

PREPARATION, PROPERTIES AND MOLECULAR STRUCTURE OF HEXAPHENOXY-CYCLOTRIPHOSPHAZENE

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By

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As was described in our earlier paper [1], hexaphenoxy-cyclotriphosphazene possesses excessively good thermal and thermo-oxidation properties. We wish to support this fact by the study of the molecular structure of the compound. The purpose of the studies was mainly to decide whether electrons in the molecules of hexaphenoxy-cyclotriphosphazene are delocalized—that is their quantum mechanical motion extends to six phenoxy rings and also the cyclotriphosphazene ring—or the phenoxy groups and cyclotriphosphazene ring form separate conjugated systems. Our experiments were based on spectrophotometric measurements in the ultraviolet range, and we have tried to arrive to conclusions as regards molecular structure on the basis of quantum chemical calculations. The ultraviolet absorption spectra were taken by a Spektromom 201 ultraviolet spectrophotometer. Ethanol was used as solvent.

First of all we wished to evaluate the energy belonging to the $\pi - \pi^*$ transition in the cyclotriphosphazene ring. Measurements have shown that the cyclotriphosphazene ring does not absorb in the ultraviolet range, as was proved by the spectrum of hexamethoxy-cyclotriphosphazene (Fig. 1). It is clear that the energy needed for the $\pi - \pi^*$ transition must be higher for the phosphazene ring than for the benzene ring of the same structure, even if a hexacentric molecular orbital is assumed to be present. There is a remarkable difference between the coulomb integrals of phosphorus and nitrogen atoms, so the formed molecular orbitals are farther apart from each other than in benzene, in which the molecular orbitals are formed of atomic orbitals of carbon atoms having the same coulomb integral. This fact can be proved by a simple variation calculation. Taking a six-membered ring of structure similar to that of cyclotriphosphazene, consisting of two sorts of heteroatom alternately situated, the following calculation can be carried out. Assuming the resonance integrals are always the same (β), and keeping the coulomb integral of one type of heteroatom constant (α) and choosing the coulomb integrals of the other type of heteroatom α , $\alpha + 0.5\beta$, $\alpha + \beta$ resp. $\alpha + 2\beta$, the $\Delta m(\pi - \pi^*)$ transition between the last filled and first unfilled molecular orbitals can be calculated in β units (Table 1).

The data in Table 1 show that for rings similar to that of phosphazene Δm increases with an increasing difference between the coulomb integrals of the two different atoms which constitute the ring.

Table I

Coulomb integral of heteroatom	Δm
α	2β
$\alpha + 0.5 \beta$	2.0616β
$\alpha + \beta$	2.2360β
$\alpha + 2 \beta$	2.8284β

Hexaphenoxy-cyclotriphosphazene, on the other hand shows a well observable maximum in the ultraviolet range. This spectrum is also presented in Fig. 1. We have attempted to decide whether the ultraviolet absorption maximum is caused by a conjugation involving the whole molecule or only by the presence of phenoxy groups, it is to decide what sort of interaction occurs between different phenoxy groups bound to the phosphorus atom of the ring. For this purpose spectra of various model compounds were taken. The ultraviolet spectra of these compounds (triphenoxy—phosphate, triphenoxy—phosphorus and anisole) are presented in Fig. 2. Wave lengths and wave numbers of the absorption maxima are given in Table 2 also with the specific absorbences belonging to them. The spectra are analogous to those of benzene derivatives. In our experiments the most intensive maximum in the α band was taken into consideration.

Table 2

Some data of the ultraviolet spectra of the compounds studied

Compound	$\lambda_{\max}(\text{nm})$	ν^* (cm^{-1})	ϵ_{\max}
Hexaphenoxy-cyclotriphosphazene	262.4	38,110	2080
Anisole	271.4	36,846	1630
Triphenoxy—phosphate	261	38,314	801
Triphenoxy—phosphorus	270	37,037	1170

Studying the spectra of the model compounds shows that the absorption maximum of triphenoxy—phosphate (in which phosphorus is in the pentavalent form) is at lower wavelength than that of triphenoxy—phosphorus (in which phosphorus is in the trivalent form). The absorption maximum of triphenoxy—phosphorus is nearly at the same wavelength as that of anisole,

showing that the electron pushing effect of the trivalent phosphorus is about the same as that of the methyl groups. If there were only inductive interaction between oxygen and phosphorus atoms in triphenoxy-phosphorus, the above

