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Phenalene–Phosphazene Complexes: Effect of Exocyclic Charge Densities on the Cyclotriphosphazene Ring System

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Received October 27, 1987

The synthesis and properties of a new series of 1,9-diamino-substituted phenalene complexes of the cyclotriphosphazene ring system is described. One of the compounds is shown to be amphoteric, and this behavior allows an examination of the response of the phosphazene linkage to variations in exocyclic charge density at the spiro center in a plane perpendicular to the cyclotriphosphazene ring system. ^{31}P NMR spectroscopy indicates that substituent lone pairs with this orientation are not effective in long-range delocalization within the phosphazene linkage (in accord with our theoretical model of spiro delocalization). An X-ray crystal structure of one compound (7) identifies the presence of clathrated molecules of chloroform together with doubly hydrogen-bonded pairs of the phenalene–phosphazene complexes in the lattice. Crystal data for 7 ($C_{13}H_8Cl_4N_5P_3 \cdot CHCl_3$): monoclinic space group $P2_1/c$, a = 12.401 (4) Å, b = 28.404 (6) Å, c = 12.962 (3) Å, β = 91.76 (2)°, V = 4564 (2) Å^3, Z = 8, R = 0.050 for 4525 reflections.

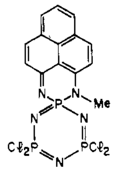
The chemistry of the cyclo- and polyphosphazenes is currently receiving a great deal of attention.[1] While a large number of derivatives have now been synthesized and studied,[2,3] the electronic structure of these compounds is not well understood.[4-7] Although the phosphazenes are conjugated systems, the cyclic compounds do not exhibit aromatic character, and the polyphosphazene backbone does not appear to support charge transport. As a result most polyphosphazenes are insulators.[1-7] Recently it has proved possible to induce electrical conductivity in polyphosphazenes by introduction of substituents that can supply a conducting pathway (outrigger polymers).[3,8-10] Nevertheless, the question of electronic spin and/or charge mobility in the polyphosphazene linkage still presents a daunting challenge and contrasts with the behavior exhibited by other classes of conjugated polymers.

The cyclophosphazenes provide useful model compounds for their polymeric analogues,[2,3] and to this end we have studied the bonding in these compounds.[7] This led to the development of a theoretically based mechanism for injection of π-electron spin density from a spiro substituent into a phosphazene linkage via the phosphorus d orbitals.[12] A phenalene–phosphazene complex based on this theoretical model provided the first evidence for the injection of electron spin density into a segment of a phosphazene linkage.[12]

In this work, we report new phenalene–phosphazene complexes designed to probe the electronic structure of the phosphazene linkage via alteration of the exocyclic charge density at the spiro center in a plane perpendicular to the cyclotriphosphazene ring system.

Results and Discussion

Preparation of Phenalene–Phosphazene Complexes. We have previously reported the synthesis of the monosubstituted phenalene–phosphazene complexes **1** and **2**.[12] Replacement of the remaining halide in these compounds by reaction with sodium trifluoroethoxide gave rise to different modes of substitution, as demonstrated by the isolation of compounds **3** and **4**; the former molecule allowed the preparation of compounds **5**$^+$ and **6**$^+$.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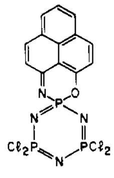
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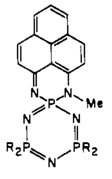
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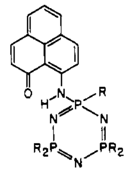
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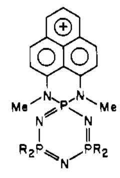
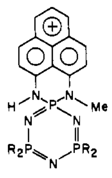
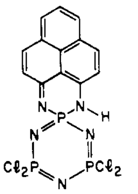

5$^+$


6$^+$

R = OCH$_2$CF$_3$

In the present study we report the synthesis of the analogous compound **7**, which is derived from the interaction of hexachlorocyclotriphosphazene and 9-aminophenalenimine. There is an essential difference between the previously prepared compounds **1** and **2** and the new molecule **7**, and this relates to the presence of an ionizable hydrogen in **7**. It is therefore conceivable that this compound could exist in the isomeric form **8** or **9**.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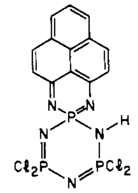
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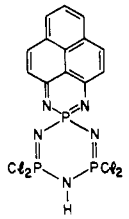
9

Reaction of **7** with sodium trifluoroethoxide leads to the fully substituted compound **10** in which the phosphorus–(exocyclic) nitrogen bonds remain intact. As expected, therefore, the substitutional chemistry of **7** parallels the behavior of **1** rather than **2**. Compound **10** proved to be a stable amphoteric compound, which allowed the generation of salts. The protonated material **11**$^+$ was isolated before spectroscopic examination, whereas the anion **12**$^-$ was generated in situ in an NMR tube without any special precautions, and the solutions appeared to be quite stable to the atmosphere.

X-ray Crystal Structure of 7. The crystallographic results are summarized in Figures 1 and 2 and Tables I–VI. Although the structure is established as that of **7** (rather than **8** or **9**), the compound crystallizes as doubly hydrogen-bonded dimeric pairs

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(1) *ACS Symp. Ser.* **1988**, *No. 360*.

(2) Allcock, H. R. *Phosphorus-Nitrogen Compounds*, Academic: New York, 1972.

