Syntheses, Stereochemistry, and Inclusion Properties of New Spirocyclophosphazenes

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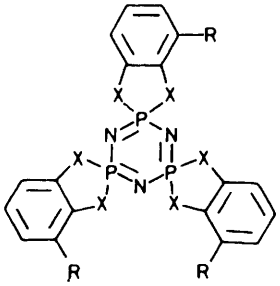
The syntheses and characterization of new spirocyclophosphazenes is reported. Variable-temperature n.m.r. measurements strongly suggest the presence of only one isomer for our compounds. Only tris-(3-methoxyphenyl-1,2-dioxy)phosphonitrile trimer has been found to form clathrate compounds with cyclohexene, n-heptane, and 1,2-dichloroethane.

The condensation reaction of hexachlorotricyclophosphazene with aromatic dihydroxy, dithio, and diamino compounds to yield spirocyclotriphosphazenes has attracted increasing interest in the last few years.[1—5]

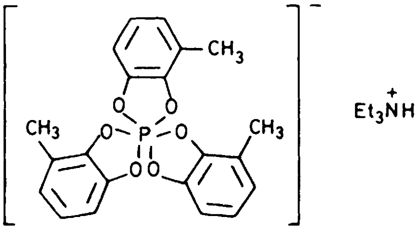
Such compounds and related polymers, because of their inclusion properties, are successfully used in organic syntheses and analytical or commercial separation processes.[6—8] For example, tris-(*o*-phenylenedioxy)phosphonitrile trimer is capable of forming clathrate inclusion adducts and large guest molecules are retained more than the smaller ones, in contrast to many other host materials.[9] Tris(naphthalene-2,3-dioxy)cyclotriphosphazene and tris(naphthalene-1,8-dioxy)-cyclotriphosphazene have been found to form inclusion compounds with a variety of aliphatic and aromatic hydrocarbons.[6]

In this work we have synthesized the spirocyclophosphazenes (**1**) and (**2**) to throw some light on the existence of different stereoisomers and also to compare their inclusion properties relative to those of unsubstituted compounds.

Since such host molecules form a channel in which the guest is accommodated, the introduction of substituents in the aromatic ring could introduce variations in the diameter of the tunnel.



(1) X = O, R = OCH_3
(2) X = S, R = CH_3



(3)

Experimental

Instrumentation.—^1H N.m.r. spectra were recorded on a Bruker WP-80FT spectrometer equipped with variable-temperature accessories. Temperatures are accurate to ±1 °C.

Saturation of the n.m.r. signals was avoided. N.m.r. samples were *ca.* 2% w/v solutions containing tetramethylsilane as internal standard.

Mass spectra were obtained on an LKB-9000S high-resolution mass spectrometer with an ionizing voltage of 70 eV.

I.r. spectra were recorded on a Perkin-Elmer 680 spectrophotometer.

Materials.—Hexachlorocyclotriphosphazene was synthesized by a procedure in the literature.[10]

Commercial 3-methoxycatechol, toluene-3,4-dithiol, and 4-methylcatechol were purified before use.

Tris-(3-*methoxyphenyl-*1,2-*dioxy*)*phosphonitrile trimer* (**1**). A solution of 3-methoxycatechol (5.80 g, 0.04 mol) and triethylamine (8.28 g, 0.082 mol) in tetrahydrofuran (150 ml) was added dropwise at room temperature to a solution of phosphonitrile chloride trimer (4.86 g, 0.014 mol) in tetrahydrofuran (200 ml) under nitrogen. After some minutes a precipitate formed. The solution was maintained at reflux temperature for 2 h and then stirred for 48 h at 30 °C. The solid formed was filtered off, washed with water, and dried (4 g, 60%). Recrystallization from chloroform yielded a *solid*, m.p. 127—129 °C (Found: C, 44.85; H, 3.15; N, 7.2. $C_{21}H_{18}N_3O_9P_3$ requires C, 45.3; H, 3.2; N, 7.4%), δ (CD_2Cl_2; 25 °C) 3.91 (9 H, s, OCH_3) and 6.58—7.18 (9 H, m, ArH), $\nu_{max.}$ (KBr) 1 225 (P=N), 1 270 (O–Ph), 830 (P–OAr), and 760 cm^{-1} (aryl).

The compound is almost insoluble in benzene, chloroform, acetone, toluene, and dimethyl sulphoxide, but it is soluble in dimethylformamide and dichloroethane.

Tris-(3-*methylphenyl-*1,2-*dithio*)*phosphonitrile trimer* (**2**). This compound has been synthesized by a procedure in the literature.[11]

Unfortunately, all the attempts to synthesize tris-(3-methylphenyl-1,2-dioxy)spirocyclotriphosphazene by changing the base (Et_3N or Na_2CO_3), the concentration of the reagents, the reaction time, the temperature (up to 100 °C) and the solvent have failed. In all cases the phosphate (**3**) was obtained, m.p. 245—248 °C (from methanol) (Found: C, 65.2; H, 6.5; N, 2.65. $C_{27}H_{34}NO_6P$ requires C, 64.9; H, 6.9; N, 2.8%); δ (DMSO; 25 °C), 1.16 (9 H, t, $^3J_{H,H}$ 7.5 Hz, CH_3CH_2), 2.13 (9 H, s, CH_3), 3.08 (6 H, q, $^3J_{H,H}$ 7.5 Hz, CH_3CH_2), and 6.37 (9 H, s, ArH), $\nu_{max.}$ (KBr) 3 120 (N–H), 1 255 (O–Ph), 840 (P–O-phenyl), and 730 cm^{-1} (phenyl).

