Phenalene–Phosphazene Complexes: Injection of Electron Spin Density into the Cyclotriphosphazene Ring System

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Received April 15, 1985

Abstract: A theoretical model is advanced which provides a mechanism for the injection of π-electron spin density from a spirosubstituent into a phosphazene linkage via the phosphorus d_π orbitals. Such p_π–d_π spirodelocalization is shown to be invariant to the d_π basic set chosen for the phosphorus atom. The 1,9-disubstituted-phenalenyl system is shown to possess a frontier molecular orbital which fulfills the requirements of the theoretical model. A series of monosubstituted-spiro [phenalene] derivatives of hexachlorocyclotriphosphazene have been prepared and characterized. Attempts to replace the remaining chlorine functionality with trifluoroethoxy groups gave rise to different modes of substitution, depending on the nature of the phenalene moiety. 4′,4′,6′,6′-tetrakis(trifluoroethoxy)-4′,4′,6′,6′-tetrahydro-1-methylspiro[phenaleno[1,9-*de*]-1,3,2-diazaphosphorine-2(1*H*),2′-[1,3,5,2,4,6]triazatriphosphorine] (**8**) retains its structural integrity in the presence of sodium trifluoroethoxide and may be isolated without complications. The compound undergoes both protonation and methylation (to produce $\mathbf{9}^+,BF_4^-$) on the exocyclic imino-nitrogen atom. This latter result has been confirmed by an X-ray crystallographic study of $\mathbf{9}^+,BPh_4^-$. Electronic and P^{31} NMR spectra provide evidence which strongly suggests that the tetrakis(trifluoroethoxy)cyclotriphosphazene system is a strong electron acceptor even when bonded to a cationic substituent (as occurs in $\mathbf{9}^+$). Both **8** and $\mathbf{9}^+,BF_4^-$ are electroactive, showing one and two reduction steps, respectively. The first reduction products have been examined by electron spin resonance spectroscopy. Analysis of the ESR spectrum obtained from **9** provides the first evidence for the injection of electron spin density into a segment of a phosphazene linkage. At least half of the cyclotriphosphazene ring nuclei are ESR-active.

The phosphazenes have been of great interest in recent years, both in their cyclic and linear (polymeric) forms.[1-3] The chemistry of these compounds is becoming increasingly well-developed and the phosphazenes probably constitute the premiere example of an inorganic homologous covalent class of compounds. The structures and bonding of the phosphazenes are of particular interest with respect to π-bonding, delocalization, and aromatic character in the ring systems, and there are a number of important outstanding questions with regard to the electronic structure of the cyclo- and polyphosphazenes.

In many respects, the chemistry of the phosphazenes parallels that of conjugated organic compounds. There is, however, an important difference: while the P–N bonds in phosphazenes are usually equal in length and presumably intermediate in character between formal single and double bonds, they do not show many of the characteristics normally associated with conjugated organic compounds such as benzene and polyacetylene. Thus, the cyclophosphazenes do not exhibit strong evidence of aromatic character (resonance energies, ring currents), and the polyphosphazenes show no dependence of the band gap on chain length. In neither the cyclo- or the polyphosphazenes has it proved possible to introduce holes or electrons into the conjugated –P–N– linkage via reductive or oxidative processes. As a result, carriers have not been generated in this conjugated system, and all the currently available materials are insulators.

Electrochemical studies[4,5] on the reduction of a variety of phosphazene derivatives in the range 0 → −3 V (SCE) led to the following observations: (i) Phosphazenes containing only the most electronegative ligands, such as F, Cl, Br, or OCH_2CF_3, could not be reduced in this potential range. (ii) Phosphazenes possessing an unsubstituted phenyl group linked through oxygen or nitrogen to phosphorus were not reduced under these conditions. (iii) Compounds containing phenyl groups linked directly to phosphorus were electroactive at these potentials [$E_{1/2}^R = -2.65$ V [$(NPPh_2)_3$]; $E_{1/2}^R = -2.45$ V [$(NP(Ph)(OCH_2CF_3))_3$]]. (iv) Reduction of an (aryloxy)phosphazene is only possible if the aromatic group itself is independently reducible in the 0 to −3 V potential range. (v) The skeletal degree of polymerization has little influence on the ease of reduction. It was therefore concluded that the phosphazene linkage is not reduced under any circumstances and that the primary site of reduction in substituted derivatives is always the aromatic side group.

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The first electron spin resonance (ESR) study of these compounds led to the detection of the biphenyl radical anion on reduction of $(NPPh_2)_3$ with sodium.[6] A subsequent investigation utilized electrochemical techniques to generate radicals within the ESR cavity, and a number of transient species were observed.[4,5] A singlet ESR spectrum at $g = 2$ was detected on reduction of $(NPPh_2)_3$, but the exact interpretation of this result is not fully resolved. The suggestions[2,7] include (i) unresolvable hyperfine splittings as a result of extensive delocalization of the unpaired spin over the molecule and (ii) line broadening from rapid inter- or intramolecular electron-exchange phenomena. The hyperfine splittings observed for the aryloxy-substituted-phosphazenes led to the conclusion that the unpaired spin density is restricted to the aromatic side group and that no interaction occurs with the phosphorus atoms or the phosphazene ring.[2,4,5]

Exposure of various cyclic phosphazenes [$(NPX_2)_{3or4}$, X = Cl or Br] to γ-rays at 77 K in the solid state was reported to give rise to paramagnetic centers whose ESR spectra were characteristic of phosphoranyl radicals.[7] It was concluded that these centers had been formed by electron attachment to a single phosphorus atom followed by a bending distortion which moved the two X ligands into axial positions, leaving the extra electron in a localized equatorial σ orbital. Insofar as we are aware, this solid-state study constitutes the only work in which an ESR hyperfine splitting by a phosphazene nucleus has been reported.

Although the previous work on the reductive chemistry and ESR spectroscopy of the phosphazenes was not particularly encouraging, and while an enormous number of substituted phosphazenes have been prepared and studied, an analysis of the bonding shows that the currently known substitution patterns are unlikely to perturb the electronic structure at phosphorus in a manner which will allow extended delocalization in these systems. In order to bring about this latter circumstance, substituents must actively engage in

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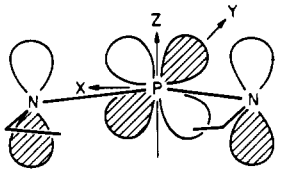

Figure 1. Atomic orbital basis functions [P(d_{xz}), N(p_z)] for phosphazene π-bonding in model 1 (M1, see text).

