801. *Electron Distribution in Cyclic $p\pi$–$d\pi$ Systems.*

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The nature of $p\pi$–$d\pi$ delocalisation and other auxiliary binding in phosphonitrilics and similar ring systems is discussed in relation to recent experimental studies. The main new theoretical feature to be added to the original suggestion of $p\pi$–$d\pi$ delocalisation is that there is some contribution to binding by at least four *d*-orbitals per phosphorus atom; the four do not, however, contribute equally. Delocalisation of the lone pairs of nitrogen atoms into *d*-orbitals of neighbouring phosphorus atoms is shown to be responsible for important features of the molecular and electronic structure. Together with repulsions between non-bonded atoms, and the steric requirements for strong π-bonding, it determines the molecular configurations adopted. In phosphonitrilics, $p\pi$–$d\pi$ bonding is strong. In " thiazyl " compounds the π-bonds are weaker, and in the extreme case of siloxane rings they are very weak indeed.

In earlier papers,[1] two principal types of cyclic π-bonds possible in planar monocyclic molecules $(AB)_n$ have been distinguished. The first and more familiar is exemplified by the borazoles, in which each ring atom provides a *p*-orbital perpendicular to the plane of the ring. In the second type, with which we are principally concerned, the π-electron system is formed from alternate *p*- and *d*-orbitals; this type of binding may be expected to occur in the cyclic phosphonitrilic derivatives and the " thiazyl " halides [2,4,6-trihalogeno-1,3,5-trithia-2,4-6-triazines].

There are now many more experimental results for these compounds. This paper is concerned with their analysis in the light of the theoretical models hitherto proposed, and with some elaboration of the theory required especially by recent studies of molecular structures. The primary question whether there are π-bonds between ring-nitrogen and ring-phosphorus in phosphonitrilic compounds, or between ring-nitrogen and ring-sulphur in " thiazyl " compounds, can be answered from the observed bond lengths: π-bonding is definitely established. It is also found that the number of *d*-electrons and *d*-orbitals involved is usually greater than the simple formulæ indicate, and that *d*-orbitals participate in the ring bonds of such compounds as siloxanes and metaphosphate ions, as well as in the phosphonitrilic and thiazyl derivatives, in which double bonds in the ring are formally required. To a smaller extent, they act as acceptor orbitals for lone-pair electrons of nitrogen or oxygen, and also form bonds with suitable exocyclic groups. The distribution of the π-electrons and molecular configuration are found to be interdependent.

Symmetry Analysis.—The phosphonitrilic compounds are planar in a number of important special cases (trimeric chloride [2] and fluoride,[3] tetrameric fluoride [4]), but not generally. Some discussion of the more general situation is thus called for. In the phosphonitrilic rings the bonds from a chosen phosphorus atom to the neighbour nitrogens

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[1] Craig and Paddock, *Nature*, 1958, **181**, 1052; Craig, *J.*, 1959, 997; *Chem. Soc. Spec. Publ.*, No. 12, 1958, p. 343.

[2] Wilson and Carroll, *J.*, 1960, 2548; Pompa and Ripamonti, *Ric. Sci.*, 1959, **29**, 1516.

[3] Becher and Seel, *Z. anorg. Chem.*, 1960, **305**, 148.

[4] McGeachin and Tromans, *J.*, 1961, 4777.

define a plane, which will be the (xy) plane for a set of local axes, the y-axis being the bisector of the NPN ring angle. The z-axis is the local normal, and in a planar ring is also normal to the ring plane (Fig. 1).

The five d-orbitals are d_{z^2}, d_{xz}, d_{yz}, d_{xy}, and $d_{x^2-y^2}$, in a scheme in which the z-axis is the axis of quantisation. If the four attached atoms were identical and tetrahedrally arranged the d-orbitals would be split into the familiar d_γ and d_ϵ sets. If we refer the orbitals to the y-axis as axis of quantisation, the d_γ set consists of d_{y^2} and d_{xz}, and the d_ϵ set of d_{yz}, d_{xy}, and $d_{x^2-z^2}$. In z-quantisation we get one d_γ and one d_ϵ orbital by linear combination of d_{y^2} and $d_{x^2-z^2}$, the other members of each set being unaffected. Thus even in the tetrahedral field the d_{xz}-orbital is split from the other two potentially π-bonding orbitals d_{yz} and d_{xy}. In the actual field about phosphorus, the bond angles are different from tetrahedral, and the exocyclic atoms differ from the ring atoms in two ways. They are of different electronegativities, and the ring-nitrogens have half-filled $2p\pi$-orbitals capable of overlapping the d_{xz}- and d_{yz}-orbitals on phosphorus. The actual field (of symmetry $\mathbf{C}_{2v}$) is thus substantially lower than tetrahedral, and the d_{xy}- and d_{yz}-orbitals are no longer degenerate with one another. The symmetry is low enough to remove all d-orbital degeneracy.

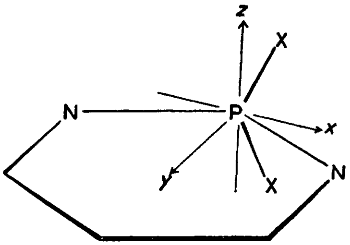

FIG. 1.

The properties of the orbitals are summarised in Table 1. Orbitals differing in symmetry with respect to the field will not behave equivalently unless through some accidental equality in energy magnitudes. Such is the complexity of causes of the splittings (electronegativity difference between cyclic and exocyclic ligand atoms, availability of π-bonding orbitals of nitrogen, etc.) that one cannot assert definitely on theoretical grounds which d-orbitals will be more and which less stable. It seems probable that the important factors are the destabilising influence of σ-bond electrons on d_{xy}- and d_{yz}-orbitals, which overlap them strongly, and the stabilising effect on the d_{xz}-orbital of $p\pi$–$d\pi$ interaction. However, the symmetry argument only makes clear that differences should exist: the question of relative importance of orbitals must be answered by analysing the consequences of each possibility, and comparing them with experiment.

TABLE 1.

Symmetry properties of atomic and molecular orbitals.

Atomic orbital symmetries in local molecular fields.

Orbital	Local symmetry tetrahedral ($\mathbf{T}_d$)	$\mathbf{C}_{2v}$
d_{z^2}	$t_2 + e$	a_1
$d_{x^2-y^2}$		a_1
d_{xy}	d_ϵ (t_2)	b_1
d_{xz}	d_γ (e)	a_2
d_{yz}	d_ϵ (t_2)	b_2
s–p_y lone-pair hybrid	—	a_1

Symmetries of proper combinations of atomic orbitals plane $(AB)_u$ molecules.

n	Ring quantum number	Atomic orbital symmetry a_1	a_2	b_1	b_2
3($\mathbf{D}_{3h}$)	0	a_1'	a_1''	a_2'	a_2''
,,	± 1	e'	e''	e'	e''
4($\mathbf{D}_{4h}$)	0	a_{1g}	a_{1u}	a_{2g}	a_{2u}
,,	± 1	e_u	e_g	e_u	e_g
,,	2	b_{1g}	b_{1u}	b_{1g}	b_{1u}

Orbital Overlap.—The extent to which the π-orbital at nitrogen overlaps the d_{xz}- and

d_{yz}-orbitals, both of which have π-symmetry in the plane ring system, gives a useful measure of the contribution made by these orbitals to the bond system, and of the way in which this contribution is affected by the displacements into the several possible non-planar configurations. In non-planar systems the d_{xy}- and $d_{x^2-y^2}$-orbitals may also overlap the nitrogen $p\pi$-orbital, and they overlap the nitrogen lone-pair orbital in a wide variety of configurations. As is discussed below, there are four potentially important non-planar configurations of the tetrameric rings. They are the tub (as in cyclo-octatetraene but with alternating atoms, symmetry $\mathbf{S}_4$), the crown ($\mathbf{C}_{4v}$), the chair ($\mathbf{C}_{2h}$), and the saddle ($\mathbf{D}_{2d}$). Each may be produced from a planar structure by up-and-downward displacements of one set of atoms (A or B in Fig. 4) or of both sets. If the displacements are equal, each configuration is uniquely specified by the ring bond-angle common to all the P atoms on the one hand, and that of all the N atoms on the other. In the known examples the NPN angle is close to 120° and the PNP angle lies in the range 130—150°, the upper limit being for the planar $\mathbf{D}_{4h}$ ring. The overlaps depend on the values of the *d*-orbital exponents, though the gross features of their change with configuration do not.