(3) Allcock, H. R. *Chem. Eng. News* **1985**, *63*(11), 22.

(4) Craig, D. P.; Paddock, N. L. In *Nonbenzenoid Aromatics*; Snyder, J. P., Ed. Academic: New York, 1971; Vol. 2.

(5) Craig, D. P.; Mitchell, K. A. R. *J. Chem. Soc.* **1965**, 4682.

(6) Salem, L. *Molecular Orbital Theory of Conjugated Systems*; Benjamin: New York, 1966; p 158.

(7) Haddon, R. C. *Chem. Phys. Lett.* **1985**, *120*, 310.

(8) Allcock, H. R.; Neenan, T. X. *Macromolecules* **1986**, *19*, 1495.

(9) Allcock, H. R.; Levin, M. L.; Austin, P. E. *Inorg. Chem.* **1986**, *25*, 2281.

(10) Haddon, R. C.; Stein, S. M.; Chichester-Hicks, S. V.; Marshall, J. H.; Kaplan, M. L.; Hellmann, M. Y. *Mater. Res. Bull.* **1987**, *22*, 117.

(11) Haddon, R. C.; Chichester, S. V.; Bowmer, T. N. *ACS Symp. Ser.* **1988**, *No. 360*, 296.

(12) Haddon, R. C.; Mayo, S. L.; Chichester, S. V.; Marshall, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 7585.

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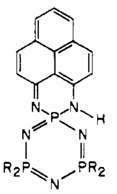

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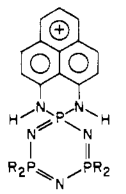
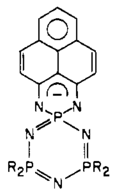


11^{+}



12^{-}

R = OCH$_2$CF$_3$

that involve the hydrogen of the exocyclic amino group (N$_2$), and N$_5$ of the cyclotriphosphazene ring as acceptor atom—perhaps suggesting that structure **8** is not an unreasonable alternative for this compound.

The compound crystallizes as a clathrate with one molecule of chloroform for each molecule of **7**. Clathration has been noted for other cyclotriphosphazene derivatives,[13] but previous reports have involved fully substituted compounds with threefold symmetry. Furthermore the packing exhibited in the unit cell of **7** is quite distinct from that found in the earlier work.[13]

In the case of **5**$^{+}$ a high degree of P–N bond length equalization in the cyclotriphosphazene ring was noted.[12] This does not hold in the structure of **7**, which exhibits a variation in ring bond lengths (Table III) typical of the heterogeneously substituted cyclotriphosphazene ring system. The cyclotriphosphazene rings in the two molecules of **7** in the unit cell are formally related by a twofold rotational axis, but this symmetry is destroyed by the crystal lattice and there are significant structural differences between them (Tables III–V). While the cyclotriphosphazene unit in molecule A is essentially planar, some of the atoms in this ring in molecule B lie outside the mean molecular plane by more that 0.1 Å. In compound **5**$^{+}$ the N$_1$–P$_2$–N$_2$ segment was found to make an angle of 26.3° to the mean molecular plane of the 1,9-diaminophenalene unit. The same distortions also occurs in **7**, but to a lesser extent: 9.2° (molecule A); 17.8° (molecule B).

The crystal structure of **7** is clearly dominated by the hydrogen bonding between pairs of molecules (Figure 2). As judged from the bond lengths (Table VI), it would seem that this is a well-developed interaction. Despite the steric obstacles to close approach between two molecules of **7**, the donor-acceptor pair (N$_2$, N$_5$) still manage to approach the distance characteristic of the nitrogen atoms in a strong N–H···N hydrogen bond (3.0 Å, as found in complementary nucleic acid base pairs),[14] and the hydrogen bonds in crystalline **7** appear to be stronger than those present in other less sterically hindered amino-substituted cyclotriphosphazenes.[15-17] The strength of the hydrogen bond in crystalline **7** is in consonance with the acidity of this proton discussed above.

NMR Spectroscopy. The amphoterism of compound **10** provides a unique opportunity to examine the effect of exocyclic charge density on the cyclotriphosphazene ring system via the ^{31}P NMR parameters.[18-21]

Table I. Refined Fractional Atomic Coordinates in Crystalline C$_{13}$H$_8$Cl$_4$N$_5$P$_3$·CHCl$_3$[a]