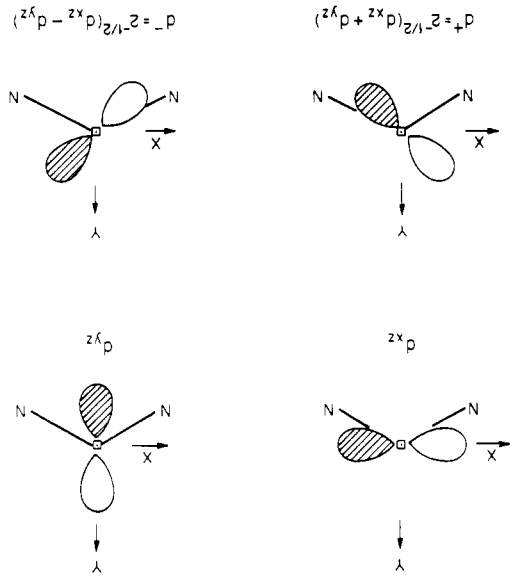

Figure 2. Projection in the X, Y plane of the phosphorus d orbitals utilized in model 2 (M2, see text) for phosphazene π-bonding ([·] = P).

conjugation with the phosphorus atom. In the present paper, we present a theoretical model for phosphazene p_π–d_π spirodelocalization, its synthetic and structural realization, and evidence for the injection of electron spin density into the cyclotriphosphazene ring system.

Theoretical Model. The nature of the bonding and the degree of delocalization in the phosphazenes has been controversial for more than 25 years.[1-3] The early, qualitative theories[8-11] of the electronic structure of cyclophosphazenes provided great impetus to research in the area. It is generally agreed that the out-of-plane π system provides the key to delocalization in the phosphazenes. In the initial (heteromorphic) model (M1)[8] of phosphazene π-bonding, this involves, a p_z function on nitrogen and a d_{xz} function on phosphorus (Figure 1). In the second model (M2)[9] of phosphazene π-bonding, an extra basis function on phosphorus (d_{yz}) is also considered (Figure 2).

Nevertheless, quite apart from the rivalry between these two models of phosphazene π-bonding, the degree of phosphorus d-orbital participation in these compounds has been repeatedly questioned.[1-3,11] Recent high-level theoretical calculations have directly addressed this question,[12,13] and from a structural point of view, it appears that phosphorus d orbitals are significant participants in the ring bonds.[13] It is of great interest to ascertain the extent to which the early, qualitative theories of the electronic structure of the phosphazenes are verified by detailed nonempirical molecular orbital(MO) calculations. This point is taken up in

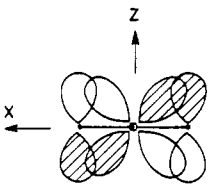

Figure 3. Projection (X, Z plane) of the overlap between substituent FMO and phosphorus d_π orbital(s) for the occurrence of p_π–d_π spirodelocalization. Note that the phosphorus d_π orbital may constitute a d_{xz} orbital alone (M1) or the d^+, d^- pair (M2) ([·] = P).

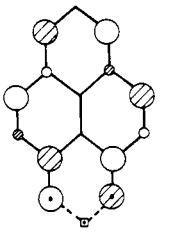

Figure 4. Lowest unoccupied molecular orbital of the 1,9-bis(methylamino)phenalenylium unit (which becomes the FMO on addition of an electron). (⊡ = P).

detail elsewhere,[13] but for the moment we note that in orbitals near the highest-occupied (HO) MO–lowest-unoccupied (LU) MO gap, the d_{xz} and d_{yz} orbitals are often important contributors and that the d_{yz} orbital sometimes occurs in the wave functions alone [delocalized model (M1)] and sometimes in combination with the d_{yz} orbital [localized (island) model (M2)].

We therefore sought a substitutional mode which would provide a frontier (F) MO with the capability of interacting with the d_{xz} orbital alone (M1)[8,9] but which also provided a mechanism to bridge the orthogonal islands resulting from the linear combinations of the pair of $d\pi$ orbitals: $d^+ = 2^{-1/2}(d_{xy} + d_{yz})$; $d^- = 2^{-1/2}(d_{xy} - d_{yz})$, arising from M2[10] (Figure 2). It should be noted that symmetry considerations preclude the involvement of phosphorus s and p functions in this interaction.

In order to achieve good orbital overlap between the substituent and phosphorus atom, the rigidity of a spirojunction seemed desirable, and together the above requirements dictate a substituent with FMO of a_2 symmetry (C_{2v} point group). The optimum substituent FMO phosphazene orbital overlap situation for p_π–d_π spirodelocalization is shown diagrammatically in Figure 3.

Calculations suggest that the 1,9-disubstituted-phenalenyl system possesses just such an FMO (Figure 4), and recent studies[14] of reduced beryllium and boron bis(1,9-oxidophenalenone) complexes (which show evidence of spiroconjugation) support this idea.

Results

Preparation and Chemical Properties of Phenalene–Phosphazene Complexes. All attempts to functionalize the phosphazene ring system with 1,9-disubstituted-phenalene derivatives possessing a single ionizable hydrogen atom (such as **1** and **2**) were unsuccessful. Even nucleophiles such as the recently reported tetrabutylammonium 9-oxidophenalenone[15] did not lead to isolable phenalene–phosphazene complexes. In this regard, the preparation of 1,9-disubstituted-phenalenes bearing a total of just two ionizable hydrogen atoms (**3** and **4**)[16] was an important precursor to the present investigation.

The reactions of **3** and **4** with hexachlorocyclotriphosphazene are not as facile as those of most primary amines, but with the correct selection of reaction conditions, quite respectable yields of the monosubstitution products **5** and **6** are obtained. Of the two compounds, **5** formed the most readily. The tetrachlorcyclotriphosphazenes **5** and **6** did not prove to be electrochemically well-behaved, and although the compounds underwent reduction these processes were not reversible (presumably as a result of

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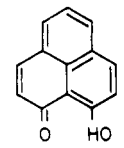

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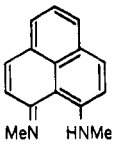

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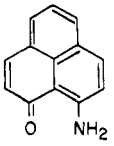

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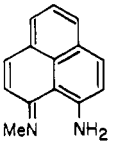

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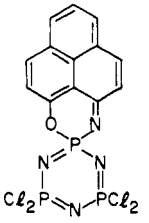

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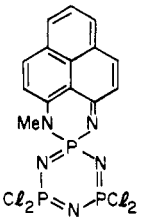
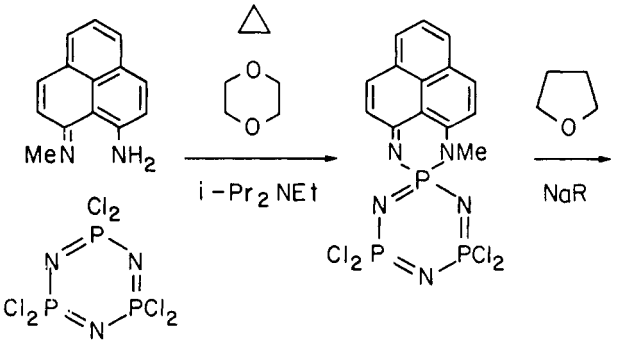


6

chloride ionization).[4,5] Replacement of the remaining halide in these compounds did not prove to be straightforward, and the interaction of **5** and **6** with sodium trifluoroethoxide lead to different structural moieties (**7** and **8**, respectively). Attempts to stoichiometrically replace the remaining four chlorines in **5** without disruption of the phosphorus–oxygen bond did not succeed. Apart from some mixed chlorotrifluoroethoxy derivatives, **7** was the only compound isolated from this reaction.

