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Incorporation of Stable Organic Radicals into Cyclotriphosphazene: Preparation and Characterization of Mono- and Diradical Adducts

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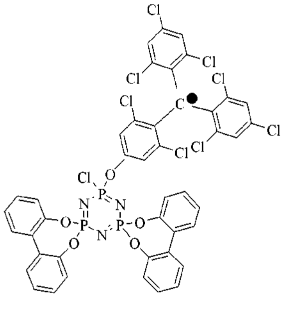
ABSTRACT



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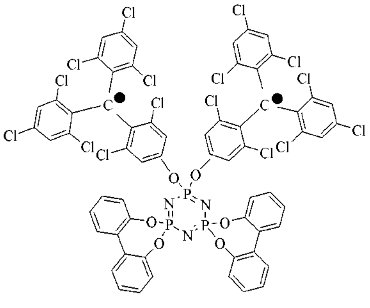

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Stable cyclotriphosphazenes 4 and 5, incorporating one and two carbon radical centers, respectively, have been easily prepared and characterized. EPR spectroscopic studies in fluid solution at room temperature were carried out for both compounds and also for diradical 5 in frozen solvent matrixes. Spectral results are consistent with a triplet or degenerate singlet triplet ground state for 5. Reductive cyclic voltammetry shows a redox couple, being monoelectronic for 4 and bielectronic for 5.

The polyphosphazenes are an important class of inorganic macromolecules consisting of $-N{=}PX_2-$ chain units, where X may be an alkoxide or aryloxide (OR), an amine (NHR), or an akyl or aryl (R) group.[1−4] It has been pointed out that the cyclic triphosphazenes are unsatisfactory as models for certain aspects of the chemistry of the high molecular weight polymers, such as the thermal, chemical, and photochemical stabilities, and that they fail to reveal the effects of the side reactions in the synthesis of the latter.[5] However, it has been suggested that the cyclic molecules may serve as essential structural models for the molecular structure of the analogous polymers.[5]

It is well established that there is no electron delocalization between consecutive NPX_2 groups because of the nature of the bonding in cyclic triphosphazenes[1,6,7] and that they do

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not have aromaticity,[8] conclusions that have been supported by recent calculations based on the AIM theory.[9] However, multinuclear magnetic resonance studies on spirocyclic cyclotriphosphazenes bearing 4-oxypyridine groups and their complexes with $W(CO)_5$ moieties have shown that a chemical modification introduced in one site of the cyclic phosphazene has measurable effects on other parts of the molecule far away from this site, suggesting some type of chemical communication through the −N=P−N=P− bonds.[10]

To date, no stable free radicals have been incorporated into polyphosphazenes. However, the presence of unpaired electrons located in different positions of a triphosphazene ring should facilitate a measurement of the degree of electronic interaction among them and an appraisal of the responsable structural and bonding effects. On the other hand, molecules with high electron-spin multiplicity as key building blocks for ferromagnets is one objective in the field of organic materials.[11] Carbon-centered organic free radicals derived from the tris(2,4,6-trichlorophenyl)methyl (TTM) radical are thermally and chemically very stable,[12] and the preparation of two functionalized derivatives of it, the amino radical **1**[13] and the phenolic radical **2**,[14] have been reported. Condensation of **1** with 1,4-diketones has yielded stable radical species anchoraged to polyheterocycles, which conveniently oxidized to cation diradicals have triplets or nearly degenerate singlet−triplet ground states. These molecules are models for polymers with high spin multiplicity. The spirocyclic triphosphazene **3** (Figure 1), having chlorine atoms easily substituted by aryloxides,[15] may be an appropriate precursor to incorporate one or two molecules of **2**.

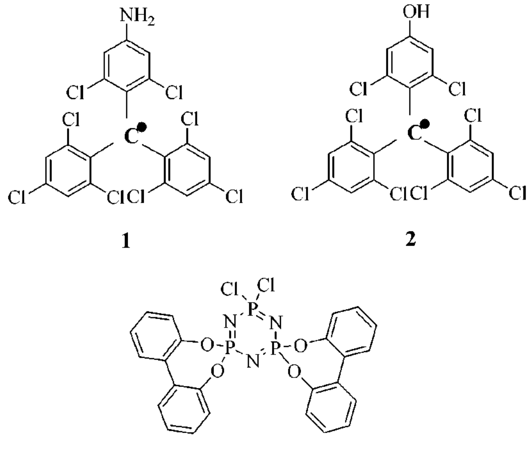

Figure 1. The structures of amino radical **1**, phenolic radical **2**, and cyclotriphosphazene **3**.

