Bonding Properties of Diphosphacyclobutadienes

Tamás Veszprémi[a], Rolf Gleiter*[a], Ekkehard Fluck[b], Jürgen Svara[c], and Bernhard Neumüller[c]

Organisch-Chemisches Institut der Universität Heidelberg[a],
Im Neuenheimer Feld 270, D-6900 Heidelberg

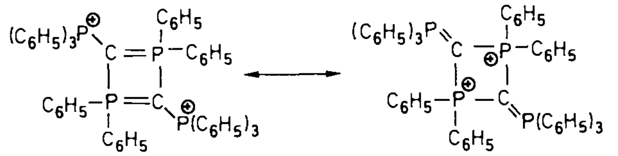
Gmelin-Institut für Anorganische Chemie der Max-Planck-Gesellschaft[b],
Varrentrappstraße 40/42, D-6000 Frankfurt/M. 90

Institut für Anorganische Chemie der Universität Stuttgart[c],
Pfaffenwaldring 55, D-7000 Stuttgart 80

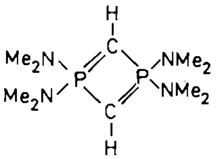
Received June 30, 1988

The He(I) photoelectron (PE) spectra of the diphosphacyclobutadienes 2 and 3 have been recorded. The interpretation of the first PE bands is based on SCF-MO calculations (MNDO method). It is found that the first two bands correspond to π-MOs which are mainly localized in the four-membered ring. The first two bands are shifted towards higher energy in the PE spectrum of 3; we ascribe this to an electron transfer from the four-membered ring in 3 to the phenyl substituents.

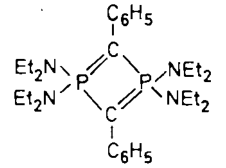
Although 1,2- and 1,3-diphosphetanes are well-known compounds[1-5)], the first diphosphacyclobutadiene derivative **1** was published in 1977[6)]. The surprisingly great stability of this compound was explained by the electron acceptor substituents which are able to reduce the electron density of the ring.



1



2



3

Therefore, the recent papers on the synthesis and structure of 1,1,3,3-tetrakis(dimethylamino)-1λ^5,3λ^5-diphosphete (**2**)[7,8)] and its phenyl derivative **3**[9)] may appear somewhat puzzling. The four-π-electron system should have antiaromatic character according to Hückel's rule, causing a reduction of symmetry. However, X-ray diffraction measurements prove planar four-membered frames with four equal P–C bonds. The P–C bond lengths in **2** with 1.725 Å and in **3** with 1.746 Å are similar to a regular P=C double bond[7,9)].

The bonding, stability, and structure of the first and only isoelectronic cyclodiphosphazene which is known as yet, namely, 2,2,4,4-tetrakis(diisopropylamino)-1,3,2λ^5,4λ^5-diazadiphosphete[10)], have been studied by ab initio calculations in recent work[11)].

It is established that the electronic structure of the planar ring is dominated by $-P^+-N^--$ charge alternation in good agreement with the "island" model[12)] of cyclic phosphonitriles which assumes weakly interacting three-centered π bonds including two phosphorus atoms and a central nitrogen atom instead of a delocalized π system. To obtain more information on diphosphacyclobutadienes we have studied the He(I) photoelectron (PE) spectra of **2** and **3**.

Results and Discussion

The PE spectra of **2** and **3** are shown in Figure 1. To interpret the spectra we used the semiempirical MNDO quantum-chemical method[13)] assuming the validity of Koopmans' theorem[14)]. Two different sets of geometrical parameters were used. The first was based on an X-ray diffraction measurement[7,9)] and the other was calculated by the MNDO method optimizing the parameters with respect to the heat of formation. Some important bond lengths and angles are summarized in Table 1. Instead of NEt_2 groups for the calculation of **3**, a simplified model was applied using NH_2 groups.