Representative values of all the overlap integrals are given in Table 2. They show that, in every configuration, at least one of the orbital interactions can be important, and

TABLE 2.

Overlap integrals * of the nitrogen $p\pi$- and lone-pair orbitals with phosphorus *d*-orbitals.†

	Structure ‡				
Overlap	Tub ($\mathbf{S}_4$)	Chair ($\mathbf{C}_{2h}$)	Saddle ($\mathbf{D}_{2d}$)	Crown ($\mathbf{C}_{4v}$)	Planar molecule ($\mathbf{D}_{4h}$)
$p\pi-d_{xz}$	0·109	0·080	0·113	0·068	0·139
$p\pi-d_{yz}$	0·063	0·046	0·065	0·039	0·080
$p\pi-d_{x^2-y^2}$	0·069	0·097	0·081	0·122	0
$p\pi-d_{xy}$	0·040	0·056	0·047	0·070	0
sp ††$-d_{xz}$	0·058	0·082	0·068	0·102	0
$sp-d_{yz}$	0·033	0·047	0·039	0·059	0
$sp-d_{x^2-y^2}$	0·147	0·123	0·150	0·112	0·166
$sp-d_{xy}$	0·042	0·056	0·040	0·062	0·012

* Magnitudes only. A number of the overlaps have negative sign with the axis convention of Fig. 1. In the tub and the chair structure the values are averages over all the overlaps of the named types. For example, the individual values for $p\pi-d_{xz}$ overlap in the tub are 0·080 and 0·137 and for $p\pi-d_{yz}$ 0·046 and 0·079.

† The *d*-orbital exponents are the same throughout, equal to 0·47. The nitrogen orbital exponents are those given by Slater's rules.

‡ Values quoted are for ring bonds of 1·64 Å, ∠P = 120°. ∠N = 135°. The values for 1·60 Å and ∠N = 132° would not be significantly different. In the planar structure the angles are ∠P = 120°, ∠N = 150°.

†† The lone-pair orbital is an *s–p* hybrid with mixing coefficient chosen to fit the nitrogen bond angle.

often more than one. Since the four *d*-orbitals considered are not equivalent in the molecular environment, their exponents are unlikely to be equal in any one molecule, and they will vary between one molecule and another. In general we expect the more electronegative exocyclic atoms (such as F) to contract the *d*-orbitals more than the less electronegative (such as C) and thus to lead to larger overlap values throughout. However, these changes do not alter the sequence of values in Table 2.

If one considers the atomic orbitals capable of π-bonding in *planar* molecules, both the d_{xz}- and the d_{yz}-orbitals are of potential significance. The first-proposed view was that the d_{xz}-orbital was the more important,* and that $d_{xz}-p\pi$ interaction produced the characteristic properties of the inorganic ring systems, with $d_{yz}-p\pi$ interaction in a less important role. The main consequences of this view, which will be examined and compared with experiment before considering others, are: (i) for the same exocyclic groups, π-electron

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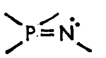
* On the ground that the environment of the phosphorus " prepares " the d_{xz}-orbital for bond formation better. Also the overlap of the d_{xz}-orbital with the nitrogen $2p\pi$ is greater.

energies per structural unit should increase steadily to a limit with increasing ring size; and (ii) for the same ring size and ring atoms, π-electron energies should increase with the electronegativity of the ligands.

In the next section these consequences are examined successively, after it has been first shown that the simplest derivatives exhibit the expected characteristics.


(A)

Comparison with Experiment.—The most straightforward test of the theory is provided by the phosphonitrilic derivatives, which are based on the repeating unit (A). To a first approximation, the 3*s*- and the 3*p*-orbitals of the phosphorus atom are taken up in the formation of σ-bonds; the σ-bonds at nitrogen are formed from two sp^2 hybrid orbitals, the third being occupied by an unshared pair of electrons. Two electrons remain to be accounted for. The ionic formulation $^+$P–N$^-$ would imply the presence of two lone pairs on the nitrogen atom, where the angle should therefore not exceed 109° 28′; in fact, it is never less than 119° (Table 5). The alternative $^-$P–N$^+$ (the electron being withdrawn from the $2p\pi$-nitrogen orbital) would give the observed bond angle at nitrogen, and perhaps make some contribution, but as will be seen below, electron donation from nitrogen occurs mainly from the sp^2 unshared pair. If we can disregard such simple ionic structures as major contributors to the bond system, additional covalent bonds are formed from alternate $d\pi$- and $p\pi$-orbitals, as envisaged in the theory. The ring bond angle (of about 120°) at phosphorus, which is remarkably constant from one molecule to another, is in nice agreement with the bond angles in other molecules with double-bonded phosphorus. Thus, the Cl–P–S angle in thiophosphoryl chloride [5] is 118°, and the exocyclic O–P–O bond angle in the tetrametaphosphate [6] ion is 121°.

For the trimeric chloride, two crystallographic investigations [2] agree in showing that the bond lengths in the ring are all equal (1·59 Å). The sum of the single covalent radii is 1·76 Å, in the phosphoramidate ion the P–N bond length [7] is 1·78 Å, and in the triamidophosphine borane $(NH_2)_3P,BH_3$ it is shortened [8] to 1·65 Å as a result of partial charge transfer from phosphorus to boron. The phosphonitrilic bond is shorter than all of these, indicating appreciable double-bond character. Thermochemical results point to the same conclusion. Among phosphonitrilic derivatives, the arbitrary division of a measured atomisation energy into parts characteristic of the individual bonds is least unsatisfactory for the halides, because only two sorts of bond are involved, and structural evidence justifies the allocation. $\bar{E}$(P–N) in the trimeric chloride [9] is 72·3 kcal., compared with a calculated value of 65 kcal. (for a single bond) and experimental values of 62 kcal. for phosphoryl isocyanate [10] and 66·8 kcal. in trisdiethylamidophosphine.[11] $\bar{E}$(P–N) is also expected to vary with the valency of the phosphorus atom (*i.e.*, for ter- and quinquecovalent phosphorus) and on the nature of the other attached atoms or groups. In view of these uncertainties, the ring bonds in triphosphonitrilic chloride are assessed as 6—10 kcal. stronger than a single P–N bond, a range consistent with the heats of formation of other phosphonitrilic derivatives.[12] The energy difference is much smaller than for benzene [in which $\bar{E}$(C–C) exceeds the single-bond energy by 38 kcal.], because the *d*-orbital is more diffuse than the *p*-orbital, and the greater part of the overlap occurs in a region where the nuclear field is low. The structural and thermochemical evidence together, therefore, establish a *prima facie* case for at least a limited electronic delocalisation in triphosphonitrilic chloride in terms of the equality, length, and energy of the ring bonds, and show also the scale of the effect.