Therefore, the reaction of triphoshazene **3** with (4-hydroxy-2,3-dichlorophenyl)-bis(2,4,6-trichlorophenyl)methyl radical **(2)**, using the cesium carbonate synthetic method,[16] gave the substituted spirocyclotriphosphazenes **4**[17] and **5**[17] (Figure 2). These red solids display electronic absorption spectra in $CHCl_3$ characteristic of the radical character of the molecule [$\lambda_{max}(\epsilon$, dm mol^{-1} cm^{-1}), 372 (34 800), 482 (800) and 536 (780) nm for **4** and 372 (69 000), 489 (1675) and 535 (1600) nm for **5**]. The molar absortivities of **5** are practically double of those of **4**, indicating the presence of two radical centers in the molecule of **5**. Similar as in the case of the TTM radical,[14] red solutions of **4** and **5** in CH_2Cl_2 treated with $SbCl_5$ give very stable dark blue solutions of the monocation $\mathbf{4}^+$ [$\lambda_{max}(\epsilon)$, 645(34 600)] and dication $\mathbf{5}^{2+}$ [$\lambda_{max}(\epsilon)$, 650(75 400)], respectively.

Cyclic voltammograms[18] of the reduction of **4** and **5** in CH_2Cl_2 in the presence of tetrabutylammonium perchlorate exhibit one redox couple, O/R, at similar potential values for both, being a monoelectronic process for **4** and bielec-

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(17) **Synthesis of Spirotriphosphazenes 4 and 5.** A mixture of $[N_3P_3Cl_2(O_2C_{12}H_8)_2]$[15] (**3**, 0.26 g, 0.453 mmol), (2,6-dichloro-4-hydroxyphenyl)-bis(2,4,6-trichlorophenyl)methyl radical (0.503 g., 0.94 mmol), and Cs_2CO_3 (0.326 g, 1 mmol) in THF (20 mL) was stirred at room temperture for 6 h. The resulting mixture was filtered from a green precipitate, and the solution was evaporated in vacuo to give an orange residue (0.679 g), which was chromatographed in silica gel eluting with hexane/chloroform (first 4: 1 and then 2: 1) to give compounds **5** and **4**. **Spirotriphosphazene 5** (0.157 g; 22%): IR (KBr) 3080(w), 1575 (w), 1557 (w), 1525 (w), 1480 (w), 1439 (w), 1369 (w), 1271 (m), 1230 (m), 1178 (s), 1096 (m), 970 (m), 951 (w), 937 (w), 911 (w), 879 (w), 860 (w), 784 (m), 752 (m) cm^{-1}; MS (MALDI-TOF) M + H, 1571.71. Anal. Calcd for $C_{62}H_{28}Cl_{16}N_3O_6P_3$: C, 47.4; H, 1.8; Cl, 36.1; N, 2.7. Found: C, 47.8; H, 2.1; Cl, 35.6; N, 2.7. **Spirotriphosphazene 4** (0, 238 g; 49%): IR (KBr) 3080(w), 1570(m), 1554(m), 1527(m), 1477(w), 1436(w), 1370 (m), 1274(m), 1228 (m), 1177 (s), 1093 (m), 970 (m), 887 (m), 860 (m), 840 (m), 788 (m), 754 (m) cm^{-1}; MS (MALDI-TOF) M + H, 1073.65. Anal. Calcd for $C_{43}H_{22}Cl_9N_3O_5P_3$: C, 48.1; H, 2.1; Cl, 29.7; N, 3.9. Found: C, 48.2; H, 2.1; Cl, 29.9; N, 3.9.

