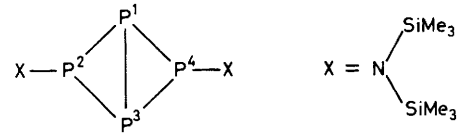
Substituent Effects on the Bonding Properties in Cyclotriphosphanes and Related Compounds. Polarization of Hückel *versus* Möbius Orbitals

Wolfgang W. Schoeller and Thomas Dabisch
Fakultät für Chemie der Universität Bielefeld, Postfach 8640, D-4800 Bielefeld, Federal Republic of Germany

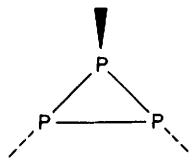
In inorganic three-membered ring systems containing ring members (P, N, O, or S) with a lone pair, a cyclic conjugated Hückel system is formed. This favours a perpendicular over a bisected orientation of electron-releasing or electon-attracting substituents, causing bond alterations opposite to those predicted previously by Hoffmann and Günther on the basis of the Walsh model.

In the bicyclo[1.1.0]tetraphosphabutane (1) [X = $N(SiMe_3)_2$] the central bond, P(1)–P(3), is considerably shortened compared with the peripheral bond(s), P(1)–P(2) [P(1)–P(4) *etc.*].[1] This has been ascribed recently [2] to an increase in olefinic character at the central bond, due to donation of electron density from the lone pairs at the amino-groups into the central bond orbitals.

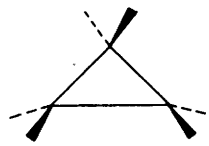
Herein we present theoretical evidence to show that these findings are of general importance for the effects of substituents on the structures of cyclotriphosphanes (2) and their derivatives.[3] Moreover we will show that our predictions are opposite to the Walsh model,[4] which has been invoked in the discussion of substituent effects on the structure of cyclopropane (3).



(1)



(2)



(3)

Results and Discussion

If we consider the system of valence orbitals of (2) in comparison with that of (3) (Figure), in the former the highest occupied and lowest unoccupied molecular orbitals occur in pairs of almost equal energy, while in the latter the frontier orbitals comprise the familiar set of Walsh orbitals (W).[4] In π_2 the PH bonds are bonding, in π_3* they are antibonding. π_1 Corresponds to W_2 contaminated with the corresponding Hückel type (π-type) orbital. Valence orbitals of (2) *versus* (3) can also be revealed using an Extended Hückel and *ab initio* STO-3G calculation but are not summarized here.[5,†]

If we then consider the interaction of a substituent p orbital either in a bisected [as in (2a)] or a perpendicular conformation [as in (2b)], interacting with the frontier orbitals of (2), then the substituent effects on the bond length alterations are as follows. (i) Perpendicular conformation (2b): (*a*) electron attracting substituents reduce the electron density in π_2. Thus the bonds P(1)–P(2) and P(1)–P(3) will be strengthened and P(2)–P(3) weakened; (*b*) electron releasing substituents do the opposite. They donate electron density into π_3*, increasing the bonding overlap between P(2) and P(3). Concomitantly, the other ring bonds will be loosened. (ii) Bisected conformation (2a): (*a*) electron releasing or (*b*) electron attracting substituents increase or decrease the antibonding interaction between P(2) and P(3).

Therefore a bisected donor orbital increases the antibonding overlap between P(2) and P(3) in a Möbius system (mixing in of W_3*), while a perpendicular donor orbital increases the bonding overlap in a Hückel system.‡ Acceptor substituents have the opposite effect. It must be noted that for symmetry reasons a perpendicular oriented donor (acceptor) orbital does not interact with the system of Walsh orbitals.

The qualitative predications are supported by energy-optimized MNDO [6] and *ab initio* STO-3G [7] calculations on various donor (CH_2^-,NH_2) and acceptor (CH_2^+,BH_2) substituted structures of (2) and (3). Both methods are in agreement with each other. Details of the former are presented in the Table.

According to the calculations, perpendicular donors and acceptors exert a significant influence on the equilibrium geometry of the parent cyclotriphosphane (2). On the contrary, in the corresponding cyclopropane system (3) such effects on the bond lengths are negligible. Here a bisected conformation is favoured over a perpendicular one.

It must be noted that the MNDO method yields bond distances which are too short for (2) (see Table). This is a general shortcoming of minimal basis-set calculations.§ Since it is our concern to discuss variations in bond lengths rather than absolute values this does not affect the conclusions reached here.