atom type[b]	fractional coordinates 10^4x	10^4y	10^4z	B,[c] Å^2 × 10
		Molecule A		
P1	985 (1)	4162 (1)	3031 (1)	30 (1)
P$_2$	2109 (1)	4593 (1)	4676 (1)	37 (1)
P$_3$	2040 (1)	3637 (1)	4590 (1)	35 (1)
Cl$_1$	3458 (1)	4973 (1)	4581 (2)	66 (1)
Cl$_2$	1322 (1)	4952 (1)	5731 (1)	63 (1)
Cl$_3$	1316 (2)	3231 (1)	5606 (1)	63 (1)
Cl$_4$	3317 (1)	3237 (1)	4307 (1)	61 (1)
N$_1$	−310 (3)	4217 (2)	2875 (3)	33 (1)
N$_2$	1438 (3)	4140 (1)	1840 (3)	29 (1)
N$_3$	1486 (3)	4613 (1)	3624 (3)	34 (1)
N$_4$	2456 (4)	4099 (2)	5141 (4)	47 (1)
N$_5$	1316 (3)	3675 (1)	3586 (3)	34 (1)
C$_1$	−788 (4)	4314 (2)	1969 (4)	30 (1)
C$_2$	−1930 (4)	4402 (2)	1958 (4)	39 (2)
C$_3$	−2471 (4)	4508 (2)	1078 (5)	43 (2)
C$_{3a}$	−1974 (4)	4522 (2)	102 (4)	38 (2)
C$_4$	−2528 (5)	4623 (2)	−820 (5)	51 (2)
C$_5$	−2019 (6)	4628 (2)	−1742 (5)	56 (2)
C$_6$	−939 (5)	4536 (2)	−1789 (4)	51 (2)
C$_{6a}$	−341 (5)	4430 (2)	−876 (4)	38 (2)
C$_7$	786 (5)	4326 (2)	−882 (4)	43 (2)
C$_8$	1360 (4)	4231 (2)	2 (4)	36 (2)
C$_9$	852 (4)	4235 (2)	957 (4)	28 (1)
C$_{9a}$	−254 (4)	4330 (2)	1004 (4)	26 (1)
C$_{9b}$	−852 (4)	4427 (2)	79 (4)	31 (1)
H$_{N2}$	2105 (31)	4061 (14)	1785 (32)	33 (10)[d]
		Molecule B		
P$_1$	2821 (1)	3018 (1)	1155 (1)	33 (1)
P$_2$	4853 (1)	2723 (1)	1855 (1)	43 (1)
P$_3$	4507 (1)	3655 (1)	1491 (1)	37 (1)
Cl$_1$	5193 (2)	2489 (1)	3271 (1)	73 (1)
Cl$_2$	5799 (1)	2312 (1)	1026 (2)	65 (1)
Cl$_3$	5036 (1)	3976 (1)	235 (1)	69 (1)
Cl$_4$	4675 (1)	4167 (1)	2532 (1)	64 (1)
N$_1$	2485 (3)	2950 (1)	−46 (3)	35 (1)
N$_2$	1678 (4)	2967 (2)	1776 (4)	35 (1)
N$_3$	3650 (3)	2625 (1)	1568 (4)	43 (1)
N$_4$	5309 (3)	3244 (2)	1770 (4)	48 (1)
N$_5$	3273 (3)	3546 (1)	1349 (3)	34 (1)
C$_1$	1475 (4)	2984 (2)	−394 (4)	34 (2)
C$_2$	1267 (5)	2976 (2)	−1493 (4)	44 (2)
C$_3$	270 (5)	3041 (2)	−1892 (5)	50 (2)
C$_{3a}$	−644 (5)	3114 (2)	−1277 (5)	42 (2)
C$_4$	−1686 (5)	3199 (2)	−1691 (5)	57 (2)
C$_5$	−2546 (5)	3264 (2)	−1059 (7)	61 (2)
C$_6$	−2413 (5)	3244 (2)	−16 (6)	51 (2)
C$_{6a}$	−1392 (4)	3157 (2)	445 (5)	37 (2)
C$_7$	−1228 (4)	3122 (2)	1517 (5)	41 (2)
C$_8$	−232 (4)	3054 (2)	1945 (4)	37 (2)
C$_9$	668 (4)	3020 (2)	1319 (4)	30 (1)
C$_{9a}$	548 (4)	3036 (2)	255 (4)	28 (1)
C$_{9b}$	−492 (4)	3103 (2)	−200 (4)	31 (1)
H$_{N2}$	1806 (36)	2968 (16)	2337 (32)	23 (12)[d]
		Solvent Molecule 1		
Cl$_{s1}$	−1553 (2)	3884 (1)	5796 (2)	101 (1)
Cl$_{s2}$	−3111 (2)	3712 (1)	4192 (2)	108 (1)
Cl$_{s3}$	−1511 (2)	3019 (1)	4696 (2)	94 (1)
C$_{s1}$	−1790 (5)	3620 (2)	4616 (5)	58 (2)
		Solvent Molecule 2		
Cl$_{s4}$	6404 (2)	6338 (1)	2182 (2)	138 (1)
Cl$_{s5}$	4525 (2)	6013 (1)	3019 (3)	157 (2)
Cl$_{s6}$	5974 (4)	5376 (1)	2330 (3)	178 (2)
C$_{s2}$	5848 (5)	5905 (2)	2906 (5)	66 (2)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1. [c] Equivalent isotropic thermal parameter, which is one-third of the trace of the orthogonalized $\mathbf{B}_{ij}$ tensor. [d] This is the actual value of the refined isotropic thermal parameter.

In a previous publication on phenalene–phosphazene complexes, we developed an orbital model for conjugation between a spiro substituent and the out-of-plane (heteromorphic) π-system of the phosphazene linkage (of **5**$^{+}$).[12] It was shown that the lowest unoccupied molecular orbital of the 1,9-disubstituted phenalenyl

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(13) Allcock, H. R. *Acc. Chem. Res.* **1978**, *11*, 81.

(14) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: New York, 1984; p 66.

(15) Begley, M. J.; Sowerby, D. B.; Bamgboye, T. T. *J. Chem. Soc., Dalton Trans.* **1979**, 1401.