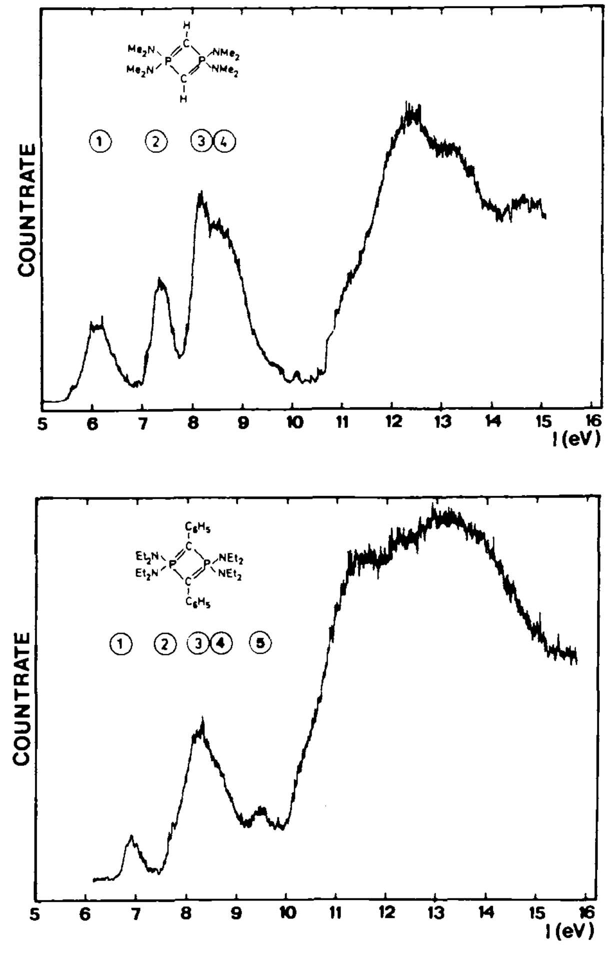


Figure 1. PE spectra of **2** and **3**

0009–2940/88/1111–2071 $ 02.50/0

The calculated and observed ionization energies and the assignments of the photoelectron bands are listed in Table 2.

Table 1. Geometrical parameters adopted for **2** and **3**

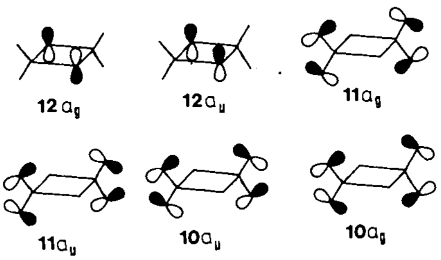
Parameter	Experiment **2**[7]	Experiment **3**[9]	Calculated **2**	Calculated **3**
P–C [Å]	1.725	1.746	1.695	1.710
P–N [Å]	1.681	1.673	1.726	1.686
C–P–C [deg]	91.4	89.5	92.9	90.2
N–P–N [deg]	97.8	100.3	96.1	102.3

Table 2. Observed and calculated ionization energies [eV]

Compound	Observed	Calculated IE a[a]	Calculated IE b[b]
2	6.1	7.41 b_{2g}, π_-	7.69 π_-
	7.4	8.13 b_{3u}, π_+	8.15 π_-
		9.65 b_{1g} n_N	9.76 n_N
		9.66 b_{2u} n_N	10.00 n_N
	8.0–9.1	9.68 b_{3u} n_N	10.21 n_N
		9.80 a_g n_N	10.66 n_N
		12.27 b_{1u} σ	12.95 σ
		12.34 b_{3g} σ	13.00 σ
3[c]	6.9	7.41 π_-	
	7.6	7.80 π_+	
		9.12 π_{ph}	
	7.7–8.9	9.12 π_{ph}	
		9.96 π_{ph}	
		10.07 π_{ph}	
	9.5	11.15 n_N	
		11.24 n_N	
		12.65 n_N	
		12.68 n_N	

[a] Using experimental geometry. — [b] Using the geometry of the most stable conformer. — [c] Calculated with NH_2 groups.