The (perpendicular) π-donation effect on (2), *i.e.* weakening (w) of the adjacent bonds and strengthening (s) of the opposite bond is shown in the structures (4) and (5).

In accordance with energy-optimized MNDO calculations ¶

† For various photoelectron spectra of substituted cyclotriphosphanes see ref. 5.

‡ For the differentiation between a Möbius and a Hückel system see W. Kutzelnigg, 'Einführung in die Theoretische Chemie,' Verlag Chemie, Weinheim, 1978.

§ See, for example, J. B. Collins, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Chem. Phys.*, 1976, **64**, 5142 (especially Table 2). A detailed test of various basis sets for *ab initio* SCF calculations indicates that they must be at least of double zeta quality including *d* orbitals at P (polarization functions) in order to reproduce P–P bond lengths properly (W. W. Schoeller, unpublished work).

¶ The optimized bond lengths (Å) are, for (4), P(1)–P(2) = 2.109, P(1)–P(3) = 2.035, P(2)–P(3) = 2.037; and for (5), P(1)–P(3) = 1.999, P(1)–P(2) = 2.068.

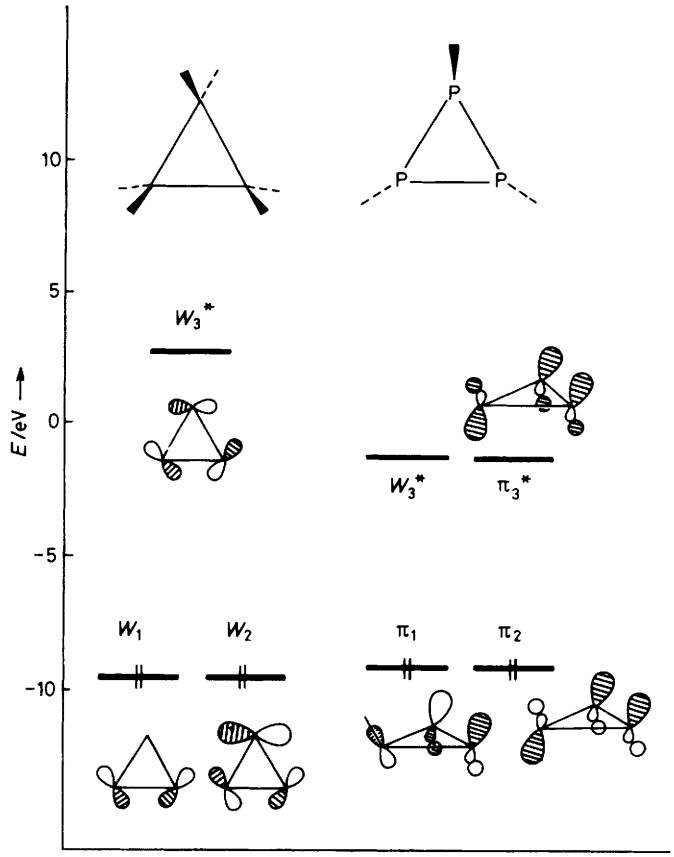
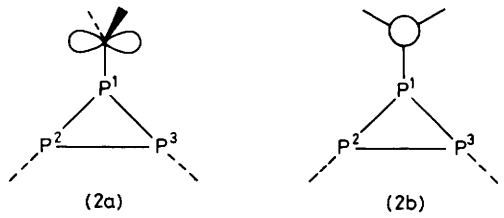


Figure. Orbital diagram of the valence orbitals of cyclotriphosphane (2) and cyclopropane (3). Orbital energies (in eV; 1 eV $\approx 1.60 \times 10^{-19}$ J) are obtained from MNDO calculations



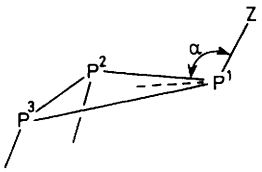
the structural elucidation [1] on (1) reveals a substantially shorter central bond, P(1)–P(3), compared with the peripheral bonds [*e.g.* P(1)–P(2)]. For the same reasons the calculations predict a strongly elongated bond * for (4). In an analogous way the effect of acceptor substituents can be rationalized.

Our theoretical findings present a new approach to the theory of substituents acting at a three-membered ring moiety, such as in (2). A perpendicular orientation of the electron-releasing or electron-attracting substituents is preferred over a bisected orientation, and causes bond alterations opposite to the expectations of the Walsh model. Our findings are based on symmetry arguments, *i.e.* the orbitals of a Hückel *versus* a Möbius system. In more general terms, the valence orbitals of a three-membered ring are isolobal [8] to a Hückel [for (2)] or a Möbius [for (3)] system.