(16) Fincham, J. K.; Hursthouse, M. B.; Parkes, H. G.; Shaw, L. S.; Shaw, R. A. *Acta Crystallogr., Sect. B: Struct. Sci.* **1986**, *B42*, 462.

(17) Shaw, R. A. *Phosphorus Sulfur* **1986**, *28*, 99.

(18) *Phosphorus-31 NMR*; Gorenstein, D. G., Ed.; Academic: New York, 1984.

(19) *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G.; Quin, L. D., Ed.; VCH: Deerfield Beach, FL, 1987.

(20) Recent work by Pomerantz and co-workers[21] has shown that ^{31}P chemical shifts in monophosphazenes are sensitive to variations in electron density.

(21) (a) Pomerantz, M.; Ziemnicka, B. T.; Merchant, Z. M.; Chou, W.-N.; Perkins, W. B.; Bittner, S. *J. Org. Chem.* **1985**, *50*, 1757. (b) Pomerantz, M.; Marynick, D. S.; Rajeshwar, K.; Chou, W.-N.; Throckmorton, L.; Tsai, E. W.; Chen. P. C. Y.; Cain, T. *J. Org. Chem.* **1986**, *51*, 1223.

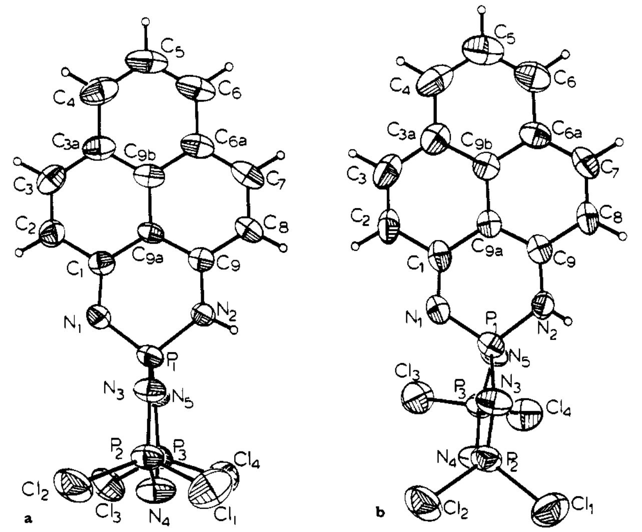

Figure 1. Perspective ORTEP drawings of the two crystallographically independent molecules of $C_{13}H_8Cl_4N_5P_3$ present in crystalline $C_{13}H_8Cl_4N_5P_3{\cdot}CHCl_3$: (a) molecule A; (b) molecule B. Non-hydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density; hydrogen atoms are represented by arbitrarily small spheres that are in no way representative of their true thermal motion.

Table II. Calculated Fractional Atomic Coordinates for Hydrogen Atoms in Crystalline $C_{13}H_8Cl_4N_5P_3{\cdot}CHCl_3$[a]

atom type[b]	fractional coordinates		
	10^4x	10^4y	10^4z
	Molecule A		
H_2	−2310	4386	2591
H_3	−3228	4576	1106
H_4	−3286	4691	−810
H_5	−2426	4696	−2366
H_6	−590	4543	−2439
H_7	1146	4323	−1527
H_8	2116	4161	−25
	Molecule B		
H_2	1852	2922	−1947
H_3	168	3039	−2629
H_4	−1801	3212	−2426
H_5	−3250	3325	−1359
H_6	−3023	3289	412
H_7	−1835	3145	1956
H_8	−140	3030	2681
	Solvent Molecule 1		
H_{s1}	−1321	3759	4125
	Solvent Molecule 2		
H_{s2}	6215	5900	3569

[a] See text. [b] Atoms are labeled in agreement with Figure 1. Hydrogen atoms have the same subscript(s) as the carbon atoms to which they are covalently bonded.

Table III. Bond Lengths in Crystalline $C_{13}H_8Cl_4N_5P_3{\cdot}CHCl_3$[a]

type[b]	length, Å		type[b]	length, Å	
	molecule A	molecule B		molecule A	molecule B
$P_1–N_3$	1.607 (4)	1.597 (4)	$C_2–C_3$	1.340 (8)	1.339 (9)
$P_1–N_5$	1.607 (4)	1.617 (4)	$C_7–C_8$	1.356 (8)	1.351 (8)
$P_1–N_2$	1.660 (4)	1.657 (5)	$C_4–C_5$	1.369 (10)	1.377 (10)
$P_1–N_1$	1.620 (4)	1.611 (4)	$C_5–C_6$	1.368 (10)	1.359 (11)
$P_2–N_3$	1.548 (4)	1.552 (4)	$C_9–C_{9a}$	1.400 (7)	1.383 (7)
$P_2–N_4$	1.581 (5)	1.588 (5)	$C_8–C_9$	1.407 (7)	1.404 (7)
$P_3–N_4$	1.574 (5)	1.568 (5)	$C_1–C_{9a}$	1.435 (7)	1.454 (7)
$P_3–N_5$	1.562 (4)	1.566 (4)	$C_{9a}–C_{9b}$	1.417 (7)	1.414 (7)
$P_2–Cl_1$	1.998 (2)	1.986 (2)	$C_1–C_2$	1.438 (7)	1.440 (8)
$P_2–Cl_2$	1.985 (2)	1.993 (2)	$C_3–C_{3a}$	1.425 (8)	1.421 (9)
$P_3–Cl_3$	1.987 (2)	1.994 (2)	$C_{3a}–C_{9b}$	1.419 (8)	1.403 (8)
$P_3–Cl_4$	1.993 (2)	1.991 (2)	$C_{6a}–C_{9b}$	1.408 (8)	1.424 (8)
$N_1–C_1$	1.328 (6)	1.322 (7)	$C_7–C_{6a}$	1.429 (8)	1.402 (8)
$N_2–C_9$	1.363 (6)	1.377 (7)	$C_{3a}–C_4$	1.390 (9)	1.405 (9)
$N_2–H_{N2}$	0.86 (4)	0.74 (4)	$C_{6a}–C_6$	1.410 (8)	1.405 (8)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1.