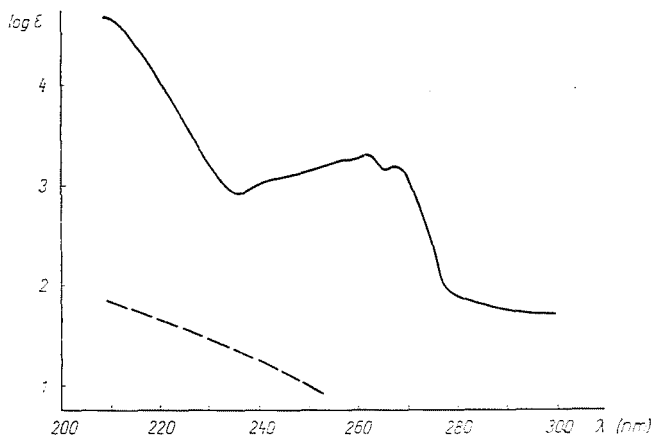


Fig. 1. Ultraviolet spectra of hexaphenoxy-cyclotriphosphazene (—) and hexamethoxy-cyclotriphosphazene (---)

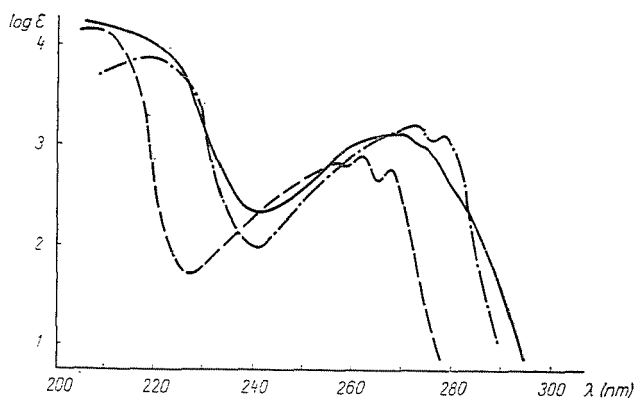


Fig. 2. Ultraviolet spectra of anisole (—) triphenoxy phosphorus (- · - · -) and triphenoxy-phosphate (---)

phenomenon could not be explained. Binding groups of decreasing electro-negativity to oxygen atoms, the absorption maxima are shifted towards higher wave numbers, as a consequence of the increase in the Δm transition between the last filled and first unfilled molecular orbitals. So for anisole, phenol and phenolate ions (in which the groups attached to the oxygen only have an inductive effect) the wave lengths belonging to the absorption maxima are 271.4 nm, 275 nm and 288 nm, respectively. The Δm difference ($\pi - \pi^*$ transition) between the last filled and first unfilled, molecular orbitals has also

been calculated by other authors [2] for anisole in β units. This was found to be 1.8274. Taking the absorption maximum of anisole at 271.4 nm into consideration and assuming that there is a direct proportionality between the energy Δm and wave number ν^* at low wave numbers, Δm can be calculated also for phenol and phenolate (Table 3). Similar calculations can be carried out for the compounds studied by us. The data contained in Table 3 have also been plotted in Fig. 3. Also electronegativities of atoms bound to the oxygen are given in the figure along with the symbols of the compounds.

Table 3

Wavelengths, wave numbers of the absorption maxima and calculated Δm values for the compounds studied

Compound	λ_{\max}	ν^*	Δm
Anisole	271.4	36,846	1.8274 β
Phenol	275	36,364	1.8008 β
Phenolate	288	34,722	1.7195 β
Triphenoxy—phosphate	261	38,314	1.9002 β
Triphenoxy—phosphorus	270	37,037	1.8369 β
Hexaphenoxy-cyclotriphosphazene	262.4	38,110	1.8901 β

Since the electronegativity of phosphorus is lower than that of carbon and hydrogen, triphenoxy phosphorus should have an absorption maximum at higher wavelength than phenol because of the inductive effect. In fact, however, the absorption maxima of triphenoxy—phosphorus show a small hypsochromic effect as compared to anisole. This is only possible if a $d\pi - p\pi$ bond exists between phosphorus and oxygen, which, working against the electron pushing inductive effect, pulls back the electrons from the oxygen.