(18) The cyclic-voltammetric measurements were carried out in a jacketed three-electrode cell under an argon atmosphere. The working electrode was a platinum sphere with an area of 0.093 cm^2, and the counter electrode was a Pt wire. The reference electrode was an SSCE (sodium chloride saturated calomel electrode) connected to the cell through a salt bridge containing a 0.1 M TBAP−CH_2Cl_2 solution. Scan rates ranging between 20 and 200 mV s^{-1} were studied. The volume of all test solutions was 25 cm^3. The temperature was kept at 25 °C.

(19) The *p*-hydrogen coupling in (2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical, $a_H = 2.1$ G,[20] is much lower than phosphorus coupling in **4**, although the nuclear magnetic moment of hydrogen ($\mu = 2.79$) is ∼2.5 as high as that of the phosphorus atom ($\mu = 1.13$).

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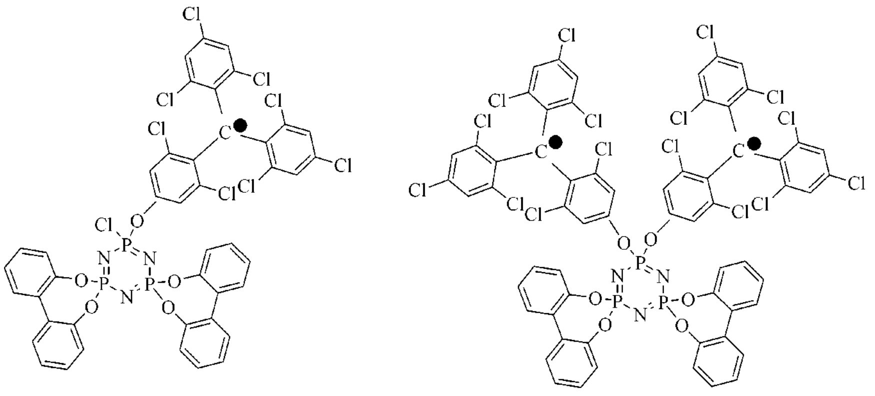
(21) EPR spectra of glassy solutions were simulated using WINEPR SimFonia, Shareware Version 1.25; Brüker Analytische Messtechnik GmbH, 1994−1996.



4 **5**

Figure 2. The structures of cyclotriphosphazenes **4** and **5**.

tronic for **5**. Their standard potentials ($E°$) were −0.55 and −0.57 V vs SSCE (sodium chloride saturated calomel electrode) for **4** and **5,** respectively. This O/R couple is associated to the equilibria $\mathbf{4} + 1e \rightleftharpoons \mathbf{4}^{-}$ and $\mathbf{5} + 2e \rightleftharpoons \mathbf{5}^{2-}$ to generate the monoanion and dianion, respectively.

Figure 3 displays the electron paramagnetic resonance spectrum of a degassed and diluted solution ($\sim 10^{-3}$ M) of **4** in CCl_4 at 253 K. This spectrum, with a g-value ($g = 2.0032$) closed to that of phenolic radical **2,** consists of an overlapped doublet of septets corresponding to the coupling with a phosphorus atom, $a(P) = 5.25$ G, and six *meta*-hydrogens, $a(6H) = 1.25$ G. At higher gain (^{13}C atom, natural abundance, 1.1%) the isotropic coupling with the ^{13}C nuclear spins of the α-carbon ($a \approx 28$ G), three bridgehead carbons ($a \approx 13$ G), and six *ortho*-carbons ($a = 10.4$ G) are displayed as small lines in the sides of the main spectrum. The coupling constant observed for the six hydrogens is identical with that of protons in the tris(2,4,6-trichlorophenyl)methyl radical,[14] and it is pertinent to mention the relative large value for the phosphorus coupling.[19]