Fortunately, **8** proved to be stable to the presence of excess sodium trifluoroethoxide and was readily obtained from **6** under mild conditions (reaction scheme). The compound is stable, shows



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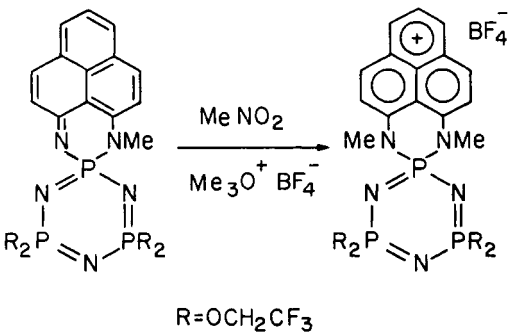


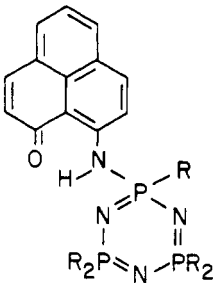
8 9⁺

good solubility properties, and undergoes a pronounced phase transition at about 140–150 °C.

Table I. P^{31} NMR Parameters for AB_2 Spectra of Phenalene–Phosphazene Complexes

compd	substitution A 1	substitution A 1	substitution B 3,3,5,5	δ_A, ppm	δ_B, ppm	J_{AB}, Hz
5	N	O	Cl	2.94	19.76	48.8
6	N	NMe	Cl	0.39	16.98	38.6
7	NH	OCH_2CF_3	OCH_2CF_3	13.58	16.10	80.2
8	N	NMe	OCH_2CF_3	8.01	12.69	64.7
9⁺	NMe	NMe	OCH_2CF_3	11.07	12.87	76.9

During our efforts to alkylate **8**, we obtained a protonated tetrafluoroborate salt. Although this compound was never isolated in pure form, NMR spectroscopy showed that protonation had occurred on the imino nitrogen of the phenalene, rather than within the phosphazene ring system. Methylation of compound **8** was



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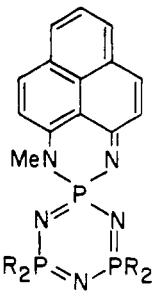
R = OCH_2CF_3



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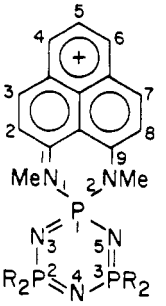
R = OCH_2CF_3



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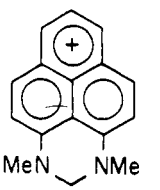
R = OCH_2CF_3



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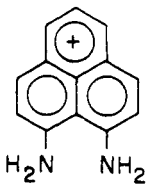

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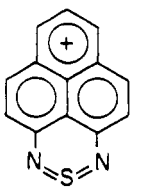

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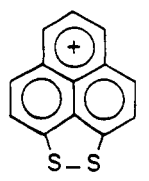

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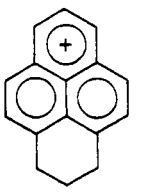

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best carried out in a drybox, although the product (**9⁺**) proved to be quite stable. Thus, we find that both protonation and alkylation occur at the exocyclic nitrogen of **8**. In many other amino-substituted-cyclotriphosphazenes, alkylation but not protonation has been found to occur at the exocyclic amino

groups,[2,3,18-20] Protonation usually occurs at a cyclotriphosphazene imino-nitrogen atom, and the fact that we observe exocyclic protonation in **8** can be ascribed to the properties of the phenalenyl nucleus.

Some of the P^{31} NMR parameters of the phenalene–phosphazene complexes are summarized in Table I. It may be seen that replacement of chlorine by trifluoroethoxy tends to equalize the phosphorus chemical shifts and also leads to an increase in the ring coupling constants. This trend is continued on methylation of **8** to give $\mathbf{9}^+$. The apparent phosphorus–methyl coupling constant also increases on passing from **8** to $\mathbf{9}^+$ (7.0 and 9.9 Hz, respectively).

Compound[21] $\mathbf{10}^+,BF_4^-$ which possesses a methylene group in place of the phosphazene ring system in $\mathbf{9}^+$ was synthesized for comparison purposes. The appearance of the two compounds is strikingly different, and this is reflected in their electronic spectra (Figure 5). If the long-wavelength band in $\mathbf{10}^+$ is interpreted as a nitrogen-to-ring charge transfer type absorption, then it is apparent that the lone pair electrons on the nitrogen of $\mathbf{9}^+$ are far less available—presumably as a result of conjugation with the cyclotriphosphazene ring system. The idea that the cyclotriphosphazene ring system withdraws electron density from the 1,9-bis(methylamino)phenalenylium unit is also supported by the proton chemical shifts: δ_{NMe} 3.28, 3.72; δ_2 7.24, 7.90; δ_3 8.28, 8.83; δ_4 8.16, 8.67; δ_5 7.64, 8.09, observed for $\mathbf{10}^+$ and $\mathbf{9}^+$, respectively.

Electrochemistry. The cyclic voltammagrams (CVs) of compounds **8**–$\mathbf{10}^+$ are compared in Figure 6, and the reduction potentials are summarized in Table II. The neutral **8** undergoes a single reduction step whereas the cationic systems $\mathbf{9}^+$ and $\mathbf{10}^+$ both exhibit two reduction waves in the range 0 → −2 V, all of which appear to be reversible one-electron processes. This latter conclusion is supported by both the ESR spectroscopy (below) and the electrochemical peak separations (Table II). Compounds **8** and $\mathbf{9}^+$ both show irregularites in their CVs in the range −0.9 V to the onset of the next reduction wave. This phenomenon is reversible (there is no dimunition of the return wave at −0.3 V in $\mathbf{9}^+$) and is tentatively assigned to an adsorption–desorption process. It seems that this behavior is brought about by the tetrakis(trifluoroethoxy)cyclotriphosphazene segment of the molecules, as the CV of $\mathbf{10}^+$ is free of this process.