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[5] Williams, Sheridan, and Gordy, *J. Chem. Phys.*, 1952, **20**, 164.
[6] Romers, Ketelaar, and MacGillavry, *Acta Cryst.*, 1951, **4**, 114.
[7] Hobbs, Corbridge, and Raistrick, *Acta Cryst.*, 1953, **6**, 621.
[8] Nordman, *Acta Cryst.*, 1960, **13**, 535.
[9] Hartley, Paddock, and Searle, *J.*, 1961, 430.
[10] Jacques and Paddock, unpublished work.
[11] Fowell and Mortimer, *J.*, 1959, 2913.
[12] Bedford and Mortimer, *J.*, 1960, 4649.

From the heat of combustion of the tetrameric chloride $(PNCl_2)_4$, $\bar{E}$(P–N) is found to be close to that in the trimeric chloride,[9] so establishing the principal difference from $p\pi$–$p\pi$ systems; in cyclo-octatetraene [13] the average value of $\bar{E}$(C–C) is 5·5 kcal. less than in benzene. The energy differences between the cyclic phosphonitrilic chlorides up to the heptamer are more accurately measured by their relative heats of polymerisation in the vapour phase.[10] The differences in $\bar{E}$(P–N) between the trimer and each higher polymer are given in the first row of Table 3, and show that the stability of the $PNCl_2$ unit increases steadily with increase in ring size. Two assumptions are involved. The first, that the same high polymer is formed in every case, cannot be justified directly, but seems very likely on the ground that the approximately determined structure of one high polymer [14] is unrelated to that of the cyclic polymer from which it was prepared and therefore may be the same for all. The second, that the stabilisation energy is confined to the ring bonds, is unjustified in detail, but it will be shown below that the strengthening of the exocyclic bonds is probably of minor importance. Again the structural evidence agrees with the thermochemical results; a refinement [15] of an early determination [16] of the crystal structure of the tetrameric chloride shows that the ring bonds are equal at 1·58 Å; this is slightly shorter than in the trimeric chloride, but not significantly so. Those in the tetrameric dimethylamide are very similar.[17]

TABLE 3.

Properties of phosphonitrilic chlorides as a function of ring size.

n in $(PNCl_2)_n$	3	4	5	6	7	Ref.
$\bar{E}(P\text{–}N)_n - \bar{E}(P\text{–}N)_3$ (kcal.)	0	0·39	0·54	0·60	0·62	10
Chemical shift (p.p.m.) relative to 85% H_3PO_4	−20	+7	+17	+16	+18	*a*
$\Delta\nu$(O–H) in phenol (cm.$^{-1}$)	135	125	115	105	95	*b*

Refs.: (*a*) Lund, Paddock, Proctor, and Searle, *J.*, 1960, 2542. (*b*) Paddock and Smith, unpublished work.

The effect of ligand electronegativity on ring stability can be assessed spectroscopically and from crystal structures. The main contributor to the E' vibrational mode of the trimeric ring at 1200—1300 cm.$^{-1}$ is the P–N stretching motion,[18] and the frequency of this mode is an approximate measure of bond strength. Some values are given in Table 4.

TABLE 4.

Frequency of E' ring stretching mode of trimeric phosphonitrilic derivatives as a function of ligand electronegativity.

X in $(PNX_2)_3$	CH_3	Br	NMe_2	Cl	OMe	F
Electronegativity	2·5	2·8	3·0	3·0	3·5	3·9
ν(P–N) (cm.$^{-1}$)	1180	1184	1195	1218	1242	1287
Ref.	*a*	*b*	*b*	18	*c*	3

Refs.: (*a*) Searle, *Proc. Chem. Soc.*, 1959, 7. (*b*) Shaw, *Chem. and Ind.*, 1959, 54. (*c*) Daasch and Smith, *Analyt. Chem.*, 1951, **23**, 853.

Results with a more direct interpretation are given by a force-constant analysis of two trimeric molecules,[19] the P–N stretching constant increasing from 8·36 md/Å in the chloride to 9·03 md/Å in the fluoride. Further concordant evidence comes from two crystal-structure determinations. In octamethyltetraphosphonitrile,[20] the P–N bond length is

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[13] Springall, White, and (in part) Cass, *Trans. Faraday Soc.*, 1954, **50**, 815.
[14] Meyer, Lotmar, and Pankow, *Helv. Chim. Acta*, 1936, **19**, 930.
[15] Hazekamp, Migchelsen, and Vos, *Acta Cryst.*, 1962, **15**, 539.
[16] Ketelaar and de Vries, *Rec. Trav. chim.*, 1939, **58**, 1081.
[17] Bullen, *Proc. Chem. Soc.*, 1960, 425, and personal communication.
[18] Daasch, *J. Amer. Chem. Soc.*, 1954, **76**, 3403.
[19] Chapman, unpublished work.
[20] Dougill, *J.*, 1961, 5471.

1·60 Å, whereas in the tetrameric fluoride it is shortened [4] to 1·51 Å. To a first approximation, therefore, the expected dependence of ring stability on ring size and ligand electronegativity is observed. However, the observed changes in bond length and dynamical properties caused by the exocyclic ligands cannot be taken to belong only to the π-electron system. The attempt to divide bond changes into σ- and π-components is more than usually unrewarding in these molecules. This is partly because of the lack of a molecular plane with respect to which σ and π can be rigorously defined. The more important point is the change in the σ-component of the P–N ring bonds which the change in exocyclic atom can be expected to cause. No precisely analogous example of the change in a P–N single bond can be cited, but values in the literature suggest that the replacement of the three radial chlorine atoms in PCl_5 to give PF_3Cl_2 reduces the axial P–Cl length from 2·19 ± 0·02 Å in the former [21] to 2·05 ± 0·03 Å in the latter.[22] So large a reduction is unexpected, but, if true, the P–N shortening in the tetrameric phosphonitrilic fluoride compared with the chloride could be largely put down to the σ-bond; and in no case can σ-bond changes be eliminated from consideration. Thus, although the lengths and vibration frequencies change in the sense expected for π-bonding, it is not clear how much of the change is derived from the π-electrons.

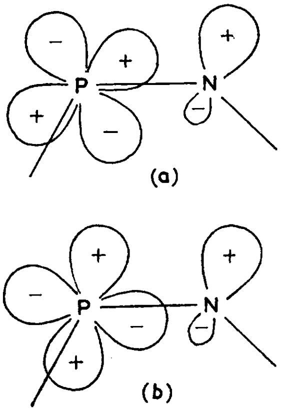

FIG. 2. Overlap schemes for (a) sp–$d_{x^2-y^2}$ and (b) sp–d_{xy} bonding. The angles at P and N are 120° and 135°, respectively, representative of actual molecules.

Lone-pair Delocalisation.—There is another formally possible type of delocalisation.[23] It can be described most simply for a planar molecule, though it occurs in non-planar molecules also. The lone pair of the nitrogen atom is in an sp-orbital with its axis in the local plane of the ring bonds and, as Cruickshank [38] has noted, the lone pair electrons may be used to give additional π-character to the P–N bonds. Each of the d_{xy}- and $d_{x^2-y^2}$-orbitals overlaps the sp-nitrogen orbitals equally and substantially (Table 2, last two lines) on both the right-hand and the left-hand nitrogen atom, and charge transfer must occur to some extent, giving a secondary system of delocalised electrons illustrated in Fig. 2. The tendency of phosphorus to gain electrons from the nitrogen lone pair increases with the electron-withdrawing power of the exocyclic group. Each of the d_{xy}- and $d_{x^2-y^2}$-orbitals overlaps the right- and the left-hand nitrogen orbitals equally. This makes possible a second set of delocalised electrons, occupying molecular orbitals symmetric to reflection in the molecular plane, but otherwise generally similar to the molecular orbitals concerned in π-delocalisation.