The spectrum of the isotropic solution ($\sim 2 \times 10^{-3}$ M) of diradical **5** in CCl_4 at room temperature displays a broad doublet ($\Delta H_{pp} = 1.5$ G) signal centered at $g = 2.0032$, which does not appreciably change at low temperatures. The following coupling constant values $a(P) = 4.20$ G and $a(12H) = 0.62$ G provides the best simulation of the spectrum. The smaller value of the coupling with phosphorus relative to that in monoradical **4** indicates most probably a change in the twisted O−C angle due to the substitution of the chlorine in **4** by the second phenoxide-radical moiety, and the value of the coupling with 12 hydrogens, half the value of the coupling with six hydrogens in **4**, shows that diradical **5** exhibits rapid electron exchange coupling. In glassy methyltetrahydrofuran (MTHF) solution at 110 K, **5** displays in the $\Delta m_s = \pm 1$ region the spectrum shown in Figure 4, simulated[21] by using the zero field splitting parameters $|D/hc| = 0.0016\ \mathrm{cm}^{-1}$ and $|E/hc| = 0.2 \times 10^{-4}\ \mathrm{cm}^{-1}$ and the anisotropic phosphorus coupling constants, $A(xx) = A(yy) = 5.30$ G and $A(zz) = 2.00$ G, with the principal values of the g tensor being $g_{xx} = 2.0041$, $g_{yy} = 2.0026$, $g_{zz} = 2.0026$. Given the line width applied in the simulation (5.4 G), the precision in these estimate values is limited. The relatively low D value is a consequence of the large distance between the unpaired electrons. It is well-

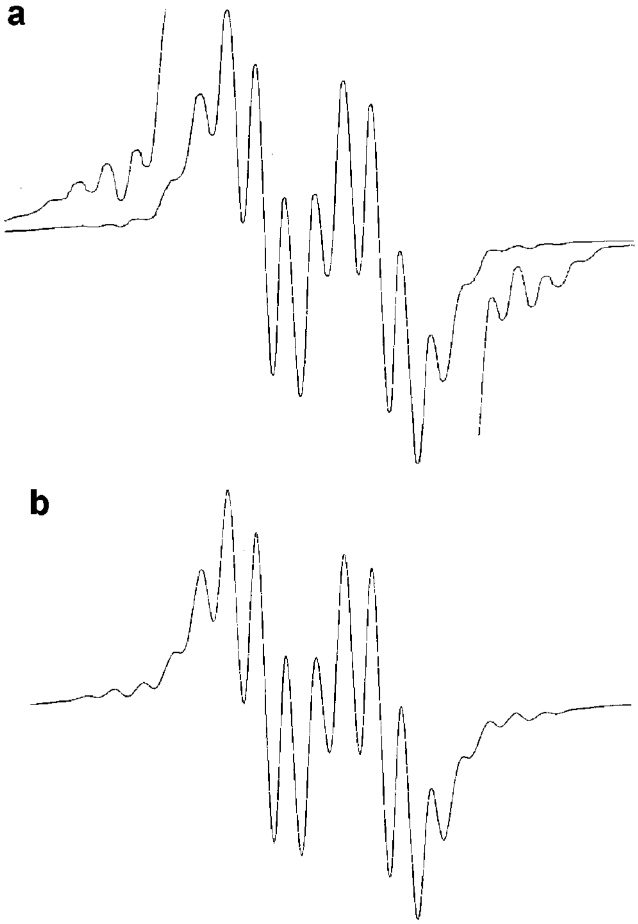


Figure 3. (a) EPR spectrum of a solution of radical **4** in CCl_4 at 253 K and amplification showing *ortho*-^{13}C couplings. (b) Computer simulation with the values given in the text.