* The optimized bond lengths (Å) are, for (4), P(1)–P(2) = 2.109, P(1)–P(3) = 2.035, P(2)–P(3) = 2.037; and for (5), P(1)–P(3) = 1.999, P(1)–P(2) = 2.068.

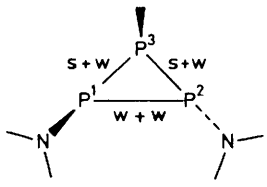
† When X = S or O and Y = PH this is substantiated by MNDO calculations.

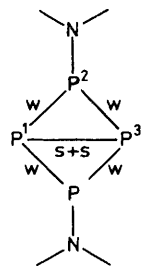
Table. Equilibrium geometries of substituted cyclotriphosphanes in a bisected (bis) or perpendicular (per) conformation of the *p* orbital (at the substituent Z) with respect to the three-membered ring moiety. Bond lengths are in Å, bond angles in degrees. The values for the derivatives (Z ≠ H) refer to changes in bond lengths with respect to the parent compound (Z = H). Values in parentheses correspond to the bonding parameters for cyclopropane and derivatives

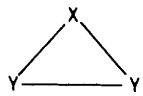


Substituent		P(1)–P(2)	P(2)–P(3)	α	P(1)–Z	ΔE *
H		2.03	2.04	104.7	1.34	
		(1.53)	(1.53)	(124.6)	(1.10)	
CH_2^+	(bis)	0.08	−0.04	111.1	1.64	37.4
		(0.09)	(−0.05)	(128.4)	(1.40)	(0.0)
	(per)	−0.03	0.08	163.4	1.59	0.0
		(0.02)	(−0.01)	(134.1)	(1.44)	(51.1)
CH_2^-	(bis)	0.06	−0.02	112.7	1.59	14.8
		(0.04)	(−0.01)	(132.1)	(1.41)	(0.0)
	(per)	0.05	−0.05	119.9	1.58	0.0
		(0.02)	(−0.01)	(131.1)	(1.42)	(19.9)
NH_2	(bis)	0.02	−0.01	110.9	1.60	10.5
		(0.02)	(0.0)	(127.6)	(1.41)	(0.2)
	(per)	0.04	−0.03	112.4	1.59	0.0
		(0.02)	(0.0)	(126.6)	(1.41)	(0.0)
BH_2	(bis)	0.01	−0.01	111.2	1.80	2.4
		(0.02)	(−0.01)	(129.0)	(1.52)	(0.0)
	(per)	−0.02	0.02	116.3	1.79	0.0
		(0.01)	(0.0)	(133.8)	(1.53)	(4.4)

* Relative energies in kJ mol^{-1}.







(6) (X,Y = PH, S, or O)

On this basis, the considerations which we have outlined by numerical calculations for the case of (2) [*cf.* (3)] and its derivatives hold equally well for other inorganic ring systems, for example (6), providing the ring atoms possess lone pairs which span a cyclic conjugated system.†

References

1 E. Niecke, R. Rüger, and B. Krebs, *Angew. Chem.*, 1982, **94**, 553; *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 544.

2 W. W. Schoeller and C. Lerch, *Inorg. Chem.*, in the press.
3 M. Baudler, *Angew. Chem.*, 1982, **94**, 520; *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 492 and refs. therein.
4 R. Hoffmann, *Tetrahedron Lett.*, 1970, 2907; H. Günther, *ibid.*, p. 5173; S. Durmaz and H. Kollmar, *J. Am. Chem. Soc.*, 1980, **102**, 6942.
5 A. H. Cowley, M. J. S. Dewar, M. Lattmann, J. L. Mills, and M. McKee, *J. Am. Chem. Soc.*, 1978, **100**, 3349; R. Gleiter, M. C. Böhm, and M. Baudler, *Chem. Ber.*, 1981, **114**, 1004.
6 M. J. S. Dewar, M. L. McKee, and H. S. Rzepa, *J. Am. Chem. Soc.*, 1978, **100**, 3607.
7 W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 1969, **51**, 2657 and subsequent publications.
8 M. Elian, M. M.-L. Chen, D. M. P. Mingos, and R. Hoffmann, *Inorg. Chem.*, 1976, **15**, 1148; R. Hoffmann, *Angew. Chem.*, 1982, **94**, 725; *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 711.

Received 4th February 1983; *Paper* 3/165