Intra-ring Bonding in Cyclic Phosphazenes

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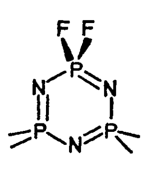
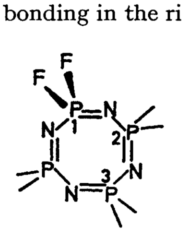
Summary Self-consistent field calculations on two cyclic phosphazenes reveal that there are surprisingly large intra-ring phosphorus–phosphorus bond orders; it is suggested that these P–P bonds are important contributors to the stability of the compounds.

THE cyclic phosphazenes, see (A) and (B), are of interest to both theoretical and experimental chemists. Although the physical and chemical properties of these compounds have been extensively studied,[1] the bonding in the rings has only been discussed qualitatively.[2,3] The basically planar structure[4] of the trimeric compounds in which the P–N distances around the ring are equal has led to the belief that they have a delocalised π electron system similar to benzene and involving the nitrogen $p\pi$ orbitals and phosphorus $d\pi$ orbitals. There is, however, disagreement over the nature of the involvement of the d orbitals of the phosphorus atoms.[2,3]



(A)



(B)

As part of an investigation into the bonding in some inorganic ring systems, we have performed calculations within the CNDO–MO–SCF framework[5] on two cyclic phosphazenes. These were the hexafluoro-derivatives of the trimer, $P_3N_3F_6$, and the octafluoro-derivative of the tetramer, $P_4N_4F_8$. The geometry of these molecules was obtained from refs. 4 and 7. The exact method and its parametrisation for the constituent atoms have been detailed elsewhere.[5,6]

The electron densities and bond orders in the two molecules are listed in the Table. The electron distribution features positive and negative charges, respectively, on the phosphorus and nitrogen atoms of the rings. Comparison of bond orders for the P–F and P–N bonds confirms the previously postulated multiple character of the P–N bonds. In the P–F and P–N bonds, the d orbital components of the bond order amount to *ca.* one-third of the total.

The most significant point which has emerged from the calculation, however, is the magnitude of all the P–P bond orders. In the tetrameric compound even the P(1)–P(3) bond order (0·15) is high enough to be significant. By contrast, the N–N interactions are almost negligible. These P–P bond orders are composed almost entirely of *s–d* and *p–d* elements and, hence, are a consequence of the inclusion of 3*d* orbitals in the calculation. This means that the trimer could be considered as a group of three bonded phosphorus atoms, one face of a P_4 tetrahedron, with three bridging nitrogen atoms. Similarly, the tetramer can be viewed as a completely flattened P_4 tetrahedron with bonds along all edges and bridging nitrogens across the short P–P bonds. Because of the close resemblance of these models to P_4 where the electron density is probably concentrated inside the cage,[8] it will be of interest to examine the electron density contours for the molecules and to compare that of the trimer with benzene.

Electron densities and bond orders in $P_3N_3F_6$ *and* $P_4N_4F_8$

		$P_3N_3F_6$	$P_4N_4F_8$
P	*s*	1·02	0·99
	p	2·22	2·18
	d	0·79	0·79
	Total	4·03	3·96
N	*s*	1·21	1·15
	p	4·16	4·25
	Total	5·37	5·40
F	*s*	1·69	1·70
	p	5·61	5·62
	Total	7·30	7·32
P–N		1·18	1·25
P–F		0·72	0·72
P(1)–P(2)		0·64	0·52
P(1)–P(3)			0·15
N–N		−0·03	−0·02

We conclude, therefore, that electron delocalisation about the phosphazene framework is augmented by intra-ring bonding and the effect is an important factor which enhances the stability of these compounds. This intra-ring bonding may be present in similar ring systems involving elements of the second row of the Periodic Table and we are undertaking further work in this direction.

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