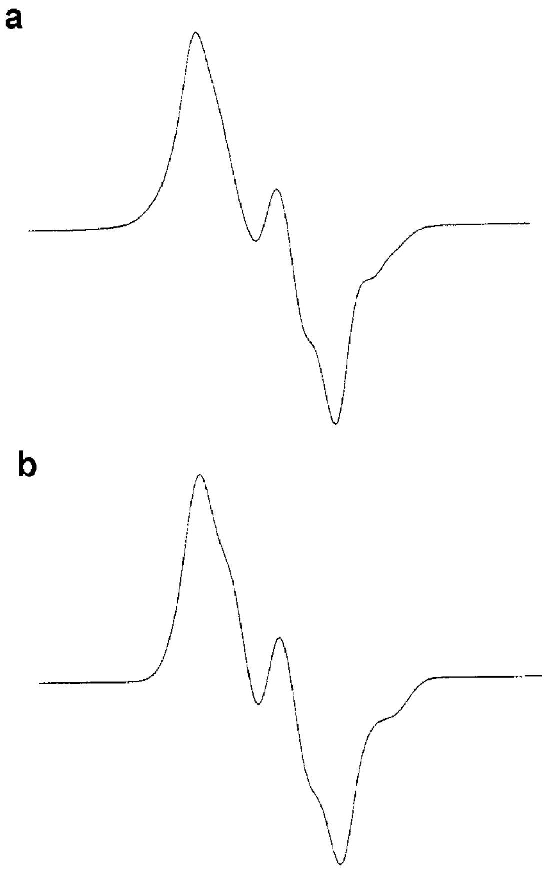


Figure 4. (a) EPR spectrum in a glassy solution of diradical **5** in methyltetrahydrofuran at 110 K. (b) Computer simulation with the values given in the text.

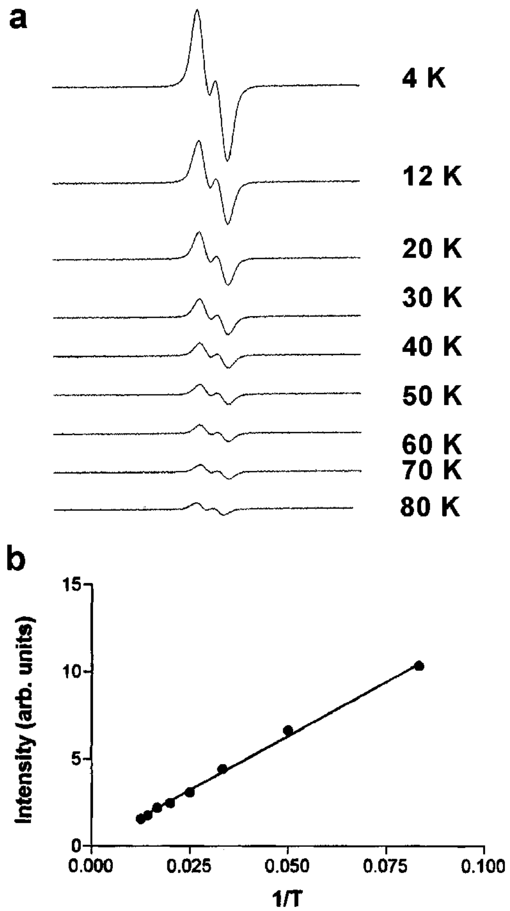


Figure 5. (a) Evolution of the $\Delta m_s = \pm 2$ signal of a glassy solution of diradical **5** in methyltetrahydrofuran from 4 to 80 K. (b) Curie plot of the $\Delta m_s = \pm 2$ signal intensities with the inverse of the temperature from 4 to 80 K.

known in the TTM radical series that the spin density is largely confined in the trivalent carbon atom as a result of the large twisted angles with phenyl rings. Further confirmation of the triplet state configuration of **5** was provided by the observation of the signal in the $\Delta m_s = \pm 2$ region, which shows a broad doublet corresponding to the phosphorus splitting. The evolution of the intensity of this signal with temperature is displayed in Figure 5 along with the Curie function of these intensities versus the inverse of the absolute temperatures in the range between 4 and 80 K. This function gives a straight line (correlation coeficient = 0.997) indicating a triplet ground state or nearly degenerate with a singlet state.

In summary, we have shown an easy access to introduce persistent magnetic species into the phosphazene pattern. The relative high hyperfine splitting due to the ^{31}P nuclear spin in monoradical **4** and the confirmation of a rapid electron exchange in diradical **5** through the multiple C−O−P−O−C bonding in fluid solution at room temperature could be brought about by a different mechanism other than spin polarization. We suggest a hyperconjugation effect originated by the overlapping between the phosphorus 3s atomic orbital and the 2p$_z$ of the adjacent carbon atom, similar to that observed in some aryl phosphates.[22] In fact, the P−O−C angles found in aryloxyphosphazenes are also around 120°,[23] although in some highly hindered cases, the value can be close to 130°.[24] In addition, diradical **5** has a triplet ground state or a very low energy triplet state. Attempts to introduce more persistent radical moieties into the phosphazene pattern to know more thoroughly the electronic communication in phosphazene ring are under way.

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