Table IV. Bond Angles in Crystalline $C_{13}H_8Cl_4N_5P_3{\cdot}CHCl_3$[a]

type[b]	angle, deg		type[b]	angle, deg	
	molecule A	molecule B		molecule A	molecule B
$N_3P_1N_5$	112.4 (2)	112.3 (2)	$P_1N_3P_2$	124.7 (3)	124.0 (3)
$N_2P_1N_3$	109.8 (2)	109.2 (2)	$P_2N_4P_3$	119.0 (3)	119.0 (3)
$N_1P_1N_3$	110.5 (2)	112.6 (2)	$P_1N_5P_3$	124.4 (3)	122.3 (2)
$N_2P_1N_5$	107.1 (2)	107.6 (2)			
$N_1P_1N_5$	112.1 (2)	109.8 (2)	$P_1N_2C_9$	125.8 (3)	124.2 (4)
$N_1P_1N_2$	104.5 (2)	105.0 (2)	$P_1N_2H_{N2}$	116 (3)	108 (4)
			$C_9N_2H_{N2}$	118 (3)	126 (4)
$P_1N_1C_1$	122.9 (3)	122.4 (3)			
$Cl_1P_2Cl_2$	101.2 (1)	100.9 (1)	$Cl_3P_3Cl_4$	99.6 (1)	100.9 (1)
$Cl_1P_2N_3$	108.8 (2)	109.7 (2)	$Cl_3P_3N_4$	109.4 (2)	107.9 (2)
$Cl_1P_2N_4$	106.5 (2)	108.0 (2)	$Cl_3P_3N_5$	109.5 (2)	109.8 (2)
$Cl_2P_2N_3$	110.3 (2)	110.1 (2)	$Cl_4P_3N_4$	107.9 (2)	109.6 (2)
$Cl_2P_2N_4$	109.1 (2)	107.0 (2)	$Cl_4P_3N_5$	109.1 (2)	107.8 (2)
$N_3P_2N_5$	119.3 (2)	119.5 (2)	$N_4P_3N_5$	119.5 (2)	119.3 (2)
$N_2C_9C_{9a}$	120.0 (4)	120.1 (5)	$C_4C_{3a}C_{9b}$	118.7 (5)	118.6 (5)
$N_2C_9C_8$	119.7 (4)	119.2 (5)	$C_{3a}C_{9b}C_{9a}$	120.5 (5)	120.8 (5)
$C_8C_9C_{9a}$	120.3 (4)	120.7 (5)	$C_{6a}C_{9b}C_{9a}$	120.4 (5)	119.4 (5)
$C_1C_{9a}C_9$	120.7 (4)	120.7 (4)	$C_{3a}C_{9b}C_{6a}$	119.0 (5)	119.9 (5)
$C_9C_{9a}C_{9b}$	119.3 (4)	119.3 (5)	$C_7C_{6a}C_{9b}$	118.1 (5)	118.8 (5)
$C_1C_{9a}C_{9b}$	120.0 (4)	119.9 (5)	$C_6C_{6a}C_{9b}$	120.0 (5)	118.8 (6)
$N_1C_1C_{9a}$	124.9 (4)	124.6 (5)	$C_6C_{6a}C_7$	121.9 (5)	122.4 (5)
$N_1C_1C_2$	117.2 (5)	118.5 (5)	$C_8C_7C_{6a}$	121.6 (5)	121.3 (5)
$C_2C_1C_{9a}$	117.8 (5)	117.0 (5)	$C_7C_8C_9$	120.3 (5)	120.4 (5)
$C_1C_2C_3$	121.0 (5)	121.0 (5)	$C_{3a}C_4C_5$	121.6 (6)	121.1 (6)
$C_2C_3C_{3a}$	122.9 (5)	123.2 (6)	$C_4C_5C_6$	121.0 (6)	120.9 (6)
$C_3C_{3a}C_{9b}$	117.7 (5)	118.0 (5)	$C_5C_6C_{6a}$	119.6 (6)	120.8 (6)
$C_3C_{3a}C_4$	123.6 (5)	123.5 (6)			

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1.