Electron Spin Resonance Spectroscopy. Electrochemical reduction of compounds **8** and $\mathbf{9}^+$ gave rise to ESR spectra at potentials close to the occurrence of the first reduction waves (Table II). As might be expected, the spectra proved to be extremely complicated. Apart from the trifluoroethoxy groups, the remaining nuclei in **9** could theoretically give rise to a spectrum of 170 100 lines. However, the accidental degeneracy in the spectrum allowed the (approximate) assignment given in Table III.

The ESR spectrum of **9** consists of a 21 line multiplet superimposed on the large 4 hydrogen (H_3, H_4, H_6, and H_7) splitting which is characteristic of the phenalenyl ring system (Table III). Of primary importance is the observation that the intensities within the multiplet follow a monotonic progression; it follows that no splitting in this multiplet may be more than twice the magnitude of any other (in order to preserve the symmetry of the line shape). Thus, a large number of nuclei are involved in the generation of this multiplet. Many possibilities were examined by computer simulation and not all of them could be rigorously eliminated. The parameters given in Table III are consistent with the hyperfine splitting constants of the model compounds and correspond to the optimum simulation of the experimental spectrum. The involvement of one phosphorus and two nitrogen atoms of the cyclotriphosphazene ring is definite, and the participation of additional nuclei remains a distinct possibility. Further unresolved cyclotriphosphazene splittings are probably responsible for the broad line width of the spectrum (0.37 g). The ESR spectrum of compound $\mathbf{8}^-$ has so far defied analysis.

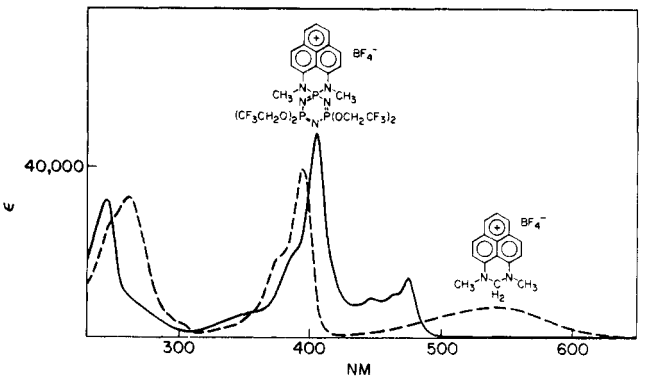

Figure 5. Electronic spectra of $\mathbf{9}^+$ and $\mathbf{10}^+$ in acetonitrile solution.

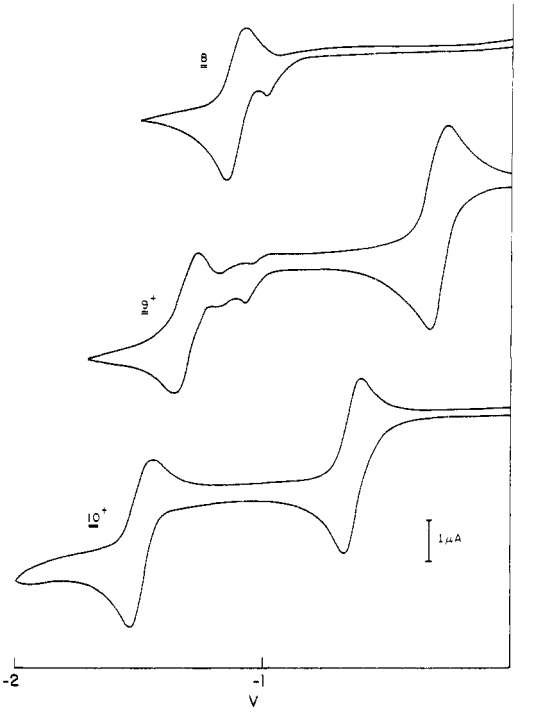

Figure 6. Cyclic voltammagrams of **8**, $\mathbf{9}^+,BF_4^-$, and $\mathbf{10}^+,BF_4^-$ in acetonitrile solution obtained with a platinum bead working electrode.

Table II. Reduction Potentials (V)

	E_1	E_2	E_3	ref
8	−1.13			*a*, *e*
$\mathbf{9}^+$	−0.30	−1.34		*b*, *e*
$\mathbf{10}^+$	−0.65	−1.52		*c*, *e*
$\mathbf{13}^+$	−0.22	−0.77	−1.55	*d*

[a] The peak potentials (V) were as follows: E_{plc} = −1.17, E_{pla} = −1.10. [b] E_{plc} = −0.34, E_{pla} = −0.27; E_{p2c} = −1.38, E_{p2a} = −1.30. [c] E_{plc} = −0.69, E_{pla} = −0.62; E_{p2c} = −1.56, E_{p2a} = −1.47. The literature values[21] apparently refer to the SHE electrode [d] Reference 27: E_{plc} = −0.25, E_{pla} = −0.19; E_{p2c} = −0.81, E_{p2a} = −0.74; E_{p3c} = −1.63, E_{p3a} = −1.48. [e] Under the conditions of our experiment, tetracyanoquinodimethane (TCNQ) showed ΔE_{p1} = 0.07, ΔE_{p2} = 0.08.

Discussion

X-ray Crystal Structure of $\mathbf{9}^+,BPh_4^-$. The crystallographic findings are summarized in Figure 7 and Tables IV and V. This appears to be the first structural characterization of an exocyclically alkylated phosphazene ring system. Although there are few precedents, the gross features found for the cation are unremarkable, and the phosphazene ring bond lengths are fairly typical for the type of substitutents employed. There is virtually

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Table III. Electron Spin Resonance Parameters for 1,9-Disubstituted-Phenalenyl Radicals

position/ nucleus	hyperfine split const, G					
	14	**13**	**12**	**11**	**10**	**9**
2,8	1.75	1.49	1.49	1.62	1.3	1.275
5	1.75	1.49	1.49	1.62	1.3	1.275
3,7 }	6.09	5.06	5.45	5.52	5.8	5.826
4,6 }	6.09	5.45	7.14	7.14	5.8	6.905
Me					1.3	1.275
N			1.49	1.62	1.3	1.275
P						1.275
N						2.55
g val	2.0027	2.0042		2.0026	2.0025	2.0025
ref	28	27	29	29	*a*	*a*

[a] Approximate analysis based on optimum simulation of experimental spectrum.

