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QUANTUM CHEMICAL CALCULATIONS OF P-N AND P-P COUPLING CONSTANTS OF CYCLOTRIPHOSPHAZENES

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Abstract Semiempirical quantum chemical calculations using the SOS approximation have been carried out in order to facilitate the interpretation of the P-N and P-P coupling constants of a series of ¹⁵N labelled hexasubstituted cyclotriphosphazenes (¹⁵NPX₂)₃. A change of sign within the series was confirmed.

INTRODUCTION

We have previously¹ studied a series of ¹⁵N labelled hexasubstituted cyclotriphosphazenes (¹⁵NPX₂)₃, where

X = F, Cl, OR(1), SR(1), NR(2)₂, CH₃

R(1) = Me, Et, Ph and R(2) = H, Me, Et.

We were interested in the influence of the substituents on the P-N ring system and on the nuclear spin-spin coupling constants ¹J_{PN} and ²J_{PP} in these compounds.

Because it was impossible to obtain the signs of the P-N and P-P coupling constants experimentally, they were supposed by us giving a linear correlation to the electronegativity of the substituents.

CALCULATIONS

In order to calculate the nuclear spin-spin coupling constants we have used a simple approximation introduced by Pople and Santry on the LCAO MO level (the so called sum-over-states treatment [SOS])², considering all contributions to the indirect coupling constant.

The wave functions and orbital energies required for the determination of the coupling constants were obtained from CNDO, INDO, or NDDO calculations. The triplet excitation energy for the Fermi contact term was calculated according to

$${}^3\Delta E_{i \rightarrow j} = \epsilon_i - \epsilon_j - J_{ij}$$

where J_{ij} is the Coulomb integral between the occupied MO_i and the unoccupied MO_j , and ϵ_i , ϵ_j are the respective orbital energies. The calculation of the spin dipole contribution was carried out in an analogous manner. In calculating the orbital term a value for the singlet excitation energy is also needed; thus in this case apart from the Coulomb integral it is necessary to take into account exchange integrals.

Two basis sets were used, the first including vacant d orbitals on atoms of the third period (spd-basis), the second neglecting these (sp-basis).

The calculations of ${}^1J_{PN}$ and ${}^2J_{PP}$ were carried out for the following six compounds: $(NPF_2)_3$, $(NP(OH)_2)_3$ (as a model compound for esters), $(NP(NH_2)_2)_3$ (as a model compound for amides), $(NP(CH_3)_2)_3$, $(NPCl_2)_3$, and $(NP(SH)_2)_3$ (as a model compound for thioesters).

${}^1J_{PN}$

The results of the calculations of ${}^1J_{PN}$ are summarized in Table 1. In the cases where various individual compounds were investigated (esters, thioesters, and amides) experimental coupling constants are mean values.

It is possible to give correct trend predictions in all cases. The correlation between experimental and calculated values of ${}^1J_{PN}$ is good, the best value being obtained when we restrict ourselves to molecules which do not contain substituent atoms of the third period (such as chlorine or sulfur). The change of sign within the series was also confirmed, at least for INDO calculations: however, the direction of the sign change is apparently opposite

TABLE I Calculated and experimental values of $^1J_{PN}$ of cyclo-triphosphazenes (in Hz) and correlation coefficients r

X	(NPX ₂) ₃ sp-Basis			spd-basis				experi- mental values
	without integrals			with integrals		without integrals		
	CNDO	INDO	NDDO	CNDO	INDO	INDO	NDDO	
F	-24.9	-25.2	-33.6	-19.8	-17.9	-16.1	-26.5	-24.9
Cl	-11.3	-6.2	-15.6	-2.4	9.6	-1.4	-15.4	+31.7
OH	-17.1	-13.8	-23.7	-9.7	-1.3	-8.8	-22.8	-7.0
SH	-5.9	2.2	-8.3	3.9	21.2	5.8	-12.2	+52.0
NH ₂	-10.1	-3.1	-12.7	-0.8	14.3	-1.2	-17.1	+7.0
CH ₃	-5.9	5.3	-5.4	3.3	24.6	6.8	-9.2	+26.1
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r(all)	0.887	0.851	0.855	0.892	0.855	0.900	0.800	
r(2 nd period)	0.989	0.994	0.992	0.978	0.990	0.934	0.988	

TABLE II Calculated and experimental values of $^2J_{PP}$ of cyclo-triphosphazenes (in Hz) and correlation coefficients r

(NPX ₂) ₃	sp-basis			spd-basis				experi- mental values
	without integrals		with integrals	without integrals				
X	CNDO	INDO	NDDO	CNDO	INDO	INDO	NDDO	
F	11.9	20.0	13.7	13.5	35.3	50.9	11.8	+160
Cl	6.3	8.4	5.2	5.3	11.3	19.7	2.1	+45
OH	7.2	10.8	8.6	15.0	21.8	30.0	6.9	+100
SH	4.6	4.4	3.4	9.7	6.9	8.3	1.1	-20
NH	4.1	4.0	4.0	7.2	5.5	6.6	2.0	+45
CH	1.5	0.7	1.7	2.7	1.1	2.6	0.7	-5
r(all)	0.901	0.929	0.959	0.704	0.938	0.938	0.956	
r(2 nd period)	0.994	0.987	0.993	0.896	0.984	0.983	0.982	

to our earlier proposal¹. Thus $^1J_{PN}$ is negative in the case of the fluoride and positive in the case of the thioesters; the signs of the experimental coupling constants in Table I are assigned on this basis.

We can however state that the contact term seems to be dominant in the sense that trends of changes in the experimental coupling constants are reproduced well by this term, whereas the orbital contributions extend across only a small range. Significant changes of the three interaction contributions by enhancement of the basis set were not observed.

$^2J_{PP}$

Table II contains the results for coupling constants $^2J_{PP}$. While the calculated absolute values are not in good agreement with the experimental coupling constants, an acceptable linear correlation was found. The correct sign cannot always be obtained from such calculations, a negative sign was found only in the case of the fictitious hexahydrido compound ($^2J_{PP}$ (INDO, sp-basis, with integrals) = -3 Hz). Nevertheless the good correlation coefficients r confirm the change of the sign of the experimental values as assumed by us. The direction of the change is opposite to that of $^1J_{PN}$, $^2J_{PP}$ increasing with increasing substituent electronegativity.

The inclusion of d orbitals in the INDO calculations yield increasing absolute values of $^2J_{PP}$, but do not influence the trend predictions. Calculation of the Fermi contact term is sufficient, spin dipolar term and orbital term being negligible in the case of geminal couplings in cyclotriphosphazenes.

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2. J. A. Pople and D. P. Santry, Mol. Phys., **8**, 1 (1963)