The PE spectrum of **2** contains three well-separated bands at 6.1, 7.4 and between 8.0 and 9.1 eV. The calculations predict that the first two bands originate from the antibonding $12a_g(\pi_-)$ and bonding $12a_u(\pi_+)$ combinations of the out-of-plane p-orbitals of the carbon atoms in the four-membered ring. It should be noted that the first PE band in the spectrum of trimethylmethylenephosphorane (which may be considered as a half four-membered ring) is at 6.81 eV[15], nearly the average of our observation. The third broad band can be assigned to four different combinations of lone-pair orbitals at the N atoms as shown schematically below.



This assignment is supported by comparison of the relative intensities of the first three bands which show roughly a 1:1:4 ratio.

According to the calculations, the four-electron π-system of the four-membered ring has a special electron distribution in which the phosphorus atoms have large positive and the carbon atoms large negative charges. Therefore, the highest occupied two MOs correspond to lone pairs which are localized on the carbon atoms. This is in good agreement with ab initio calculations carried out on cyclophosphazenes[11]. The calculated atomic and group charges are listed in Table 3. To study the effect of rotation of the NMe_2 groups, we carried out some model calculations using NH_2 groups. Maintaining the optimized geometry of P–N bonds and the cyclic framework, we examined the conrotatory rotation of the four NH_2 groups. In Figure 2 the variation of the total energy (E_t) and the energy of the HOMO are plotted as a function of the twist angle (Θ).

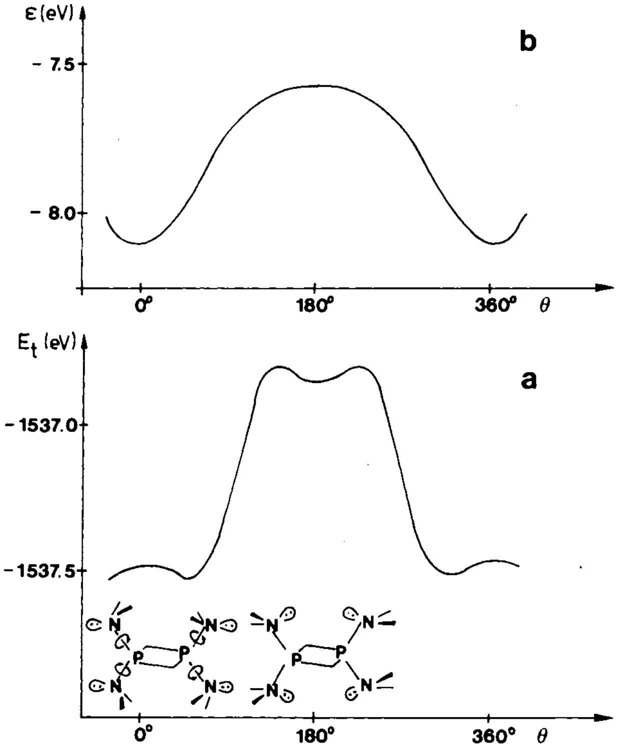


Figure 2. Variation of the total energy (a) and of the HOMO (b) as a function of the rotation angle (Θ) around the P–N bond. The calculations were carried out with the MNDO method.

Table 3. Calculated net atomic and groups charges (MNDO) using the experimental geometries

Group	Compound **2**	Compound **3**
P	0.92	0.86
C	−0.73	−0.60
N	−0.49	−0.35[a]
H	0.10	–
NMe_2	−0.14	−0.10[a]
Phenyl	–	−0.06

[a] Using NH_2 groups (see text).

Since the amino groups are not planar (both experiment and calculations give pyramidal $P-NH_2$ and $P-NMe_2$ groups) the rotation is symmetrical about $\Theta = 180°$. The energy difference between the conformation with lowest and highest energy is found to be $E \approx 69.4$ kJ/mol (16.6 kcal/mol). The energy minimum occurs at a twist angle of $\Theta \approx 45°$ which is very similar to the experimentally found conformation of **2**[7]. Around the minimum, the total energy varies only slightly. However, the change of the HOMO is considerable with the variation of Θ. Therefore, although the rotation of NMe_2 groups is more complicated due to the steric constraints of the methyl groups, they can probably turn in the gas phase covering a considerable angle and thus causing a broadening of the respective photoelectron bands.