We shall refer to the subsidiary bond-system as π' bonding if it involves orbitals in the *local plane* defined by phosphorus and its neighbour nitrogens. In out-of-plane rings, $d\pi'$–$p\pi$ interactions may of course be stronger than $d\pi$–$p\pi$ insofar as they are determined by orbital overlap (Table 2). $d_{x^2-y^2}$-Orbitals have the same local symmetry properties

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[21] Rouault, *Ann. Phys.*, 1940, **14**, 78.

[22] Brockway and Beach, *J. Amer. Chem. Soc.*, 1938, **60**, 1836.

[23] Paddock, " Inorganic Polymers," Elsevier Publ. Co., Amsterdam, in the press.

(site symmetry) under group $\mathbf{C}_{2v}$ as the nitrogen lone-pair *sp* hybrid orbitals. The two types of orbital combine in the molecule in sets belonging to the same symmetry species (Table 1). A consequence is that the sequence of molecular orbitals in the planar molecule, and the change of their characteristics with the number of atoms in the ring, is in the pattern of $p\pi$–$p\pi$ molecular orbitals. Their contributions to molecular stability should follow Hückel's $4n + 2$ rule, and π' energies should alternate along the series of increasing ring size.

d_{xy}-Orbitals do not have the same local symmetry as the lone-pair orbitals, nor in general do their combinations in the molecule transform in the same way under the molecular point groups (Table 1). In this case the molecular orbitals resemble in their sequence and variation with ring size the $p\pi$–d_{xz} (heteromorphic) delocalised system, and should lead to smooth variation along the series of increasing ring size. In π' delocalisation there is again uncertainty as to which *d*-orbital predominates. Experimental results, to be mentioned below, give as yet no evidence of an alternation of properties with ring size, although they do indicate that delocalisation of lone pairs occurs and contributes to the bonding. Thus it is indicated that type (*b*) overlap is somewhat more important than type (*a*), though the occurrence of both types must be expected on the grounds of overlap, and some degree of alternation would not be unexpected in other physical properties.

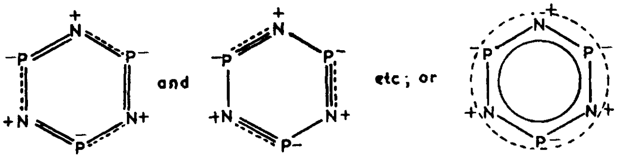

FIG. 3. Possible representations of mixed π- and π'-bonding.

If the postulated charge transfer from nitrogen to phosphorus occurred to the extent of a full electronic charge, which it almost certainly does not, we could indicate the valency situation by structures of the type shown in Fig. 3.

Feedback of electrons into the π-orbitals of phosphorus has also been proposed on the thermochemical grounds for phosphoryl compounds[24] and for phosphinimines.[25] The phosphonitrilic derivatives provide a wider field in which the ideas can be tested and offer the possibility of discriminating between the contributory effects.

There are several types of evidence for the reality of partial transfer from the unshared electron pair on the nitrogen atoms. It must be remembered that increase of electronegativity at phosphorus will cause an electron drift from the nitrogen $p\pi$-orbital, in spite of its higher ionisation potential, as well as from the lone-pair orbital. The former transfer is, however, accompanied by a loss of π-bonding energy, while the latter gives an increase, and we expect the lone-pair transfer to be the bigger. But it is important to distinguish evidence of a *general* electron drift from nitrogen and evidence of a drift specifically affecting the lone-pair electrons. The most interesting evidence of the latter type concerns the ring angle PNP. Transfer of an electron from the lone pair would result (in an unstrained system) in an increase of the angle to 180°. Less transfer, and the constraints of the ring system, would give smaller increases. Thus, the ring angle at nitrogen should be a sensitive index of the migration of lone-pair electrons.

It is thus significant that we find the angle at nitrogen in the tetrameric molecules to be appreciably greater than 120° (Table 5); in the fluoride, the angle is widened to such an extent that the ring becomes flat, and, in agreement with the expectation of a large electron loss, tetraphosphonitrilic fluoride is so weak a base that it barely dissolves in sulphuric acid.

Other evidence of partial electron transfer from nitrogen, but relating to a general

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[24] Chernick and Skinner, *J.*, 1956, 1401.
[25] Claydon, Fowell, and Mortimer, *J.*, 1960, 3284.

TABLE 5.

Molecular geometry of phosphonitrilic compounds $(PNX_2)_{3,4}$.

	$(PNCl_2)_3$	$(PNMe_2)_4$	$(PNCl_2)_4$	$[PN(NMe_2)_2]_4$	$(PNF_2)_4$
∠P (ring)	119·6°	119·8°	121·2°	120°	122·6°
∠P (exocyclic)	101·9	104	102·8	104	99·9
∠N (ring)	120·0	132	132	133	147
P–N (ring)	1·59 Å	1·60 Å	1·58 Å	1·58 Å	1·51 Å
P–X	1·99	1·80	1·99	1·68	1·51
P–X in POX_3	1·99	1·81	1·99	—	1·52
Ref.*	2, *a*	20, *b*	15, *a*	17	4, 5

* The first reference in each column is to the phosphonitrilic, the second to the phosphoryl compound. (*a*) Badgley and Livingston, *J. Amer. Chem. Soc.*, 1954, **76**, 261. (*b*) Wang, Forsvarets-forskningsinstitutt (Norway) Intern. Rapport IR-K-225 (1960).

transfer rather than one from the lone-pair orbital, is of two kinds. The first is the reduction in frequency of the O–H stretching vibration of phenol by hydrogen-bonding with phosphonitrilic chlorides at ring nitrogen atoms. It is found (Table 3) that the frequency displacement decreases steadily with increase of ring size, indicating reduced electron availability. The phosphorus nuclear magnetic resonance shifts, on the other hand, increase with ring size, the greater shielding of phosphorus being correlated with electron loss from nitrogen; thus electron transfer increases with ring size.

These two complementary indications of increasing transfer of electrons from nitrogen to phosphorus in the π'-orbital system are correlated with a slow increase of the angle at the nitrogen atom in rings of increasing size. The lone-pair orbital changes in hybridisation and shape, and its overlap with the *d*-orbitals at phosphorus goes up, giving easier electron transfer. Observationally, the change in phosphorus chemical shift from the trimer to the tetramer (27 p.p.m.) is greater than any subsequent change. This is associated with an angle change at nitrogen from 120° to 132°. We may anticipate further increases, though smaller ones, in the larger systems. As confirmation of the electron transfer from nitrogen, we note that if the lone-pair electrons are localised by protonation of the phosphonitrilic chlorides in sulphuric acid, the phosphorus shielding constants are reduced in all cases to values near that of the neutral trimeric chloride.[26] In terms of the π'-delocalisation theory, we offer the tentative interpretation that this delocalisation is very weak in the trimeric chloride (consistent with a ring angle at nitrogen close to 120°) and that its increase along the series is measured (indirectly) by the excess of the chemical shift over that of the trimeric chloride.