Table IV. Bond Lengths Involving Selected Atoms in Crystalline $9^+,BPh_4^-$

type	length,[a] Å	type	length,[a] Å
P_1–N_1	1.671 (3)	P_1–N_3	1.580 (3)
P_1–N_2	1.667 (3)	P_1–N_5	1.575 (4)
P_2–N_3	1.585 (3)	P_3–N_5	1.582 (3)
P_2–N_4	1.567 (4)	P_3–N_4	1.568 (4)
P_2–O_1	1.578 (2)	P_3–O_3	1.570 (5)
P_2–O_2	1.564 (4)	P_3–O_4	1.570 (3)
N_1–C_{10}	1.483 (4)	N_2–C_{11}	1.484 (6)
N_1–C_1	1.365 (5)	N_2–C_9	1.367 (5)
C_1–C_2	1.421 (6)	C_5–C_6	1.375 (9)
C_1–C_{9a}	1.413 (5)	C_6–C_{6a}	1.395 (7)
C_2–C_3	1.350 (6)	C_{6a}–C_7	1.396 (7)
C_3–C_{3a}	1.409 (6)	C_{6a}–C_{9b}	1.413 (5)
C_{3a}–C_4	1.395 (6)	C_7–C_8	1.362 (7)
C_{3a}–C_{9b}	1.397 (6)	C_8–C_9	1.417 (5)
C_4–C_5	1.376 (7)	C_9–C_{9a}	1.417 (6)
		C_{9a}–C_{9b}	1.430 (6)
O_1–C_{12}	1.404 (5)	O_3–C_{16}	1.468 (10)
O_2–C_{14}	1.405 (8)	O_4–C_{18}	1.423 (7)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.

no evidence of the P–N bond length alternation found in other heterogeneously substituted cyclotriphosphazene derivatives.[19] This may be a reflection of the fact that some degree of convergence of the effective electronegativities of the ring substitutents occurs on alkylation of **8** to product 9^+. This point is supported by the P^{31} chemical shifts (Table I) which show a much smaller spread in 9^+ than in **8**. Likewise the phenalene unit shows bond lengths which are fairly typical of a positively polarized phenalenyl system.[14,15,23] The cyclotriphosphazene ring and the 1,9-diaminophenalenylium unit each attain a high degree of planarity in crystalline $9^+,BPh_4^-$. However, the N_1–P_2–N_2 segment lies 26.3° out of the best molecular plane for the 1,9-diaminophenalenylium unit, presumably to accommodate a somewhat smaller N_1–P_1–N_2 angle (which is found to be 99.8°), than would be possible in C_{2v} sysmmetry. Such a deformation is expected to exert a minor effect on the π-orbital overlap within this segment of the molecule. This will be particularly true for the P_1–N_1 and P_1–N_2 p_π–d_π overlap because the d orbitals are only weakly oriented by the field of the ligands[24] and are able to maintain conjugation in nonplanar conformations.[25] The point may be quantified for the p_π orbitals in the C_1–N_1 and C_9–N_2 bonds by use of the π-orbital axis vector (POAV1) analysis.[26] From the atomic coordinates in 9^+, it follows

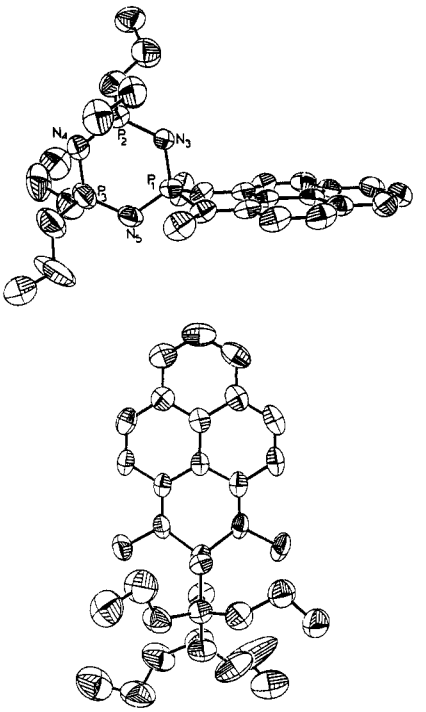

Figure 7. ORTEP diagram of 9^+. Hydrogen and fluorine atoms are omitted for clarity.

Table V. Bond Angles Involving Selected Atoms in Crystalline $9^+,BPh_4^-$

type	angle,[a] Å	type	angle,[a] Å
$N_1P_1N_2$	99.8 (1)	$N_2P_1N_3$	109.8 (1)
$N_1P_1N_3$	110.4 (2)	$N_2P_1N_5$	109.5 (2)
$N_1P_1N_5$	109.6 (2)	$N_3P_1N_5$	116.5 (2)
$N_3P_2N_4$	117.3 (2)	$N_5P_3N_4$	119.2 (2)
$N_3P_2O_1$	108.9 (1)	$N_5P_3O_3$	110.1 (2)
$N_3P_2O_2$	111.4 (2)	$N_5P_3O_4$	104.1 (2)
$N_4P_2O_1$	112.2 (2)	$N_4P_3O_3$	105.6 (2)
$N_4P_2O_2$	105.7 (2)	$N_4P_3O_4$	112.1 (2)
$O_1P_2O_2$	99.9 (2)	$O_3P_3O_4$	104.9 (2)
$P_1N_1C_1$	123.1 (2)	$P_1N_2C_9$	124.0 (3)
$P_1N_1C_{10}$	115.5 (3)	$P_1N_2C_{11}$	114.8 (3)
$C_1N_1C_{10}$	119.7 (3)	$C_9N_2C_{11}$	119.4 (3)
$P_1N_3P_2$	123.5 (2)	$P_1N_5P_3$	121.6 (2)
$P_2N_4P_3$	121.1 (2)		
$P_2O_1C_{12}$	124.6 (2)	$P_3O_3C_{16}$	121.4 (4)
$P_2O_2C_{14}$	120.9 (3)	$P_3O_4C_{18}$	123.0 (3)
$N_1C_1C_2$	119.9 (3)	$N_2C_9C_8$	120.8 (4)
$N_1C_1C_{9a}$	121.1 (3)	$N_2C_9C_{9a}$	120.3 (3)
$C_2C_1C_{9a}$	119.0 (3)	$C_8C_9C_{9a}$	118.9 (4)
$C_1C_2C_3$	120.6 (3)	$C_7C_8C_9$	120.8 (4)
$C_2C_3C_{3a}$	122.5 (4)	$C_{6a}C_7C_8$	122.5 (4)
$C_3C_{3a}C_4$	121.8 (4)	$C_6C_{6a}C_7$	122.0 (4)
$C_3C_{3a}C_{9b}$	118.2 (4)	$C_7C_{6a}C_{9b}$	118.1 (4)
$C_4C_{3a}C_{9b}$	120.0 (4)	$C_6C_{6a}C_{9b}$	119.9 (4)
$C_{3a}C_4C_5$	120.9 (5)	$C_5C_6C_{6a}$	120.6 (4)
$C_4C_5C_6$	120.0 (5)		
$C_1C_{9a}C_9$	121.9 (3)	$C_{3a}C_{9b}C_{6a}$	118.6 (4)
$C_1C_{9a}C_{9b}$	119.0 (3)	$C_{3a}C_{9b}C_{9a}$	120.8 (3)
$C_{9b}C_{9a}C_9$	119.0 (3)	$C_{6a}C_{9b}C_{9a}$	120.6 (4)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.

that the σ bonds around N_1 and N_2 make an (average) angle of 4.5° to the plane normal to the POAV (by adopting $s^{0.012}p$ hybridization). As a result, the p_π-orbital misalignment across the C–N bond is reduced to a value of 10.6° (which may be compared with the formal value of 18.4° calculated from the peripheral dihedral angles).