The electronegativity of pentavalent phosphorus (in triphenoxy—phosphate) is somewhat higher than that of trivalent phosphorus, so it can be expected that triphenoxy—phosphate shows a small hypsochromic effect as compared to triphenoxy—phosphorus. In the spectra of the two compounds, however, a remarkable shift can be observed. This shift can be explained by the changes in the coulomb (and to a slight extent also in the resonance) integrals. The free electron pair on the phosphorus atom in triphenoxy—phosphorus pulls the electrons from the phosphorus to a lower extent than the oxygen atom bound to the phosphorus atom by double bond in triphenoxy—phosphate molecules. Thus, in consequence of the strong inductive effect of oxygen in the latter compounds pulls the electron cloud to itself, consequently, the $+I$ effect of phosphorus atom is reduced, while its $-M$ effect increases ($+I > -M$) as compared to the phosphorus atom in triphenoxy—phosphorus

($+I \gg -M$). The increased $-M$ effect pulls the electron cloud from oxygen in the phenoxy group, that is, increases its electronegativity and coulomb integral. The electron cloud shifted towards the empty d-orbitals of phosphorus from the oxygen of the phenoxy group decreases the electronegativity and coulomb integral of phosphorus. This change in the coulomb integrals causes a hypsochromic shift as compared to triphenoxy-phosphorus. This fact has been proved by quantum chemical calculations, using a variation method. The one-electron LCAO-MO calculations are simplified by the fact that not

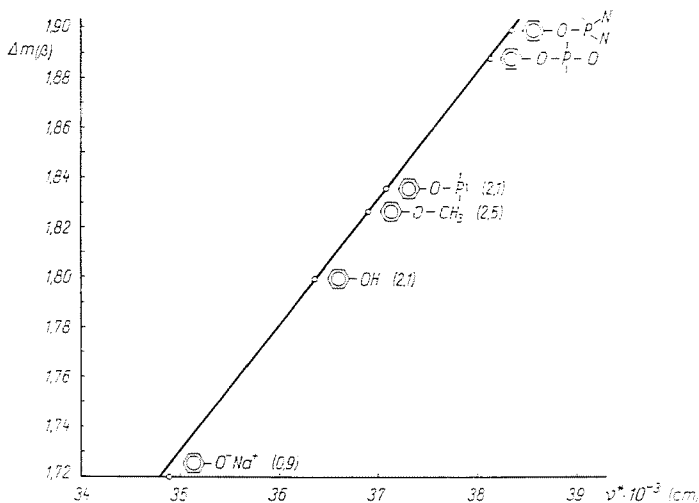


Fig. 3. Δm transition ($\pi - \pi^*$) of the compounds studied as function of the wave numbers belonging to the absorption maxima

all the phenoxy groups attached to the phosphorus atoms must be taken into account, it is sufficient to carry out the calculations for one phosphorus-phenoxy group, so an eight electron model can be chosen as the starting point. This simplification is justified by the fact that the wave-lengths belonging to the maxima in the ultraviolet spectra are practically independent of the number of phenyl [3] or phenoxy groups attached to the phosphorus atom. Consequently, for three phenoxy groups the conjugation does not spread to the whole system. The phosphorus atom and the four attached oxygen atoms are situated in triphenoxy-phosphate as shown in Fig. 4. Oxygen atoms are situated near to the peaks of a tetrahedron, and two d-orbitals on each oxygen are capable of overlap. In consequence of the symmetry of the d-orbitals no conjugation can exist between them through the phosphorus atom. The values of the overlap and resonance integrals between the phosphorus and oxygen atoms are lower than for normal $\pi - p\pi$ bonds, where p- and d-

orbitals are situated in the same plane. The value of the overlapping integral can be calculated for this case as follows:

$$S = S_0 \sin \Theta \sin 2\alpha$$

where Θ is the angle between the d-orbitals

α is the angle between the tetrahedral valence directions and the z axis,

S_0 is the overlap integral for the case when the d- and p-orbitals are in the same plane.

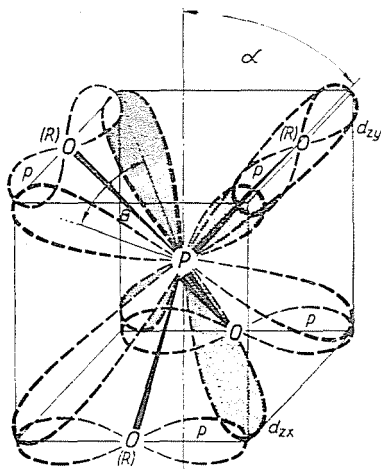


Fig. 4. Overlapping of the atomic orbitals of phosphorus and oxygen atoms in triphenoxy phosphate molecules

In order to facilitate the calculations, we have assumed that the values of the resonance integrals between phosphorus and nitrogen atoms are nearly equal to β . It can also be assumed that the values of the overlap integral are not markedly different for triphenoxy—phosphorus and triphenoxy—phosphate, which is also proved by the bond lengths. So keeping the values of resonance integrals constant in the calculations, different variation values were chosen for the coulomb integrals of the phosphorus atom and oxygen in the phenoxy group as compared with triphenoxy—phosphorus.