Any important participation by the in-plane *d*-orbitals $d_{x^2-y^2}$ and d_{xy} of phosphorus, as well as the $d\pi$-orbitals, will lead to a diminished resistance to ring deformation. The availability of several different *d*-orbitals at phosphorus must have the effect that the *total* *d*-overlap of the $p\pi$-orbital at nitrogen, and the lone-pair orbital, change only slowly with change in configuration. Thus the energy penalty incurred in deforming the molecular structure should be much reduced, giving a flexible molecule. The slight deviation of the trimeric chloride molecule in the crystal [2] from its planarity in the vapour phase and in solution [18, 27] shows that it is easily deformable, though this must be attributed mainly to the general weakness of the π-system as compared with benzene. The tetrameric fluoride on the other hand, while flat in the crystal, displays a variety of mobile configurations in solution and in the vapour,[3,28] as a consequence of π'-contributions. For the higher fluorides, the vibrational spectra [29] indicate that a high pseudo-symmetry is attained statistically, some infrared bands being broadened by flexural deformation. Configurational isomerism, as found in normal hydrocarbon rings and chains,[30] has not been detected in

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[26] Gillespie and White, unpublished work.

[27] de Ficquelmont, Magat, and Ochs, *Compt. rend.*, 1939, **208**, 1900.

[28] Chapman and Paddock, *J.*, 1962, 635.

[29] Chapman, Paddock, Paine, Searle, and Smith, *J.*, 1960, 3608.

[30] Kohlrausch and Köppl, *Z. phys. Chem.*, 1934, **26**, *B*, 209; Billeter and Günthard, *Helv. Chim. Acta*, 1958, **41**, 338.

the spectra of the phosphonitrilic fluorides, showing that the particular types of deformation are impermanent. All the phosphonitrilic fluorides have very low viscosities and low activation energies for viscous flow;[29] the activation volume is small and only slightly dependent on ring size. The general result is that both flexure and flexibility increase with ring size; the fluorides are more flexible than the chlorides, the molecular motion involving principally bond torsion.

Hydrocarbons are comparatively inflexible[31] because of the barrier to the mutual displacement of adjacent methylene groups; there is also a high barrier to rotation in the aliphatic disulphides,[32] arising from the interaction of unshared pairs of electrons. In phosphonitrilic derivatives the nitrogen atoms carry no substituents, and the lone-pairs are largely delocalised, especially in the fluorides. In a comparison of phosphonitrilics with molecules which contain these barriers, it is therefore easy to overestimate the intrinsic torsional flexibility of the P–N bond, and the results do not necessarily indicate the near-equality of π- and π'-bonding in these systems, although the presence of both types is clearly established by other lines of argument.

Our conclusion is that phosphorus can act as an acceptor when π-bonded to electronegative elements carrying lone-pairs; consequently, the number of *d*-electrons is greater than simple structural formulæ indicate. In phosphonitrilic derivatives in general, the additional bonding is chiefly π', arising from the delocalisation of lone-pair electrons and (in puckered structures) from d_{xy}–$p\pi$ and $d_{x^2-y^2}$–$p\pi$ interaction; it is weaker than π-bonding. The theory is applicable also to such compounds as siloxanes and the cyclic metaphosphate ions, in which unsaturation in the ring is not formally required; here the new bonds are much weaker. They can be formed only to the extent that the oxygen lone-pair can be delocalised in the π and π' systems.

Molecular Configuration.—For given ring angles the molecular configuration will depend on the balance between optimum auxiliary (π and π') bond formation, and minimum repulsions between non-bonded atoms. In solution and in the vapour phase, the trimeric phosphonitrilic fluoride[3] and chloride[18, 28] are planar, with $\mathbf{D}_{3h}$ symmetry, as expected. The crystal structures of four tetrameric phosphonitrilic derivatives are known and are more informative about the electronic structure. One of them, the fluoride, is planar; the other three are non-planar, with closely similar ring structures.

The known structures of the phosphonitrilic compounds and of some other $(AB)_4$ systems all display the minimum symmetry of a tetrahedron ($\mathbf{S}_4$). The simplest cyclic $(AB)_4$ structure of this symmetry consists of two equal tetrahedra of alternate A and B atoms. This is shown in projection in Fig. 4a, where the signs denote equal displacements above and below the plane of projection. If A = B, this becomes the skeletal (" tub ") structure of cyclo-octatetraene, in which there is strong $p\pi$–$p\pi$ interaction between the adjacent atoms on the same side of the plane, and weak interaction otherwise. This is consistent with the bond lengths in cyclo-octatetraene,[33] which are short when parallel to the plane and long when across it.

Two structures closely related to the $\mathbf{S}_4$ tub structure both belong to $\mathbf{D}_{2d}$. In one, the four nitrogen atoms have been brought into the plane, leaving the phosphorus atoms at the corners of a tetrahedron. In the other the phosphorus atoms are coplanar, and the nitrogens tetrahedral (Fig. 4b). These two structures have the unique property of equalising successive π-interactions round the ring; the two-fold axes ensure that the interactions of a phosphorus atom (A) with the nitrogen atoms (B) on each side are equal, and the inverse four-fold axis equalises them all round the ring. In contrast to configuration (4a), the axes of orbitals on adjacent atoms are never parallel to one another, but make equal angles with their neighbours. If the bond angle at nitrogen is 132° and that at

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[31] Gee, *Proc. Chem. Soc.*, 1957, 111.

[32] Scott, Finke, McCollough, Gross, Pennington, and Waddington, *J. Amer. Chem. Soc.*, 1952, **74**, 2478; Fava, Iliceto, and Camera, *J. Amer. Chem. Soc.*, 1957, **79**, 833.

[33] Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, 1957, **27**, 1311.

phosphorus 120°, as in several examples, the angle between the local z-axes of adjacent atoms is 45°.

There are two other possible symmetrical configurations, the " chair " and the " crown," the first, of some importance to our problem, being illustrated in Fig. 4c. The A and the B sets are each coplanar, and π-overlap can be improved by increasing the symmetry to $\mathbf{C}_{2h}$ (Fig. 4d). The interactions of the π-orbitals on the A atoms of the diads with their neighbours is the same as in configuration (4b), but the B–A–B π-bonds across the symmetry plane are weak, there being a large angle between the normals to the planes at B and those at A in the symmetry plane.

The crown structure ($\mathbf{C}_{4v}$) is made from a planar structure by displacing the nitrogen atoms equally to one side of the common plane until the ring angles assume chosen values.

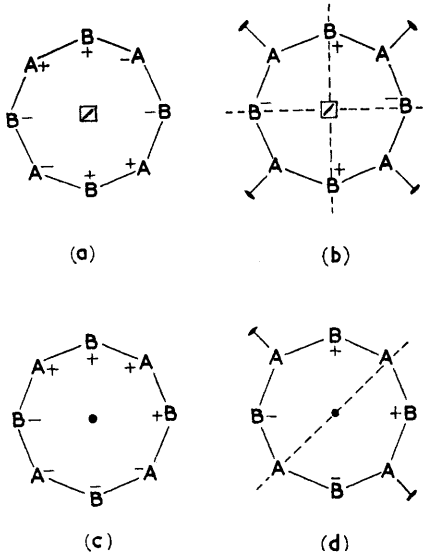

FIG. 4. Projections of the ring structures of $(AB)_4$ molecules, of symmetry $\mathbf{S}_4$(a), $\mathbf{D}_{2d}$(b), $\mathbf{C}_i$(c), and $\mathbf{C}_{2h}$(d). Broken lines denote planes of symmetry. Structures (d) and (b) have two-fold axes through one and two pairs of A atoms, respectively. Signs denote equal displacements above and below the plane.

The overlap of π-orbitals in the crown structure is small, on account of the large angles between adjacent local z-axes.