Electrochemistry and Electron Spin Resonance Spectroscopy. As previously noted in connection with the electronic and NMR spectra of 9^+ and 10^+, the tetrakis(trifluoroethoxy)cyclotriphosphazene system appears to act as an electron acceptor, even

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toward the cationic 1,9-bis(methylamino)phenalenylium unit. This point is further substantiated by the reduction potentials of the two compounds, and it may be seen from Table II that the first electron may be added to 9^+ with an ease approaching that of the highly electroactive 13^+.[27] These observations indicate that in the reduced (neutral) compound **9**, the FMO of the 1,9-bis(methylamino)phenalenyl unit will be polarized to inject electrons (rather than holes) into the cyclotriphosphazene ring system. Of course, this argument assumes that the primary site of reduction is the phenalenylium unit rather than the cyclotriphospazene ring itself. Support for this point of view comes from previous studies[2,4,5] which found that $[NP(OCH_2CF_3)_2]_3$ could not be reduced in the potential range $0 \rightarrow -3$ V. Furthermore, the ESR parameters found for **9** are quite similar to those reported for other 1,9-disubstituted-phenalenyl radicals[27-29] (Table III). The results obtained for **9** make it quite clear that for the first time, electron spin density has been injected into a segment of a phosphazene linkage. At least half of the cyclotriphosphazene ring nuclei are ESR-active.

Finally we note that while the presence of electron spin density in the cyclotriphosphazene ring system seems unequivocal, the mechanism offered at the beginning of this paper (Theoretical Model) is supported (but not proved) by the present findings.

Experimental Section

4′,4′,6′,6′-Tetrachloro-4′,4′,6′,6′-tetrahydrospiro[2*H*-phenaleno[1,9-*de*]-1,3,2-oxazaphosphorine-2,2′-[1,3,5,2,4,6]triazatriphosphorine] (5). A solution of 9-aminophenalenone[16] (**3**, 0.5 g, 2.6 mmol), hexachlorocyclotriphosphazene (1.1 g, 3.2 mmol), and triethylamine (1.5 mL, 11 mmol) in dry dichloromethane (25 mL) was refluxed overnight. The reaction mixture was cooled and the solids separated by filtration (0.83 g). The filtrate was chromatographed on a silica gel column using toluene/dichloromethane as the eluant to give a (combined) crude yield of 1.19 g. Recrystallization from chlorobenzene (25 mL) gave rise to 0.86 g (72%) of chunky brown-yellow crystals, mp 298 °C. Anal. Calcd for $C_{13}H_7N_4OP_3Cl_4$: C, 33.22; H, 1.50; N, 11.92; P; 19.77; Cl, 30.18. Found: C, 32.93; H, 1.54; N, 11.86; P, 19.60; Cl, 30.16. IR (CsI) 1629 cm^{-1} (m), 1584 (s), 1521 (s), 1437 (vw), 1380 (m), 1220 (vvs, vbr), 1007 (s), 967 (s), 915 (m), 871 (w), 840 (m), 830 (m), 759 (w), 750 (w), 690 (m), 580 (vs), 550 (vs), 520 (vs), 480 (w), 425 (m); UV (CH_2Cl_2) λ_{max} 242 (ϵ 23 000), 264 (16 000), 272 (15 000), 354 (12 000), 369 (19 000), 406 (9200), 427 (12 000), 450 (8200); ^{1}H NMR ($CDCl_3$, 50 °C, Me_4Si) δ 7.0–8.4; ^{31}P NMR ($CDCl_3$, 50 °C, ext H_3PO_4) (AB_2) δ_A 2.94, δ_B 19.76 (J_{AB} = 48.8 Hz).

4′,4′,6′,6′-Tetrachloro-4′,4′,6′,6′-tetrahydro-1-methylspiro[phenaleno-[1,9-*de*]-1,3,2-diazaphosphorine-2(1*H*),2′-[1,3,5,2,4,6]triazatriphosphorine] (6). A solution of 9-(methylamino)phenalenimine[16] (**4**, 1.04 g, 0.005 mol), hexachlorocyclotriphosphazene (2.09 g, 0.006 mol), and diisopropylethylamine (3.5 mL, 0.02 mol) in dry dioxane (40 mL) was refluxed overnight and then the solvent was removed under a stream of nitrogen. The dark residue was extracted with boiling toluene (100 mL) which on cooling deposited 2.94 g of discolored yellow needles. Recrystallization (charcoal) from a further 100 mL of toluene gave rise to yellow needles (1.59 g, 66%): mp 275–276 °C; exact mass, *m/e* calcd for $C_{14}H_{10}P_3N_5{}^{35}Cl_4$ 480.889 772, found 480.882 775, *m/e* calcd for $C_{14}H_{10}P_3N_5{}^{35}Cl_3{}^{37}Cl_1$ 482.886 822, found 482.884 682; IR (CsI) 1628 cm^{-1} (m), 1584 (s), 1519 (s), 1463 (vw), 1440 (w), 1424 (vw), 1364 (w), 1290 (w), 1220 (vvs, br), 1170 (vvs, br), 1135 (s), 1020 (m), 947 (s), 908 (vw), 846 (m), 833 (s), 821 (m), 757 (w), 732 (m), 713 (w), 692 (w), 661 (vw), 585 (vs), 550 (vs), 510 (vs), 428 (m); UV (CH_2Cl_2) λ_{max} 249 nm (ϵ 37 100), 272 (11 800), 282 (11 000), 357 (17 100), 374 (32 700), 415 (3830), 438 (7160), 464 (8430); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 3.55 (d, br, J' = 8.4 Hz, 3 H), 7.2–8.4 (m, 7 H); ^{31}P NMR ($CDCl_3$, ext H_3PO_4) (AB_2) δ_A 0.39, δ_B 16.98 (J_{AB} = 3.86 Hz).