Taking the above said into consideration, the calculations were carried out for one phenoxy—phosphorus group, that is, for an eight-centre model.

The coulomb integrals were taken as the same (α) for all carbon atoms in the phenyl ring, and also the resonance integrals for the carbon-carbon bond (β). $\alpha - \beta$ was chosen as the coulomb integral of phosphorus atom, and $\alpha + 2\beta$ for that of oxygen atom. The exchange integrals for both the carbon-oxygen bond and phosphorus-oxygen bond were chosen as β . The C_6H_5-O-P

group belongs to the C_{2v} symmetry group. A quadratic and a sextic matrix can be written for the energy of the molecular orbitals:

$$\begin{vmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{vmatrix} = 0$$

where $H_{11} = H_{22} = \alpha - \varepsilon$ and $H_{12} = H_{21} = \beta$, resp.

$$\begin{vmatrix} H_{11} & H_{12} & H_{13} & H_{14} & H_{15} & H_{16} \\ H_{21} & H_{22} & H_{23} & H_{24} & H_{25} & H_{26} \\ H_{31} & H_{32} & H_{33} & H_{34} & H_{35} & H_{36} \\ H_{41} & H_{42} & H_{43} & H_{44} & H_{45} & H_{46} \\ H_{51} & H_{52} & H_{53} & H_{54} & H_{55} & H_{56} \\ H_{61} & H_{62} & H_{63} & H_{64} & H_{65} & H_{66} \end{vmatrix} = 0$$

where

$$\begin{aligned} H_{11} &= \alpha - \beta - \varepsilon \\ H_{12} &= H_{21} = H_{23} = H_{45} = H_{54} = \beta \\ H_{22} &= \alpha + 2\beta - \varepsilon \\ H_{33} &= H_{44} = H_{55} = H_{66} = \alpha - \varepsilon \\ H_{34} &= H_{43} = H_{56} = H_{65} = \sqrt{2}\beta \\ H_{13} &= H_{14} = H_{15} = H_{16} = H_{24} = H_{25} = H_{31} = H_{35} = H_{36} = H_{41} = \\ &= H_{42} = H_{46} = H_{51} = H_{52} = H_{53} = \\ &= H_{61} = H_{62} = H_{63} = H_{64} = 0. \end{aligned}$$

With $(\alpha - \varepsilon)/\beta = x$ substitution the eigenvalues of the molecular orbitals can be calculated by means of the roots of the quadratic and sextic equations obtained from the two matrixes.

The eight eigenvalues for the above case are:

$$\begin{aligned} \varepsilon_1 &= \alpha + 2.786\beta & \varepsilon_5 &= \alpha - \beta \\ \varepsilon_2 &= \alpha + 1.844\beta & \varepsilon_6 &= \alpha - \beta \\ \varepsilon_3 &= \alpha + \beta & \varepsilon_7 &= \alpha - 1.386\beta \\ \varepsilon_4 &= \alpha + 0.818\beta & \varepsilon_8 &= \alpha - 2.064\beta \end{aligned}$$

Fig. 6 shows the situation of the orbitals. The first four molecular orbitals can hold 2—2 electrons, so the highest filled orbital is the one of ε_4 energy, the first unfilled orbital is the one of ε_5 energy. The difference of ε_4 and ε_5 is the Δm , corresponding to the $\pi - \pi^*$ transition. Δm is equal to 1.8184β for the given case.

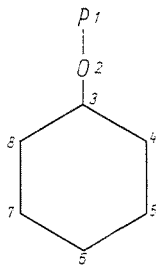


Fig. 5. Numeration of the phenoxo—phosphate group

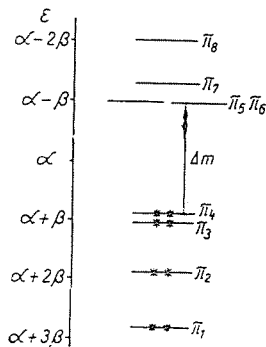


Fig. 6. Molecular orbitals of triphenoxo—phosphorus

In triphenoxo—phosphate the coulomb integral of oxygen is higher, that of phosphorus is lower than in triphenoxo—phosphorus. Therefore, calculations were also carried out in which the coulomb integral of oxygen was increased while that of phosphorus reduced. Choosing $\alpha - 1.1\beta$ for α_o , and $\alpha + 2.1\beta$ for α_p , then in the quadratic matrix

$$H_{11} = H_{22} = \alpha - \varepsilon \text{ and } H_{12} = H_{21} = \beta$$

and in the sextic matrix

$$H_{11} = \alpha - 1.1\beta - \varepsilon \text{ and } H_{22} = \alpha + 2.1\beta - \varepsilon.$$

Further values are the same as those for the former sextic matrix. In this case not all eight eigenvalues were calculated only those belonging to the last two filled and the first two unfilled molecular orbitals ($\varepsilon_3 - \varepsilon_6$) in order to make the calculation of the Δm for the important $\pi - \pi^*$ transition possible. It is important to calculate ε_6 also because in this way it becomes apparent whether one of the orbitals 5 and 6, found to be degenerated in the first calculation, gets under the $\alpha - \beta$ orbital.