Table V. Bond Lengths and Angles Involving Solvent Non-Hydrogen Atoms in Crystalline $C_{13}H_8Cl_4N_5P_3{\cdot}CHCl_3$[a]

type	length, Å	type	length, Å
$C_{s1}–C_{s1}$	1.721 (7)	$C_{s2}–Cl_{s4}$	1.705 (7)
$C_{s1}–Cl_{s2}$	1.732 (7)	$C_{s2}–Cl_{s5}$	1.680 (7)
$C_{s1}–Cl_{s3}$	1.745 (6)	$C_{s2}–Cl_{s6}$	1.686 (7)
type	angle, deg	type	angle, deg
$Cl_{s1}C_{s1}Cl_{s2}$	110.5 (4)	$Cl_{s4}C_{s2}Cl_{s5}$	109.1 (4)
$Cl_{s1}C_{s1}Cl_{s3}$	110.2 (4)	$Cl_{s4}C_{s2}Cl_{s6}$	110.7 (4)
$Cl_{s2}C_{s1}Cl_{s3}$	110.5 (4)	$Cl_{s5}C_{s2}Cl_{s6}$	107.8 (4)

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

system fulfilled the requirements of the theoretical model and should therefore be capable of interacting with the phosphorus dπ orbital. In apparent agreement with this scheme, electroreduction of $\mathbf{5}^+$ was shown to lead to a radical that provides the first evidence for the injection of electron spin density into a segment of a phosphazene linkage. The amphoterism exhibited by compound **10** provides another test of this model as the changes in exocyclic electron density in the 1,9-diaminophenalenyl unit as a result of the protonation/deprotonation of **10** are quite different from those produced in the reduction of $\mathbf{5}^+$.

The bonding models are illustrated in Figure 3, and it is clear that while the LUMO of the 1,9-disubstituted phenalenyl moiety (Figure 3a) is of the correct symmetry to interact with the dπ orbital of phosphorus to produce spirodelocalization, the in-plane nitrogen lone-pair orbitals (Figure 3b) possess the wrong symmetry to support an interaction with the phosphorus dπ orbitals.

On the basis of this simple model, it would therefore be expected that variations in the availability of the exocyclic in-plane nitrogen lone-pair orbitals would influence the environment of the spiro-

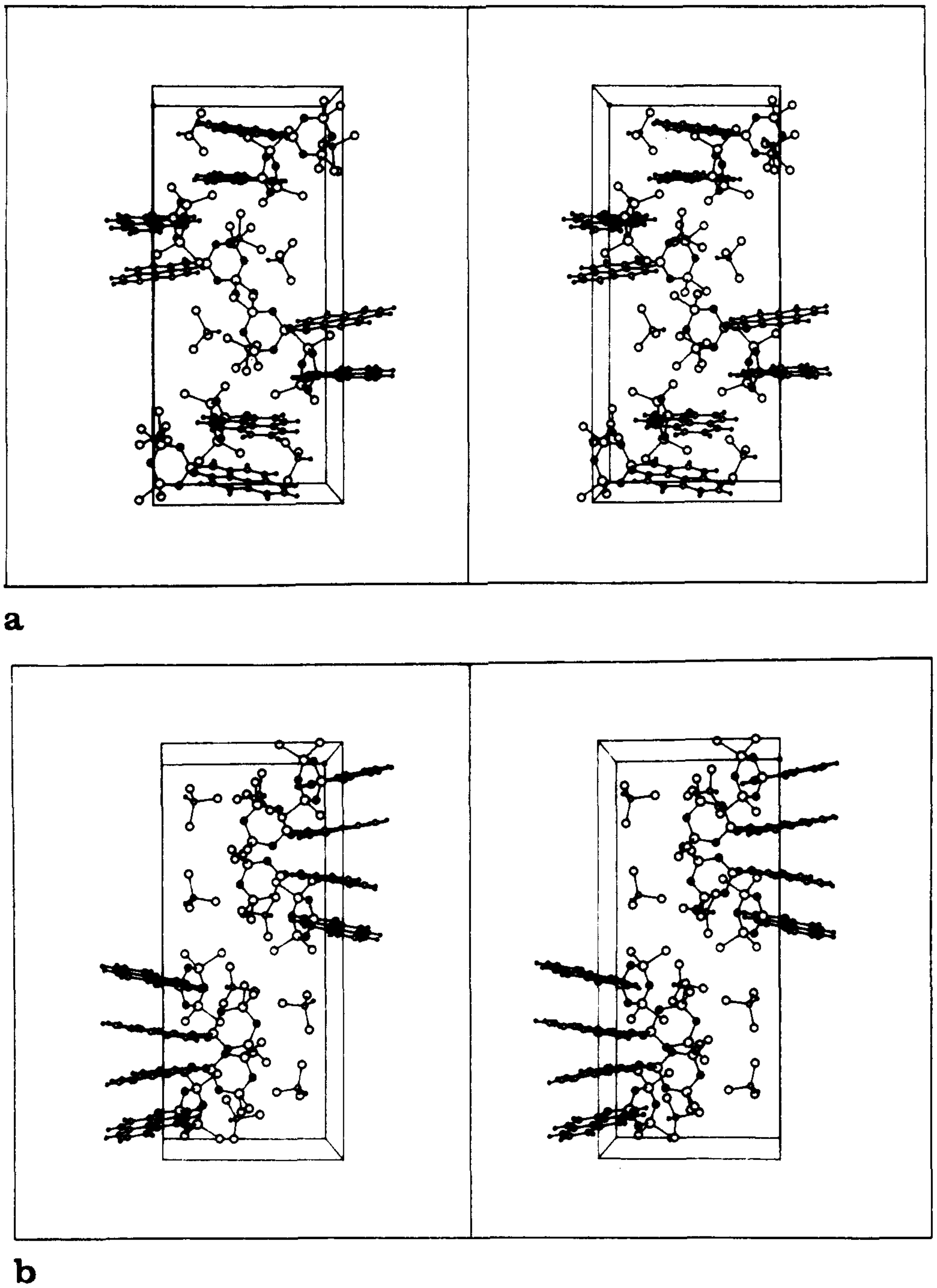

Figure 2. ORTEP stereoview of the unit cell of crystalline $C_{13}H_8Cl_4N_5P_3 \cdot CHCl_3$, viewed down (a) the *x* axis or (b) the *z* axis.