2-[(9-Oxo-9*H*-phenalen-1-yl)amino]-2,4,4,6,6-pentakis(trifluoroethoxy)-2,2,4,4,6,6-hexahydro-1,3,5,2,4,6-triazatriphosphorine (7). A solution of sodium trifluoroethoxide (19.1 mL, 0.015 mol) in tetrahydrofuran was added dropwise to a solution of **5** (1.17 g, 0.0025 mol) in dry tetrahydrofuran and the mixture allowed to stir overnight. The reaction mixture was filtered to remove sodium chloride and partitioned between water and ether. The ether layer was washed and dried over magnesium sulfate and the solvent removed on a rotary evaporator to give a yellow solid (1.5 g). Recrystallization from heptane (80 mL) gave rise to yellow plates (1.2 g, 65%), mp 126–127 °C. Anal. Calcd for $C_{23}H_{18}N_4O_6P_3F_{15}$: C, 33.51; H, 2.20; N, 6.80; P, 11.27. Found: C, 33.67, H, 2.10; N, 7.07; P, 11.17. IR (CsI) 1632 cm^{-1} (m), 1594 (m), 1490 (w), 1450 (vw), 1440 (vw), 1420 (w), 1350 (vw), 1310 (s, br), 1260 (vs br), 1160 (vs, br), 1070 (vs, br), 1010 (w), 960 (s), 930 (vw), 885 (m), 845 (s), 815 (s), 795 (m), 753 (w), 732 (vw), 705 (w), 650 (w, br), 555 (s), 525 (m), 493 (m), 475 (w), 460 (m), 412 (vw). UV (CH_2Cl_2) 240 nm (ϵ 24 900), 266 (19 600), 274 (23 600), 345 (12 900), 369 (25 300), 402 (6800), 422 (10 400), 446 (9580); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 4.1–4.6 (m, 10 H), 6.8–8.3 (m, 7 H), 13.32 (d, br, J' = 14 Hz, 1 H); ^{31}P NMR ($CDCl_3$, ext H_3PO_4) (AB_2) δ_A 13.58, δ_B 16.10, (J_{AB} = 80.2 Hz).

4′,4′,6′,6′-Tetrakis(trifluoroethoxy)-4′,4′,6′,6′-tetrahydro-1-methylspiro[phenaleno[1,9-*de*]-1,3,2-diazaphosphorine-2(1*H*),2′-[1,3,5,2,4,6]-triazatriphosphorine] (8). A solution of sodium trifluoroethoxide (10.2 mL, 0.008 mol) in tetrahydrofuran was added dropwise to a solution of **6** (0.97 g, 0.002 mol) in dry tetrahydrofuran and the mixture allowed to stir overnight. The reaction mixture was filtered to remove sodium chloride and partitioned between water and ether. The ether layer was washed and dried over magnesium sulfate and the solvent removed on a rotary evaporator to give a yellow solid (1.13 g). Recrystallization from heptane (50 mL) gave rise to yellow needles (1.01 g, 69%), mp 142, 152–157 °C (see text). Anal. Calcd for $C_{22}H_{18}N_5O_4P_3F_{12}$: C, 35.84; H, 2.46; N, 9.50; P, 12.60; F, 30.92. Found: C, 35.79; H, 2.44; N, 9.46; P, 12.66; F, 30.79. IR (CsI) 2960 cm^{-1} (vvw), 1630 (m), 1587 (s), 1524 (s), 1444 (w), 1418 (m), 1285 (vvs, br), 1220 (vvs, br), 1170 (vvs, br), 1075 (vvs, br), 1015 (m), 960 (vs), 860 (s), 833 (vs), 818 (vs), 797 (vs), 692 (w), 656 (m), 610 (m), 558 (vs), 515 (w), 475 (w), 430 (w); UV (CH_2Cl_2) λ_{max} 249 nm (ϵ 36 500), 273 (13 500), 283 (12 400), 355 (17 400), 372 (31 700), 416 (4250), 439 (7800), 465 (8500); ^{1}H NMR (CD_3CN, Me_4Si) δ 3.45 (d, br, J' = 7.0 Hz, 3 H), 4.4–4.6 (m, 8 H), 7.0–8.4 (m, 7 H); ^{31}P NMR ($CDCl_3$, ext H_3PO_4) (AB_2) δ_A 8.01, δ_B 12.69 (J_{AB} = 64.7 Hz).

4′,4′,6′,6′-Tetrakis(trifluoroethoxy)-4′,4′,6′,6′-tetrahydro-1,3-dimethylspiro[phenaleno[1,9-*de*]-1,3,2-diazaphosphorinium-2(1*H*),2′-[1,3,5,2,4,6]triazatriphosphorine] (9^+) Tetrafluoroborate and Tetraphenylborate. Compound **8** (0.59 g, 0.8 mmol) was weighed into a 10-mL fask containing a magnetic stirrer and the reaction vessel transferred to a drybox. Trimethyloxonium tetrafluoroborate (0.24 g, 1.6 mmol) was weighted into the flask and 4 mL of dry nitromethane added. The solution was stirred for 15 min and removed from the drybox and the solvent evaporated with a stream of nitrogen. The orange solid residue was twice extracted with boiling 1,2-dichloroethane (30 mL, 30 min). The extracts gave 0.28 and 0.06 g of yellow-orange cubes on cooling (51%), mp 279–281 °C. Anal. Calcd for $C_{23}H_{21}N_5O_4BP_3F_{16}$: C, 32.92; H, 2.52, N, 8.35; B, 1.29; P, 11.07. Found: C, 32.62; H, 2.55; N, 8.06; B, 1.13; P, 11.09. IR (CsI) 1620 cm^{-1} (m), 1590 (w), 1573 (s), 1507 (m), 1480 (vw), 1440 (vw), 1420 (m), 1290 (s, br), 1220 (vs, br), 1170 (vvs, br), 1070 (vvs, br), 957 (s), 885 (w), 840 (m), 825 (m), 796 (s), 690 (vw), 655 (w), 610 (vw), 558 (m), 525 (w); UV (CH_2Cl_2) λ_{max} 244 nm (ϵ 31 900), 406 (47 400), 447 (9500), 464 (10 200), 475 (14 000); ^{1}H NMR (CD_3CN, Me_4Si) δ 3.72 (d, br, J' = 9.9 Hz, 6 H), 4.4–4.7 (m, 8 H), (AB) δ_A 7.90, δ_B 8.83 (J_{AB} = 9.5 Hz, 4 H), (AB_2) δ_A 8.09, δ_B 8.67 (J_{AB} = 7.7 Hz, 3 H); ^{31}P NMR (CD_3CN, ext H_3PO_4) (AB_2) δ_A 11.07, δ_B 12.87 (J_{AB} = 76.9 Hz).

The residue from above was boiled with methanol (30 mL), and the mixture cooled, filtered, and treated with a solution of sodium tetraphenylborate in methanol. A brown solid (9^+,BPh_4^-) was isolated by filtration (0.21 g, 24%).