In the phosphonitrilics the auxiliary bonds may be of both π- and π'-type, and there are special considerations of non-bonded repulsions between exocyclic atoms. Non-bonded repulsions are greatest in the first of the two $\mathbf{D}_{2d}$ structures, in which the nitrogen atoms are coplanar. In this structure two pairs of *trans*-exocyclic atoms fall unacceptably close, and the structure itself must be ruled out. The other $\mathbf{D}_{2d}$ structure (4b) and the crown structure have reduced non-bonded repulsions and are nearly equal to one another in this respect. The smallest repulsions occur in the $\mathbf{S}_4$ tub (4a) and in the chair (4c, d), and they are again nearly equal.* Figs. 5a, b, c, show perspective views along A–A directions for configurations (a) staggered, (b) eclipsed, (c) staggered. Observed configurations may be expected to show some compromise between those favouring strong π-bonding and those minimising non-bonded interactions.

The wide variety of bond possibilities given by the several available d-orbitals of, for example, phosphorus affects the consideration of auxiliary bonding in the various molecular configurations. Both d_{xz}- and d_{yz}-orbitals may take part in π-bonds, and both of the d_{xy}- and $d_{x^2-y^2}$-orbitals in π'-bonds. In the tub structure ($\mathbf{S}_4$) there is good overlap between the nitrogen $2p\pi$-orbital and phosphorus d_{xz} or a linear combination of d_{xz} and d_{yz}. There is also good overlap of the in-plane (π') d-orbitals with the $2p\pi$-orbital of the

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* Both configurations occur in the same crystal of octamethylcyclotetrasilazane.[34]

[34] Smith and Alexander, Abs. Meeting Amer. Cryst. Assoc., 1961.

other neighbour nitrogen, which in turn overlaps another adjacent phosphorus π-orbital. There is still no cyclic conjugation, but one could have three-centre " islands " of conjugation round the ring, analogous to those postulated by Dewar *et al.*,[35] leading to equal bond lengths. Moreover, the configuration has the smallest possible non-bonded repulsions between exocyclic atoms. There are, however, two important qualifications. This electronic structure implies that the d-orbitals are all of roughly equal overlapping power; and lone-pair delocalisation must take place, if at all, into an orbital of phosphorus which has π-character with respect to the local plane, *i.e.*, it must be a linear combination of d_{xz} and d_{yz}.

In both chair and tub structures, there is substantial overlap of the $p\pi$- and lone-pair orbitals of nitrogen with one or more of the d-orbitals of phosphorus, these being assumed equi-energetic. It is thus probable that, if all the d-orbitals were available, the preferred configurations of the tetramers would be the cyclo-octatraene $\mathbf{S}_4$ tub and the chair structure. In fact, these seem to occur only when non-bonded repulsions are the controlling factor, *i.e.*, when auxiliary bonds are weak. The known tetramers of the phosphonitrilics have neither of these structures. The tub is found only in the tetramer of thiazyl fluoride[36] in which, as we shall discuss, lone-pair delocalisation does not occur significantly and the ring bonds are alternately long and short; it appears that only one sulphur d-orbital is used and that the electronic structure is essentially that of cyclo-octatetraene. Thus so far as the phosphonitrilics are concerned the configuration which both minimises non-bonded repulsions and would give best auxiliary bonds from a set of equi-energetic d-orbitals is not realised in any reported example. These conform, more or less closely, to the condition that the overlaps of π-orbitals are as large as possible and are equal round the ring, even at the expense of increased non-bonded repulsions. The structures are, strictly, $\mathbf{S}_4$, but approach $\mathbf{D}_{2d}$ in all cases, the compromise structure adopted being dependent on relative magnitudes of π- and π'-bonding, and on the importance of steric factors. Thus, in the methyl derivative[20] the angle between successive local planes is alternately 31° 4′ and 54° 27′. In the chloride,[15] where a greater π' contribution would be expected, the inequalities in angle are greater, being 15° 34′ and 57° 18′. In the dimethylamido-derivative, feed-back from the exocyclic groups should diminish π'-contributions and reduce the angular inequalities; the similarity of its skeletal structure to that of S_4N_4 has already been noted.[17] The tetrameric fluoride is a special case, as previously seen.

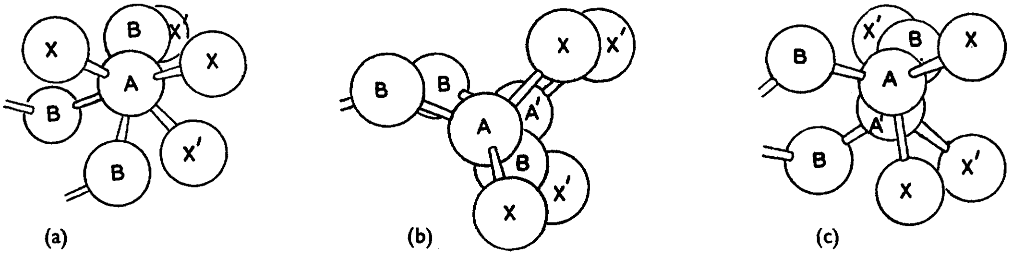

FIG. 5. Views along AA vectors of molecules $(ABX_2)_4$ (a) of symmetry as in Fig. 4a; (b) as in Fig. 4b; (c) as in Fig. 4d. The atoms XX belong to A, X′X′ to A′ behind A. A′ is obscured in (a).

When π-bonding is weaker, the configuration may be controlled by the non-bonded interactions. In " tetrathiazyl " fluoride (tetrafluoro-1,3,5,7-tetrathia-2,4,6,8-tetrazocine)[36] the three bonds to sulphur make angles lying between a right angle and the tetrahedral angle, and the vacant position of the near-tetrahedron is occupied by the lone-pair of sulphur. This prevents any substantial delocalisation of the nitrogen lone-pair, in agreement with the observed angle of 123° at nitrogen. The non-bonded repulsions

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[35] Dewar, Lucken, and Whitehead, *J.*, 1960, 2423.
[36] Wiegers and Vos, *Acta Cryst.*, 1961, **14**, 562.

(including repulsions of the lone-pairs) in a ring with so small an angle at nitrogen are greatly increased in the $\mathbf{S}_4$- or $\mathbf{D}_{2d}$- configuration, and impose the configuration (4a) on the molecule. The π-bond system is then limited to a cyclo-octatetraene-like set of pairs of double-bonded atoms, and the bond lengths alternate. There is no delocalisation in this case. However, there is another important feature of the actual configuration, already briefly referred to. Not only is there a large overlap between the $d\pi$-orbital of sulphur with the $2p\pi$-orbital of one of its neighbour nitrogen atoms, reflected in double-bonding and a short N–S distance, but also the $d_{x^2-y^2}$-orbital is favourably oriented toward the $2p\pi$-orbital of its other neighbour nitrogen. If the $d_{x^2-y^2}$-orbital were of the right size to give energetically important overlap it would also participate in double-bonding and there would be more nearly equal bond lengths round the ring. The fact that it does not is evidence that the $d_{x^2-y^2}$-orbital is not polarised sufficiently by its environment to bond strongly. In this molecule it seems very clear that only π-bonding occurs.

In the tetrametaphosphate ion,[6, 37] the only π-bonding in the ring comes from the delocalisation of lone-pairs on oxygen, induced by the exocyclic π-bonds. It is therefore weak, and the configuration of symmetry $\mathbf{C}_{2h}$ is again controlled by the non-bonded repulsion, in this case of PO_2^-, and the bond lengths [37] are consequently unequal in pairs, those from the phosphorus atoms on the diad axis being shorter (1·584 Å) than those intersecting in the atoms on the mirror plane (1·635 Å). A refinement [38] of an earlier structure [6] shows inequalities in the same sense. π-Bonding must be relatively weak here too.