Table VI. Close Contacts Involving Hydrogen Atoms in Crystalline $C_{13}H_8Cl_4N_5P_3 \cdot CHCl_3$[a]

donor atom (D)[a]	acceptor atom (A)	D···A,[b] Å	H···A,[b] Å	D–H···A, deg	H–D···A, deg	H···A–P,[c] deg	assymmetric unit of A[d]
N_{a2}–H_{Na2}	N_{b5}	2.919 (6)	2.15 (4)	149 (3)	22 (3)	116 (3) (P_{b1}) 120 (3) (P_{b3})	*x*, *y*, *z*
N_{b2}–H_{Nb2}	N_{a5}	3.133 (6)	2.66 (4)	124 (3)	45 (3)	116 (3) (P_{a1}) 109 (3) (P_{a3})	*x*, *y*, *z*

[a] The hydrogen atom involved in the interaction is also indicated. [b] Figures in parentheses are the estimated standard deviations in the last significant digit. [c] P denotes the phosphorus atoms that are covalently bonded to the acceptor nitrogen atoms. [d] All donor atoms belong to the asymmetric unit for which the fractional atomic coordinates are given in Table I.

phosphorus through σ-donation but would be ineffective in transmitting electron density to more distant atoms of the ring (via the cyclotriphosphazene π-system). The number of nonbonded lone pairs at the amino groups increases in the order **11**$^+$ (0), **10** (1), and **12**$^-$ (2), and it may be seen (Table VII) that the ^{31}P chemical shift of the spiro phosphorus (δ_A) is sensitive to this parameter, particularly in the presence of excess charge. This is in accord with the strong electron-acceptor character of the cyclotriphosphazene ring system.[12] The ^{31}P coupling constants also respond to the variation in electron density at the spiro phosphorus atom and exhibit the expected dependence on effective electronegativity of the substituent. Note, however, the invariance in ^{31}P chemical shift of the distant phosphorus atoms (δ_B) to the presence of exocyclic charge density and changes in lone-pair

Table VII. NMR Parameters of Phenalene–Phosphazene Complexes[a]

	substitution		^{1}H						^{31}P		
compd	X	Y	δ_2	δ_3	δ_4	δ_5	$J_{2,3}$, Hz	$J_{4,5}$, Hz	δ_A	δ_B	J_{AB}, Hz
5$^+$	NMe	NMe	7.90	8.83	8.67	8.09	9.5	7.7	11.07	12.87	76.9
6$^+$	NH	NMe							5.52	12.40	79.8
11$^+$	NH	NH	7.58	8.63	8.53	7.99	9.0	7.8	0.04	11.78	83.3
10	NH	N	7.22	8.11	8.05	7.64	9.2	7.5	3.39	12.30	68.1
12$^-$	N	N	7.07	7.78	7.80	7.35	9.2	8.5	18.40	11.48	48.9

[a] Measured in CD_3CN, with Me_4Si (^{1}H) and external H_3PO_4 (^{31}P) as references.

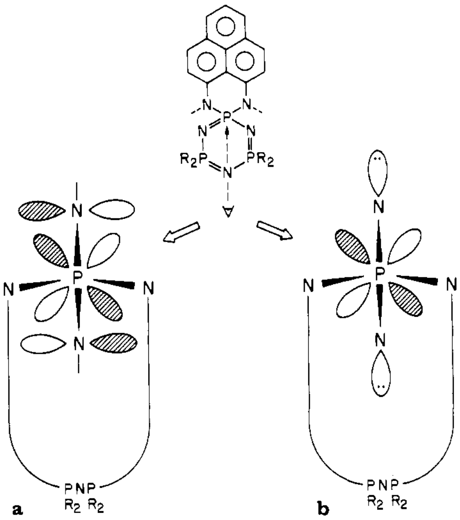

Figure 3. Schematic diagrams for the interaction of exocyclic charge density with the dπ orbital of the spiro phosphorus. In part a the exocyclic orbitals involve the phenalene LUMO, whereas in part b they are nitrogen lone-pair orbitals.

availability. Given the known sensitivity of ^{31}P chemical shifts to solvent effects,[21] the observed variations in δ_B may be within experimental error. The distant ^{31}P chemical shifts provide an interesting contrast with the proton chemical shifts of the phenalenyl nucleus, which show a significant variation with protonation/deprotonation even though the number of π electrons does not change.

It is concluded that substituent lone pairs with the orientation shown in Figure 3b are not effective in long-range delocalization within the phosphazene linkage.