X-ray crystallography: performed by C. S. Day, Crystallytics Co., Lincoln, NE 68501. Slow cooling of a 1,2-dichloroethane solution of 9^+,BF_4^- gave rise to yellow-orange cubes in which the tetrafluoroborate anion was shown to be disordered on preliminary crystallographic examination. Vapor diffusion of hexane into a 1,2-dichloroethane solution of 9^+,BPh_4^- produced red chunky crystals which were suitable for X-ray crystallographic study. The crystal selected for examination had dimensions 0.30 × 0.55 × 0.80 mm (rectangular parallelipiped): M_r 1071.6, triclinic P_1–C_i^1, a = 11.198 (4) Å, b = 21.358 (5) Å, c = 11.613 (5) Å, α = 87.64 (3)°, β = 118.50 (3)°, γ = 100.27 (2)°, V = 2398 (2) Å^3, ρ(calcd) = 1.484 g/cm^3, Z = 2. Scan technique: ω. Direct methods were employed to solve the structure. The number of independent data was 5473. The number of parameters refined was 656. Hydrogen atoms were inserted at calculated positions (apart from the methyl hydrogens which were subjected to independent refinement). R = 0.058. R_w = 0.060. GOF = 2.75. Full details of the structure solution are included in the supplementary material.

Electrochemistry. Cyclic voltammetry was carried out in acetonitrile solution with tetrabutylammonium hexafluorophosphate as the supporting electrolyte using PAR equipment. The cell contained a platinum

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bead as the working electrode and an SCE electrode with a salt bridge as the reference.

Electron Spin Resonance Spectroscopy. The ESR apparatus consisted of a modified x-band Varian spectrometer employing 100-kHz field modulation.[30] ESR signal averaging and the spectral computer simulations were performed on an AT&T PC6300 microcomputer equipped with an 8087 numeric coprocessor.[31] Hyperfine splitting (hfs) constants are given in gauss (G). The radicals were generated by electrochemical or zinc metal reduction of acetonitrile or dimethylsulfoxide solutions of the appropriate parent compound. In all cases, the appearance potential for the ESR signal coincided closely with the first reduction wave observed in the cyclic voltammetry. The experimental and computer-simulated spectra obtained for **9** are included as supplementary material.

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Acknowledgment. We are grateful to W. D. Reents for exact mass measurements and S. H. Glarum for consultations on the ESR spectroscopy.

Registry No. 3, 56496-29-8; **4**, 98304-01-9; **5**, 98304-02-0; **6**, 98330-18-8; **7**, 98330-19-9; **8**, 98304-03-1; $9^+BPh_4^-$, 98304-00-8; $9^+BF_4^-$, 98304-04-2; 10^+, 69461-26-3; 11^+, 98304-05-3; 12^+, 75961-51-2; 13^+, 68377-40-2; 14^+, 98304-06-4; hexachlorocyclotriphosphazene, 940-71-6.

Supplementary Material Available: Experimental and computer simulated spectra of **9** and details of the structure solution of 9^+, BPh_4^- (26 pages). Ordering information given on any current masthead page.

Solvation Effects on the Alkaline Hydrolysis of Some *p*-Nitrophenyl Esters

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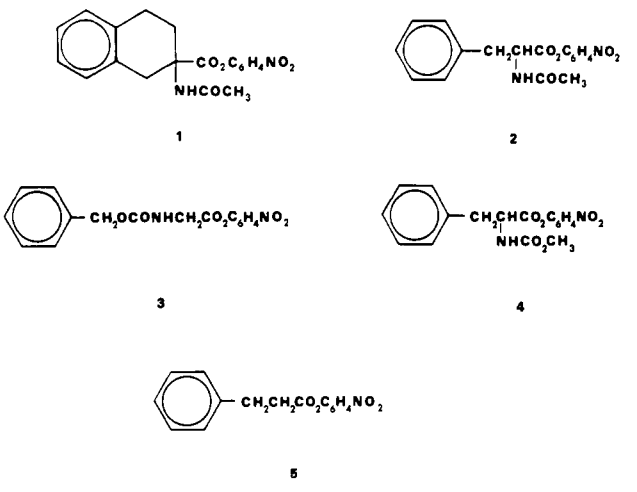
Abstract: The alkaline hydrolyses of six *p*-nitrophenyl esters were investigated. Two of the esters [2-acetamido-1,2,3,4-tetrahydro-2-naphthoate **1** and *N*-acetylphenylalaninate **2**] hydrolyze by a mechanism in which an oxazolinone is formed. The remaining esters [*N*-(benzyloxycarbonyl)glycinate **3**, *N*-(methoxycarbonyl)phenylalaninate **4**, 3-phenylpropanoate **5**, and acetate (NPA)] hydrolyze by a mechanism involving addition of hydroxide ion to the ester carbonyl group. Rather unexpectedly, esters **1–5** form an isokinetic series (estimated isokinetic temperature 87 K). Less unexpectedly, solvation changes upon activation appear to be responsible for the relationship: changes in ΔG^* for the series are linearly correlated with the logarithms of the inverse kinetic H_2O–D_2O solvent isotope effects (KSIEs). Small, nonspecific reorganizations of solvent molecules about similar R-group structures appear to be important in maintaining the regularity of change in ΔG^* and to contribute significantly to the KSIEs. The dissimilarity between the NPA R group and those of the other esters may explain the departure of this ester from the isokinetic relationship. Solvation models generated to rationalize the KSIEs (measured in 50:50 H_2O–D_2O mixtures and in the pure isotopic waters) imply that some specific as well as nonspecific solvent reorganizations accompany heavy-atom reorganization upon activation. Cooperativity among these solvation processes in turn produces the observed isokinetic behavior.

Many excellent studies have focused on the mechanism of alkaline hydrolysis of esters.[1] For ordinary esters with good leaving groups such as *p*-nitrophenoxide, the addition of hydroxide ion to the ester carbonyl group is generally thought to be rate determining, although partial rate limitation by a step preceding the addition and involving desolvation of the reactant hydroxide ion has been proposed.[2] In contrast, hydrolyses of substituted phenyl esters of carboxylic acids containing α-*N*-acylamino functions proceed in discrete steps leading to formation of oxazolinone intermediates (Scheme I). In the formation of 5-phenyloxazolin-2-one from *N*-benzoylglycine *p*-nitrophenyl ester, the only example of the oxazolinone mechanism which has been thoroughly investigated,[3-5] the expulsion of the leaving group from a quasi-tetrahedral intermediate is completely rate-controlling.[5]

Alkaline hydrolysis of esters **1–5** and *p*-nitrophenyl acetate (NPA) includes examples of both kinds of ester acyl group structure. Thus, alkaline hydrolysis of esters **1** and **2**, with α-*N*-acylamino functions, is expected to be dominated by the oxazolinone pathway. The nucleophilic addition mechanism should predominate alkaline hydrolysis of esters **3–5** and NPA.



During the course of studies of the alkaline hydrolysis of esters **1–5** and NPA, we have discovered a limited isokinetic series whose members include representatives of both hydrolytic mechanisms. As a rule, compounds forming an isokinetic series react by identical mechanisms, and even this is often an insufficient condition.[6] It was therefore unanticipated that esters **1–5**, which span 3.8×10^3 times in reactivity and represent at least two distinct hydrolytic

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