The effect of decreased π-character is clearly shown by comparing the configuration of octamethylcyclotetrasiloxane [39] (Fig. 4c) with that of the isoelectronic octamethylcyclotetraphosphonitrile (Fig. 4b). The extent of π-bonding in the siloxane can be assessed by comparison of its properties with those of tetra-alkyl orthosilicates, in which the Si–O bonds are probably nearly single. As expected if π-bonding is absent, the angle at oxygen [40] in tetramethyl orthosilicate is small (113°); the availabilities of lone-pair electrons at oxygen [41] (as measured by hydrogen-bonding techniques) are comparable in tetraethyl orthosilicate and orthocarbonate, and the silicate forms a complex with iodine.[42] The base strengths of the dimethylsiloxanes, whether linear or cyclic, are much less,[41] and the angles at oxygen are larger; the increase from hexamethylcyclotrisiloxane [43] (136°) to octamethylcyclotetrasiloxane [39] (142·5°) is accompanied by a reduced availability of lone pairs at oxygen and an increased shielding of the silicon nuclei.[44] At the same time, the average bond energy increases; the trimeric derivative polymerises exothermically [45] ($\Delta H_{\text{pol}} = -3{\cdot}5$ kcal./mole), whereas the polymerisation of the tetramer is almost athermal.[46] Partial donation of the lone-pairs therefore occurs, and it contributes a $p\pi$–$d\pi$ component to the Si–O bond. An increased angle at oxygen is accompanied by a stronger Si–O bond.

The magnitude of this component is nevertheless small, as expected if electron transfer is a pre-condition of π-bonding. $\bar{E}$(Si–O) in hexamethylcyclotrisiloxane (108 kcal.), calculated from its heat of combustion,[47] is only slightly larger than $\bar{E}$(Si–O) in tetramethyl orthosilicate [48] (105 kcal.). The further increase on polymerisation (about 0·8 kcal. per SiO bond) [45,46] must be attributed largely to the relief of steric strain, because bond strength is greater [49] and base strength less [41] in linear siloxanes than in cyclic molecules

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[37] Ondik, Block, and MacGillavry, *Acta Cryst.*, 1961, **14**, 555.

[38] Cruickshank, *J.*, 1961, 5486.

[39] Steinfink, Post, and Fankuchen, *Acta Cryst.*, 1955, **8**, 420.

[40] Yamasaki, Kotera, Yokoi, and Ueda, *J. Chem. Phys.*, 1950, **18**, 1414.

[41] West, Whatley, and Lake, *J. Amer. Chem. Soc.*, 1961, **83**, 761.

[42] Shinoda and Hildebrand, *J. Phys. Chem.*, 1957, **61**, 788.

[43] Peyronel, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1954, **16**, 231.

[44] Holzman, Lauterbur, Anderson, and Koth, *J. Chem. Phys.*, 1956, **25**, 172, and personal communication (P. C. L.).

[45] Piccoli, Haberland, and Merker, *J. Amer. Chem. Soc.*, 1960, **82**, 1883.

[46] A. J. Barry, personal communication, quoting the work of O. K. Johannson.

[47] Tanaka, Takahashi, Okawara, and Watase, *Bull. Chem. Soc. Japan*, 1955, **28**, 15.

[48] Tanaka and Watase, *J. Chem. Phys.*, 1954, **22**, 1268.

[49] Tanaka, *Bull. Chem. Soc. Japan*, 1960, **33**, 282.

containing the same number of siloxane units. Steric strain is likely to be more important in these molecules than in phosphonitriles, first, because the occurrence of π-bonding in them depends on the delocalisation of lone-pairs and therefore on the attainment of a large angle at oxygen and, secondly, because the π-electrons would be more closely held to the more electronegative oxygen, their mutual repulsion and angular separation being thereby the greater. The two effects are balanced; steric strain cannot arise without π-character.

As a consequence of the weakness of the π-system, octamethylcyclotetrasiloxane is centrosymmetrical,[39] the average ring angle at silicon being restricted to 109° by the ring strain imposed at oxygen. The effect is greater in the trimeric molecule,[43] in which the OSiO angle is 104°. Although the average Si–O bond length in octamethylcyclotetrasiloxane is short (1·64 Å) compared with the corrected sum of the covalent radii (1·76 Å), it is the same in tetramethyl orthosilicate,[40] and it is evidently not a good measure of changes in π-character. It is, therefore, not surprising that the ring bonds are equal in length, within experimental error. Finally, the structure of sulphur nitride itself[50] is forced into a configuration of symmetry $\mathbf{D}_{2d}$ by the formation of weak bonds between p_z-orbitals of alternate sulphur atoms.[51] The $d\pi$–$p\pi$ interactions and bond lengths are thereby automatically equalised.

For π'-bonding, similar deductions can be made for the different molecular symmetries, but, because the π- and π'-orbitals are mutually perpendicular, each is strong where the other is weak. In configuration (Fig. 4a), for instance, we have noted that p_z interacts equally, and strongly, with $d_{xy}(\pi)$ on one side, and $d_{x^2-y^2}(\pi')$ on the other. If the two orbitals were energetically equal, we should expect them to participate equally and equalise the bond lengths, especially as exocyclic interactions are small. The inequalities observed in the bond lengths of both tetrathiazyl fluoride and of the tetrametaphosphate ion, and the relative positions of the long and the short bonds in the two molecules, show that whether the bonds are primary or induced by delocalisation of lone-pair electrons, π-bonding is stronger than π'-bonding.

From a study of the observed configurations, we therefore draw the two conclusions: (1) π-bonding is stronger than π'-bonding; and (2) configurations which favour strong π-bonding and those which minimise the repulsion of non-bonded groups are mutually exclusive, a compromise between them being made differently in different molecules.

π-Bonding to Exocyclic Groups.—We have so far considered only π- and π'-bonds within the ring, but some interaction must also occur with the exocyclic groups, to the extent that they are able to act as electron donors; in this respect they compete with donor atoms in the ring. There is no useful distinction between exocyclic π- and π'-bonding, because the local symmetry about the bond axis is often close to $\mathbf{C}_{3v}$, in which the two are degenerate. Of the phosphorus orbitals involved, d_{z^2} is probably the major contributor.

The strongest exocyclic π-bonding is expected in amido-derivatives, by donation from the nitrogen $2p\pi$-lone-pair. The length of the exocyclic P–N bond in the refined[17] structure of the octadimethylamidotetraphosphonitrile (1·68 Å) corresponds to appreciable double-bonding, and the dimethylamido-group is flatter than in the parent amine. Both are consequences of electron release from the lone-pair; correspondingly, the frequency of the E' mode of the hexakisdimethylamidotriphosphonitrile corresponding to ring stretching is 23 cm.$^{-1}$ less than in the chloro-compound (Table 4) although the electronegativities of nitrogen and chlorine are usually taken to be the same. π'-Bonding in the ring is proportionately reduced, and the electron density on the ring-nitrogen atom increased, by the exocyclic feed-back, so that the fully substituted amine derivatives are comparatively strong bases.[52] The feed-back also accounts[53] for orientational effects in the amine

[50] Clark, *J.*, 1952, 1615.
[51] Lindqvist, *J. Inorg. Nuclear Chem.*, 1958, **6**, 159.
[52] Ray and Shaw, *Chem. and Ind.*, 1961, 1173.
[53] Chapman, Paine, Searle, Smith, and White, *J.*, 1961, 1768.

substitution reactions of triphosphonitrilic chloride.[54] However, although the exocyclic P–N bonds are shorter than pure single bonds, they are still much longer than the ring P–N bonds (1·58 Å). The difference cannot all be put down to the different hybridisation of the cyclic and exocyclic nitrogen atoms, and it seems clear that $p\pi$–$d\pi$ bonding is much stronger in the ring bonds than in the exocyclic ones, even in this particularly favourable case.