Inclusion Properties.—The following methods were used to test the inclusion properties of our compounds.

(a) Recrystallization: the compound (100 mg) was dissolved in hot solvent (2 cm^3) and after precipitation the crystals were filtered off.

(b) Spontaneous evolution of the solvent: this method was

Table. Mass spectral data

Compound (1)	Compound (2)	Compound (3)
550 (100)	597 (37)	400 (1)
549 (100 × 4)	440 (19)	399 (0.62)
534 (40)	427 (10)	293 (8)
519 (12)	408 (5)	292 (44)
504 (8)	297 (5)	291 (4)
428 (12)	288 (7)	276 (25 × 10)
413 (24)	265 (14)	275 (69 × 10)
396 (24)	199 (10)	261 (6)
290 (17)	186 (15)	260 (42)
275 (72)	185 (50)	199 (12)
230 (13)	168 (5)	196 (5)
213 (12)	167 (6)	195 (11)
107 (64)	154 (100)	186 (26)
95 (52)	153 (65)	185 (27)
79 (40)	121 (21)	170 (44)
51 (44)	110 (7)	169 (26)
	92 (20)	154 (62)
	91 (39)	153 (76 × 10)
		124 (76)
		101 (100)

Data are for m/z with relative intensities in parentheses.

generally preferred due to the difficulty of recrystallizing the compounds because of their low solubility. The compound (100 mg) and solvent (some cm^3) after heating at temperatures below 100 °C were left for 24 h. The solid product was then filtered off.

In both cases the clathrate was dried under reduced pressure (0.5 mmHg) at room temperature for 24 h before measurements (multiple ^{1}H n.m.r. integrations).

Results and Discussion

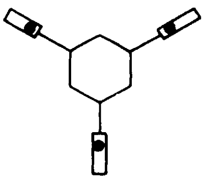
Mass Spectrometry.—The electron-impact 70 eV mass spectra were measured in order to obtain information on the chemical species derived from fragmentation in the vapour phase of compounds (**1**)—(**3**). The related mass spectral data are reported in the Table.

The spectrum of phosphate (**3**) shows a low-intensity peak at m/z 398 derived from the molecular ion after the loss of triethylamine and a ten times more intense peak at m/z 292, due to the fragmentation ion $(CH_3C_6H_3O_2)_2POH^+$.

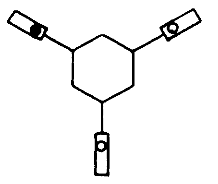
The base peak is present at m/z 275 corresponding to $(CH_3C_6H_3O_2)_2P^+$. Other interesting peaks are m/z 275 $(CH_3C_6H_3O_2)_2P^+$, 186 $(CH_3C_6H_3O_2)POOH^+$, and 170 $(CH_3C_6H_3O_2)POH^+$. The peak at m/z 153 $(CH_3C_6H_3O_2)P$ shows an intensity very close to that of the base peak. The peaks at m/z 124 and 101 are attributable to 4-methylcatechol and triethylamine, respectively.

The spectra of the spirocyclotriphosphazenes (**1**) and (**2**) show peaks corresponding to the molecular ions at m/z 549 and 597 which in the latter corresponds to the base peak. It is also noteworthy that for compound (**2**) all the other peaks are of very low intensity and not as numerous as for compound (**1**), indicating probably the greater stability of compound (**2**) because of the presence of a sulphur-containing ring rather than an oxygen one.

Stereochemistry.—Previous *X*-ray studies have showed that all spirocyclophosphazenes assume an achiral 'paddle-wheel' conformation with the side aromatic groups twisted at right angles to the central phosphorus–nitrogen ring. Therefore, in this arrangement, two different stereoisomeric forms (**4**) and (**5**) are possible for our compounds. In form (**4**) the aromatic ring substituents are all in the same site with respect to the phosphazene plane, and in form (**5**) one group is above and the others below the plane.



(**4**)



(**5**)

When both forms are present the n.m.r. spectra of compounds (**1**) and (**2**) should show three signals both for the methoxy and methyl groups. In fact, isomer (**4**) should show only one signal due to the three equivalent substituents and isomer (**5**) two sets of signals, with one double the intensity of the other.

On the other hand, the room-temperature n.m.r. spectra of the compounds show only one sharp signal (δ 3.91 and 2.25 for methoxy and methyl groups, respectively). When the temperature is decreased to −75 °C for compound (**1**) (CD_2Cl_2) and −58 °C for compound (**2**) (DMF) these signals did not show any broadening or substantial modification.

This strongly suggests the presence of only form (**4**) for the compounds (**1**) and (**2**), and that no stereochemical mobility is observable on the n.m.r. time-scale for such molecules.

The presence of only form (**4**) for our compounds was confirmed by the fact that in the ^{1}H n.m.r. spectra of the crude reaction mixtures no signal for any other isomer was found in appreciable amount. Attempts to isolate other compounds by column chromatography failed probably due to hydrolysis of the products on silica gel.

Inclusion Properties.—The following solvents were tested: chloroform, methanol, ethanol, acetonitrile, ethyl methyl ketone, benzene, toluene, *m*-xylene, mesitylene, cyclohexene, n-heptane, and 1,2-dichloroethane.

In the case of compound (**1**) clathrate compounds were formed with the following solvents: cyclohexene (1:3), n-heptane (1:2), and 1,2-dichloroethane (1:2). Our host/guest mole ratios are comparable with the values obtained by others.[9] No clathrates were obtained with the spirocyclophosphazene (**2**) probably due to the greater dimensions of its channel.

Acknowledgements

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