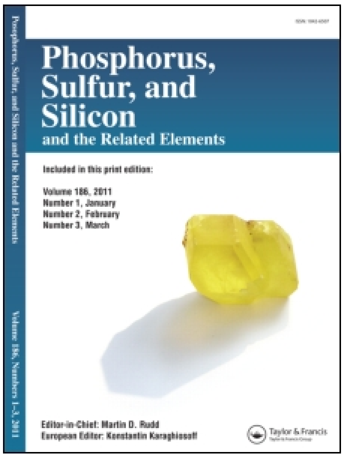

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FORCE FIELD PARAMETERS AND MOLECULAR MECHANICS, MOLECULAR DYNAMICS AND QUANTUM MECHANICAL AB INITIO STUDIES OF 2,2,4,4,6,6-HEXAKIS-(*P*-PHENOXY-PHENOXY)-$2\lambda^5,4\lambda^5,6\lambda^5$-CYCLOTRIPHOSPHAZA-1,3,5-TRIENE

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The solid-state structures and conformations of hexa(aryloxy)cyclotriphosphazenes bearing bulky aryloxy-groups have been previously studied by us using X-ray diffraction analysis.[1-3] These data thus refer to static structural and conformational properties in the solid. The conformational characteristics, molecular dynamics and intramolecular interactions of these molecules would remain quite unknown unless theoretical force-field computational methods become applicable.

In the present study force field parameters have been developed for cyclotriphosphazenes using the Dinur and Hagler method[4] of second derivatives of the energies. The energies were obtained through MO-SCF ab-initio calculations at the 4-31G* level explicitly including *d*-orbitals. Molecular mechanics (MM2) modelling and molecular dynamic (MD) simulations have been carried out for the title compound $[NP(O-C_6H_4-OC_6H_5)_2]_3$ using the MacroModel and CharmM programs, respectively. The calculated bond lengths and angles (Table I) resulted in agreement with the values determined by X-ray diffraction analysis of the crystal[5] (triclinic, space group P1, with a = 15.345(2) Å, b = 15.440(3) Å, c = 15.999(3) Å, α = 80.43(1)°, β = 66,67(1)°, γ = 60.62(1)°, V = 3031.3(9) $\AA^3$, and Z = 2; R = 0.057 and R_w = 0.066). Calculated and X-ray structure data for the torsional angles are in poor agreement due to relevant crystal packing forces determining the conformation in the solid. The MD simulation (run by starting from X-ray coordinates after a 10 ps equilibration at 298 K; transients usually collected 600 ps) attained a nearly symmetric equilibrium conformation and showed that the fluxional mobility of the phenoxy groups increases on going from the P-O bonds of the phosphazenic core to the external fragments of the molecule. The force field parameter set for MD well reproduces the energy difference beetwen solid and gas phase conformation calculated by ab-initio (STO-3G*) method.

The ab initio calculations indicated that the highest occupied band shows difference in the energy levels as a consequence of the conformational change. This implies that the energy of these orbitals, to whom contribute the P and, by larger extent, N atoms of the ring, may fluctuate giving rise to a continuous band. The calculated small energetical differences beetwen the MO levels indicate the possible *quasi*-band structure for bonding electrons. A perturbation of the electronic system localized on the atoms of the external phenyl groups can therefore easily propagate towards the P and N atoms of the cyclophosphazenic ring.

TABLE I. Mean values of calculated and experimental bond lengths (Å) and bond angles (°) and percent differences (%) from the mean experimental values.

	MM2	%	MD	%	exptl
P-N	1.585	0.6	1.569	0.4	1.576
P-O	1.554	1.5	1.552	1.7	1.578
O-C	1.366	2.6	1.386	1.1	1.402
N-P-N	115.37	1.2	117.02	0.2	116.77
P-N-P	124.43	1.7	122.08	0.2	122.33
O-P-N	110.44	0.0	109.95	0.4	110.41
C-O-P	122.64	2.0	124.50	0.5	125.13
O-P-O	98.09	1.5	98.07	1.52	96.6

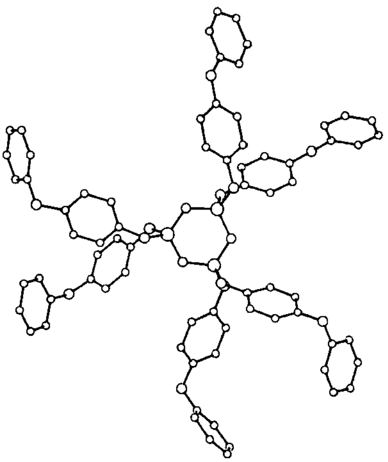

FIGURE 1. Perspective view of the molecule in the conformation from the simulation, after averaging of atomic positions and subsequent minimization.

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