The most conspicuous difference between the PE spectra of **2** and **3** is that the first and second ionic states of **3** are shifted to higher energy as compared to the first two ionic states of **2**. This observation can be rationalized by assuming a transfer of negative charge from the ring C-atoms to the phenyl groups. This will cause a considerable stabilization of the ionic states which arise from ionizations from π_+ and π_-. These arguments are confirmed by considering the atomic and group charges (Table 3). It can be seen that the net charge at the C atom of the ring decreases in **3** as compared to **2** and that the phenyl group accomodates about 6% of the negative charge. A similar effect was found by studying the PE spectrum of benzylidenetrimethylphosphorane[15, 16]. From the viewpoint of the phenyl group, the PCPC moiety can be considered as an electron donor substituent with lone electron pairs of extremely low IE.

Unfortunately, the exact positions of the π orbital signals of the phenyl groups cannot be located in the broad, structureless band of the PE spectrum between 7.7 and 8.9 eV, because this band contains the ionizations from four lone-pair combinations of the nitrogens, too.

We are grateful to *Alexander Flatow* for recording the PE spectra. We thank the *Fonds der Chemischen Industrie* and the *BASF Aktiengesellschaft*, Ludwigshafen, for financial support. T.V. thanks the *Alexander von Humboldt* foundation for a stipend.

Experimental

The syntheses of **2** and **3** have been described in the literature[7–9]. The He(I) photoelectron spectra of the analytically pure compounds have been recorded on a Perkin-Elmer PS 18 instrument. The recording temperatures were: **2**: 80°C and **3**: 160°C. The calibration was carried out with Ar and Xe.

CAS Registry Numbers

2: 103678-18-8 / **3**: 112313-40-3

---

[1] W. Mahler, *J. Am. Chem. Soc.*, **86** (1964) 2306.

[2] T. C. Wallace, R. West, A. H. Cowley, *Inorg. Chem.*, **13** (1974) 182.

[3] A. H. Cowley, M. J. S. Dewar, D. W. Goodman, M. C. Padolina, *J. Am. Chem. Soc.*, **96** (1974) 3666.

[4] G. Becker, W. Becker, G. Uhl, *Z. Anorg. Allg. Chem.*, **518** (1984) 21.

[5] R. Appel, V. Barth, F. Knoch, *Chem. Ber.*, **116** (1983) 938.

[6] R. Appel, F. Knoll, H. D. Wihler, *Angew. Chem.*, **89** (1977) 415.

[7] J. Svara, E. Fluck, H. Riffel, *Z. Naturforsch. Teil B*, **40** (1985) 1258.

[8] B. Neumüller, E. Fluck, *Phosphorus Sulfur*, **29** (1986) 23.

[9] E. Fluck, B. Neumüller, H. Riffel, *Z. Naturforsch.*, im Druck.

[10] A. Baceiredo, G. Bertrand, J.-P. Majoral, G. Sicard, J. Jaud, J. Galy, *J. Am. Chem. Soc.*, **106** (1984) 6088.

[11] G. Trinquier, *J. Am. Chem. Soc.*, **108** (1986) 568.

[12] M. J. S. Dewar, E. A. C. Lucken, M. A. Whitehead, *J. Chem. Soc.*, **1960**, 2423.

[13] M. J. S. Dewar, W. W. Thiel, *J. Am. Chem. Soc.*, **99** (1977) 4899, 4907.

[14] T. Koopmans, *Physica*, **1** (1934) 104.

[15] K. A. Ostoja Starzewski, H. tom Dieck, H. Bock, *J. Organomet. Chem.*, **65** (1974) 311.

[16] H. Bock, *Pure Appl. Chem.*, **44** (1975) 343.

[174/88]