Calculations were carried out for the above eight-centre system also for the case when the coulomb integral of oxygen was increased to $\alpha + 2.2\beta$, while that of phosphorus reduced to $\alpha - 1.2\beta$. In this case $H_{11} = \alpha - 1.2\beta - \varepsilon$ and $H_{22} = \alpha + 2.2\beta - \varepsilon$ in the sextic matrix. The results of our calculations are summarized in Table 4.

One can conclude from the variation calculations that Δm increases with increasing coulomb integral of oxygen and decreasing coulomb integral of phosphorus, so the absorption maximum undergoes a hypsochromic shift. As is demonstrated in Table 1, the absorption maximum of triphenoxy—phosphate is really at a lower wave length than that of triphenoxy—phosphorus.

The above results are supported by the ultraviolet spectroscopic studies of K. Lemmann on tetraphenoxy-phosphonium-hexafluoro—phosphate $[P(OC_6H_5)_4]^+PF_6^-$. Four equivalent oxygen atoms are attached in this com-

Table 4

Results of the quantum chemical calculations for phenoxy—phosphorus group

Calculation	1.	2.	3.
Coulomb int. O	$\alpha + 2 \beta$	$\alpha + 2.1 \beta$	$\alpha + 2.2 \beta$
Coulomb int. P	$\alpha - \beta$	$\alpha - 1.1 \beta$	$\alpha - 1.2 \beta$
ϵ_3	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$
ϵ_4	$\alpha + 0.818 \beta$	$\alpha + 0.824 \beta$	$\alpha + 0.8305 \beta$
ϵ_5	$\alpha - \beta$	$\alpha - \beta$	$\alpha - \beta$
ϵ_6	$\alpha - \beta$	$\alpha - 1.021 \beta$	$\alpha - 1.037 \beta$
$\Delta m(\pi - \pi^*)$	1.818 β	1.824 β	1.8305 β

pound to the phosphorus atom, there is no oxygen showing strong inductive effect attached to phosphorus. Phosphorus exerts a strong +I and a smaller -M effect on the oxygens in the phenoxy groups (+I \gg -M), so the conditions are nearly the same as in the triphenoxy—phosphorus. Tetraphenoxy-phosphonium-hexafluoro—phosphate has an absorption maximum at 272 nm, very near to that of triphenoxy—phosphorus. Phosphorus atoms in the ring of hexaphenoxy—cyclotriphosphazene are surrounded by similar groups as phosphorus in triphenoxy—phosphate. -I effect of the doubly bound oxygen is substituted by the -I effect of nitrogen atoms next to phosphorus atoms in the phosphazene ring. Phenoxy—groups are attached to phosphorus on the other side. The ultraviolet absorption maxima of the two compounds are near to each other (262.4 nm for hexaphenoxy-cyclotriphosphazene, and 261 nm for triphenoxy—phosphate). From this one can conclude that the π -octetts of phenoxy—groups are not bound to the π -sextett of the phosphazene ring, that is the conjugation does not spread to the whole of the molecule. The reason for this fact can be that phosphorus atoms form $d\pi - p\pi$ bonds with oxygen and nitrogen atoms by separate empty d-orbitals. Therefore, nitrogen atoms in the ring only have an inductive effect on the phenoxy—phosphorus group.

Summary

1. It has been proved that the triphosphazene ring has absorption maximum only in the far ultraviolet range.

2. The bond between phosphorus and oxygen atoms is not simply a σ bond, but a σ and a dative $p\pi - d\pi$ bond.

3. It has also been proved by means of one-electron LCAO-MO method, that triphenoxy-phosphorus should show a bathochromic shift as compared to triphenoxy-phosphate.

4. Hexaphenoxy-cyclotriphosphazene has a structure similar to that of triphenoxy-phosphate which is due to a similar electronic structure.

5. On the basis of the above-said it has been stated that the π sextett of the phosphazene ring in hexaphenoxy-cyclotriphosphazene is not bound to the octetts of the phenoxy groups, but all the rings form separate conjugated systems.

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