Exocyclic π-bonding appears to be weaker in other phosphonitrilic derivatives. In the methyl derivatives π-bonding would necessarily be hyperconjugative; analogous examples are the easy elimination of hydrogen chloride from 2-chloroethyl phosphonates [55] and the exchange of the hydrogen atoms of the tetramethylphosphonium ion with heavy water,[56] and some interaction of the same sort may be expected in the phosphonitriles. For the fluorides, measurements of fluorine chemical shifts should be sensitive to electron donation and the formation of a double bond. The observed changes [26] in shift are small (8 p.p.m. from trimer to undecamer) and in the sense of a decrease in the bigger rings, indicating a slowly increasing π-bonding. The π-bonding in all cases is undoubtedly small, and the relatively large increase in electron density on phosphorus with increasing ring size indicated by a difference of 50 p.p.m. in the phosphorus resonance between the trimer and the undecamer is to be associated, as in the chlorides listed in Table 3, with lone-pair donation from the ring-nitrogen atoms rather than from the exocyclic atoms.

The P–X bond lengths in a series of phosphonitrilic derivatives are similar to those in the related phosphoryl compounds (Table 5), but the σ- and π-effects in such bonds have not yet been clearly distinguished. Thermochemically, $\bar{E}$(P–X) + $\bar{E}$(P–N) is found [12] to increase with the electronegativity of X, but the division of the sum between the two components has to be made on structural grounds.

In all cases, the ring angle at phosphorus is close to 120°, indicating, by analogy with the structures of simple phosphorus compounds, that the π-bonds are concentrated in the ring. The small changes in ring angle (Table 5) also suggest that ring π-bonding predominates increasingly over exocyclic π-bonding with increasing electronegativity. The same conclusion follows from a study of changes in the exocyclic angles; there appears to be the least π-character in the P–F bonds. The variation suggests that the increased bond strength is in fact a σ-effect; but these are clearly marginal differences, and independently of them we can draw the main conclusion that the π-electrons in the phosphonitrilic derivatives are mainly in the ring system.

In the tetrametaphosphate ion,[37] the primary π-bonding is to exocyclic oxygen, and the exocyclic angles at phosphorus (120°, 123·5°) are consequently larger than the angle in the ring. Furthermore, the ring angle is larger (108·5°) at the phosphorus atoms which are the more strongly bound within the ring than at the atoms in the symmetry plane of the molecule (100·5°). This is consistent with our interpretation of the effect of π-bonding on inter-bond angles.

In the siloxanes, π-bonds can be formed only to the extent that lone-pair electrons on the ring atoms are delocalised, competitively with electrons from the exocyclic groups. The exocyclic bond angles at silicon (average 107° in three dimethylsiloxane structures) [39, 43, 57] are small, and suggest that π-bonding is not a major feature. The Si–C bond lengths are those expected for single bonds, and the solution chemistry of the dimethylsiloxanes gives no evidence of hyperconjugative contributions.

Our conclusion on the distribution of π-orbitals between the ring and exocyclic groups is that to a first approximation the π-bonds are where they appear to be on the basis of simple structural formulæ, additional π-bonds being provided elsewhere by the

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[54] Becke-Goehring and John, *Angew. Chem.*, 1958, **70**, 657; Ray and Shaw, *Chem. and Ind.*, 1959, 53; Becke-Goehring, John, and Fluck, *Z. anorg. Chem.*, 1959, **302**, 103.

[55] Ford-Moore and Williams, *J.*, 1947, 1465; Kosolapoff, *J. Amer. Chem. Soc.*, 1948, **70**, 1971.

[56] Von E. Doering and Hoffmann, *J. Amer. Chem. Soc.*, 1955, **77**, 521.

[57] Roth and Harker, *Acta Cryst.*, 1948, **1**, 34.

delocalisation of other electrons, principally lone-pairs. In the case of greatest interest at present, the phosphonitrilic derivatives, it seems likely that exocyclic π-bonding is in general of minor significance.

d-*Orbital Distribution and Delocalisation.*—According to the arguments in preceding sections, in cases of relatively strong auxiliary binding, ring π-bonding is stronger than exocyclic π-bonding, and, within the ring, π-bonding is stronger than π'-bonding. In the tetrathiazyl fluoride molecule, the tetrametaphosphate ion, and octamethylcyclotetrasiloxane, the configuration is controlled by non-bonded interactions, the π-bonds being localised, and steric strain playing an important part in the siloxanes.

The greater stability of the siloxane unit in a chain than in a ring of the same number of units [49] raises the problem of the comparative stability of rings and chains in the phosphonitriles. Strain is less in the chains, and this will offset the expected greater π-electron stability in rings. Thermochemical data on the point are lacking, but there is an interesting observation that the nuclear magnetic resonance spectra of the linear chlorides [26, 58] show a greater shielding at phosphorus in short chains than in rings of the same number of units. This can be explained by greater lone-pair delocalisation, with the implication of greater π'-bond energy in the chain molecules, or by partial transfer of the nitrogen $p\pi$-electron to phosphorus. Such a transfer must be accompanied by a loss of delocalisation energy, and since in a linear molecule the delocalisation energy is less, electron transfer is easier in a chain than in a cyclic molecule. It is thus to be expected that phosphorus shielding is greater in the linear molecules. In any case, the ring angle at phosphorus is invariably greater than at silicon, showing the relatively smaller importance of steric effects in phosphonitriles.

π-Bonds can be formed from either d_{xz}- or d_{yz}-orbitals, or both. If these two alone were used, and used equally, the system of bonds in the ring divides into a series of 3-centre PNP " islands," the heat of formation of a unit of the ring being independent of ring size.[35] It is difficult to reconcile this with the thermochemical evidence we have discussed. Further, the theory cannot account for the observed ring flexure and flexibility, since two adjacent " islands " are hinged by the z-axis, so that the z-axes of all the atoms should remain parallel. It thus becomes clear that the main new theoretical feature to be added to the original suggestion of $p\pi$–$d\pi$ delocalisation is not that there are *two* $d\pi$-orbitals participating equally, but that some contribution by at least four d-orbitals must be allowed (the fifth d orbital, d_{z^2}, contributes to exocyclic π-bonding). The four do not, however, contribute equally. Thus the in-plane d_{xy}- and $d_{x^2-y^2}$-orbitals accept electrons from the nitrogen lone-pairs to some extent, but when it is sterically possible for them to replace the $d\pi$-orbitals in the π-system they do so only to a reduced extent.

If the contributions of d_{xz} and d_{yz} are unequal, then the π-system must be cyclically delocalised. The three effects of lone-pair delocalisation, improved overlap with increasing ring size, and decreasing strain energy can now be recognised as contributors to the change of apparent π-electron energies with ring size, so weakening this line of experimental evidence for the reality of delocalisation stability. Chemical evidence is at present limited, though it is consistent with our argument that successive substitution of chlorine atoms in tetrameric phosphonitrilic chloride occurs in the *trans*-position.[59] The strong interactions between the vibrations of remote P–N bonds in the trimeric chloride and fluoride [19] confirm the existence of a delocalised system over at least four P–N bonds, in agreement with the orbital distribution deduced above.

The results taken together emphasise that the distribution of d-electrons is sensitively dependent on detailed environment, and they justify the basic assumption of d-orbital participation. The distribution is not controlled solely by symmetry, but also by interactions which vary from molecule to molecule and can have large effects on molecular

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[58] Lund, Paddock, Proctor, and Searle, *J.*, 1960, 2542.

[59] John, Moeller, and Audrieth, *J. Amer. Chem. Soc.*, 1960, **82**, 5616.

structure; in all cases the discrimination of finer causes, and the assignment of detailed effects to the *d*-electrons, remain a matter for experimental study.

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