	14.7211(3)
b [Å]	10.7597(3)	11.9459(3)
c [Å]	23.7161(5)	14.9661(4)
β [°]	90	105.089(2)
V [Å^3]	3094.16(13)	2541.15(11)
Z	4	4
Density (calcd.) [Mg/m^3]	1.720	1.809
Absorption coefficient [mm^{-1}]	0.751	0.895
F(000)	1400	1400
Crystal size [mm]	0.45 × 0.40 × 0.40	0.12 × 0.10 × 0.01
$\theta_{max.}$ [°]	27.49	27.46
Reflections collected	25948	34251
Independent reflections	3716	5808
Final *R* indices $F^2 > 2\sigma F^2$	*R*1 = 0.1102 *wR*2 = 0.2708	*R*1 = 0.0362 *wR*2 = 0.0754
$\Delta\rho_{max./min.}$ [e·Å^{-3}]	1.333/–1.104	0.369/–0.427

CCDC-245906 and CCDC-245907 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Reaction of Compound 1 with 1,3-Propanediol To Give Compounds 2a–d: Compound **1** was prepared as in the literature.[3] To a stirred solution of compound **1** (2 g, 2.92 mmol) dissolved in dry tetrahydrofuran (20 mL) at –15 °C under argon was first added dropwise 1,3-propanediol (0.4 g, 5.84 mmol) in dry tetrahydrofuran (20 mL), then sodium hydride (0.28 g, 11.68 mmol) in dry tetrahydrofuran (20 mL) was added dropwise and finally 15-crown-5 (0.5 g) was

added. The reaction mixture was stirred for a further 2 days at room temperature and the reaction was followed by TLC indicating four products and no starting material remaining. The precipitated salt (NaCl) was then filtered off, the solvent was removed under reduced pressure and four products were isolated by column chromatography [silica gel 60 (70–230 mesh) as adsorbent and ethyl acetate/*n*-hexane (1:2) as eluent]. The order of compounds eluted is **2d**, **2b**, **2a** and **2c** . Compound **2c** was crystallized from benzene and **2d** was crystallized from dichloromethane/hexane (3:1). **2a:** Yield 0.30 g (14.85%), m.p. 208 °C. (found: C 18.96, H 2.85, N 12.05. MS: *m*/*z* = 690.8 $[M + 1]^+$). **2b:** Yield 0.05 g (2.47%), decomp. 200 °C, (found: C 21.06, H, 2.86, N 12.11. MS: *m*/*z* = 691.0 $[M + 1]^+$). **2c:** Yield 0.08 g (3.97%), m.p. 170 °C, (found: C 20.25, H 2.89, N 12.12. MS: *m*/*z* = 690.7 $[M + 1]^+$). **2d:** Yield 0.07 g (3.47%), decomp. 140 °C, (found: C 20.21, H 2.74, N 11.96. MS: *m*/*z* = 690.7 $[M + 1]^+$). $C_{11}H_{20}Cl_4N_6O_8P_6$: calcd. C 19.09, H 2.91, N 12.15. MS: *m*/*z* = 690.0 $[M^+]$.

Acknowledgments

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[7] The starting material, compound **1**, is a linear tri-spirane, in which all the organophosphate and cyclotriphosphazene spirane moieties are six-membered and the shape of the ring system may be described as planar/chair/chair/planar. The introduction of spiro substituents creates further six-membered spirane rings, whereas ansa substituents form eight-membered rings giving rise to fused bicyclic systems. Thus the spiro-spiro derivative, **2a**, is a penta-spirane with the two terminal spirane rings at an angle to the linear central four. The ansa-ansa compound, **2b**, is a tri-spirane with both ends having fused bicyclic units. The two spiro-ansa isomers, **2c** and **2d**, are tetra-spiranes and have one end with a fused bicyclic structure. The ring system of the *syn* compound **2c** may be described as chair/planar/chair/disordered-chair/fused-envelope and the *anti* compound **2d** as chair/planar/twisted-chair/chair/fused-envelope. All the CH_2 groups are staggered with respect to their nearest neighbours and eclipsed with those two bonds away, except in the twisted chair, where they are staggered.

[8] The fused bicyclic ansa structures exhibit a boat-chair form. The ring N atom sandwiched between the two P–O ansa segments is forced out of the rest of the plane of the N_2P_3 ring to such an extent that it is nearly parallel with the adjacent P–Cl bonds. This distortion causes a ring compression. The respective non-bonded P···P distances for the spiro and ansa N_3P_3 rings for these two diastereoisomers are for the *syn* compound **2c** (spiro 2.724, 2.729 and 2.763 Å and ansa **2.636**, 2.725 and 2.726 Å) and for the *anti* compound **2d** (spiro 2.745, 2.760 and 2.764 Å and ansa **2.637**, 2.735 and 2.741 Å).

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