Experimental Section

Preparation of 1,1-(9-Amino-1-iminophenalene-*N*,*N*′-diyl)-3,3,5,5-tetrachlorocyclotriphosphazene (7). A solution of 9-aminophenalenimine[22–24] (0.4 g, 0.002 mol), hexachlorocyclotriphosphazene (1.0 g, 0.003 mol), and triethylamine (1.2 mL, 0.008 mol) in dry tetrahydrofuran was refluxed overnight. The reaction mixture was allowed to cool, and the solids were removed by filtration through Celite. Hexane was added to the filtrate to induce crystallization (0.68 g, 72%); mp >300 °C. IR (CsI) (cm^{-1}): 3220 (m, br), 2997 (vw), 1630 (m), 1590 (s), 1570 (s), 1520 (s), 1490 (vw), 1440 (w), 1393 (m), 1364 (m), 1345 (m), 1200 (vvs, br), 1012 (s), 980 (m), 912 (m), 836 (vs), 812 (m), 750 (s), 696 (m), 680 (w), 665 (w), 570 (vs), 550 (vs), 510 (vs), 426 (m). UV (CH_2Cl_2): [nm (ϵ, M^{-1} cm^{-1})]: 245 (22000), 270 (8000), 279 (7000), 355 (10000), 371 (18000), 404 (3600), 428 (5500), 453 (5800). ^{1}H NMR (CD_2Cl_2, Me_4Si): δ 7.1–8.2 (m). ^{31}P NMR ($CDCl_3$, 50 °C, external H_3PO_4) (AB_2): δ_A −5.79, δ_B 16.02, J_{AB} = 43.9 Hz.

Preparation of 1,1-(9-Amino-1-iminophenalene-*N*,*N*′-diyl)-3,3,5,5-tetrakis(trifluoroethoxy)cyclotriphosphazene (10). A solution of sodium trifluoroethoxide (10.3 mL, 0.009 mol) in tetrahydrofuran was added dropwise to a solution of **1** (0.7 g, 0.0015 mol) in dry tetrahydrofuran and the mixture allowed to stir overnight. The reaction mixture was partitioned between water and ether and the organic layer washed and dried over magnesium sulfate. The solvent was removed on a rotary evaporator to give a brown solid, which was chromatographed on silica by using dichloromethane/ether as eluant. The product was obtained as large, chunky yellow needles after recrystallization from hexane/ether (0.65 g, 60%); mp 115–117 °C. Anal. Calcd for $C_{21}H_{16}N_5O_4P_3F_{12}$: C, 34.87; H, 2.23; N, 9.68; P, 12.85. Found: C, 34.93; H, 2.27; N, 9.46; P, 12.64.

Preparation of Salts. The protonated species **6**$^+$ and **11**$^+$ were prepared by treating dichloromethane solutions of the neutral precursors with tetrafluoroboric acid in ether. The salts separated as solids, which were characterized by NMR spectroscopy. The anionic species **12**$^-$ was generated in situ by treatment of a CD_3CN solution of the neutral precursor (**2**) with excess solid sodium hydride.

X-ray Data and Structure Determination for 7. The diffraction data were taken with a Nicolet autodiffractometer, and the structure was solved with the Nicolet SHELXTL package (Crystalytics Co., Lincoln, NE 68501).

Crystal data for $C_{13}H_8Cl_4N_5P_3.CHCl_3$: M_r = 588.3; crystal selected from a sample recrystallized from chloroform; near cube of dimension 0.56 mm; monoclinic space group $P2_1/c$; cell dimensions at 20 °C, a = 12.401 (4) Å, b = 28.404 (6) Å, c = 12.962 (3) Å, and β = 91.76 (2)°; V = 4564 (2) Å^3; Z = 8; Mo K$_\alpha$ (λ = 0.71073 Å); d_{calcd} = 1.71 g cm^{-3}; ω scan/background = 2, max 2θ = 48°; 7289 unique reflections measured, of which 4525 were ultimately used in the refinement of 532 parameters; anomalous dispersion correction applied to P and Cl.

All hydrogen atoms covalently bonded to ring carbon atoms were included in the structure factor calculations as idealized atoms (assuming sp^2 hybridization of the carbon atoms and a C–H bond length of 0.96 Å) "riding" on their respective carbon atoms. The solvent hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp^3 hybridization of the carbon atoms and a C–H bond length of 0.96Å) "riding" on their respective carbon atoms. The isotropic thermal parameters for these hydrogen atoms were fixed at 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded. The two hydrogen atoms covalently bonded to nitrogen atoms were treated as separate isotropic atoms, and their parameters were varied in least-squares refinement cycles. Final R = 0.050; R_w = 0.047.

Final atomic positional parameters are given in Tables I and II while selected bond distances and angles appear in Tables III and IV, respectively.

Registry No. **2**, 98304-02-0; **3**, 98304-03-1; **6**$^+$, 114198-71-9; **7**, 114198-69-5; **7**·$CHCl_3$, 114198-74-2; **10**, 114198-70-8; **11**$^+$, 114198-72-0; **12**$^-$, 114198-73-1; 9-aminophenalenimine, 67618-27-3; hexachlorocyclotriphosphazene, 940-71-6.

Supplementary Material Available: Full details of the structure solution together with a table of anisotropic thermal parameters (Table SII) (9 pages); a table of structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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(22) Franz, K. D.; Martin, R. L. *Tetrahedron* **1978**, *34*, 2147.
(23) Neidlein, R.; Behzadi, Z. *Chem. Ztg.* **1978**, *102*, 150.
(24) Haddon, R. C.; Chichester, S. V.; Mayo, S. L. *Synthesis* **1985**, 639.