5398 *Inorg. Chem.* **2000,** *39,* 5398−5399

Gas-Phase Structure of Hexakis(trifluoromethyl)-cyclotriphosphazene, $[(CF_3)_2PN]_3$

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Received May 11, 2000

Introduction

The utilization of trimethyl(trifluoromethyl)silane as a nucleophilic trifluoromethylating reagent has made it possible to synthesize hexakis(trifluoromethyl)cyclotriphosphazene, **1**, from hexafluorocyclotriphosphazene in 90% isolated yield.[1] In addition to the usual spectral characterization, we have reported its structure determined by single-crystal X-ray diffraction and compared it with that of the hexafluoro compound. **1** is a solid and stable indefinitely at room temperature and exhibits a sublimation pressure of ∼3 Torr at 22 °C.[2] In the solid, **1** adopts a structure with a planar P_3N_3 ring and deviates only slightly from the ideal D_{3h} symmetry. In this study we report the structure of the free molecule, using gas electron diffraction (GED) and quantum chemical calculations. Only few molecular structures have been determined in the solid state as well as in the gas phase. The comparison of such structures provides interesting information about intermolecular interactions (packing effects) and about systematic differences between solid-state structures determined by X-ray diffraction and gas-phase structures derived by GED.

Experimental Section

The GED intensities were recorded with a gas diffractograph KD-G2[3] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of approximately 60 kV. The sublimation pressure at room temperature was sufficient for recording the scattering intensities. The photographic plates were analyzed with the usual methods,[4] and averaged molecular intensities in the s ranges 2−18 and 8−35 Å^{-1} in steps of $\Delta s = 0.2$ Å^{-1} are presented in Figure 1 ($s = (4\pi/\lambda)\sin\theta/2$, λ = electron wavelength, θ = scattering angle).

Results

The geometry of **1** was fully optimized with HF/3-21G*, HF/6-31G*, and B3LYP/6-31G* approximations. All three methods predict a planar P_3N_3 ring and D_{3h} overall symmetry. The vibrational frequencies were calculated with the HF/3-21G* method. All quantum chemical calculations were performed with the Gaussian 98 program suite.[5] Vibrational amplitudes were derived with the program ASYM40[6] from the calculated Cartesian force constants applying a scale factor of 0.85 for stretching and bending constants. Torsional force constants were not scaled. Calculated geometric parameters are included in Table 1, and vibrational amplitudes are given together with the experimental values as Supporting Information.

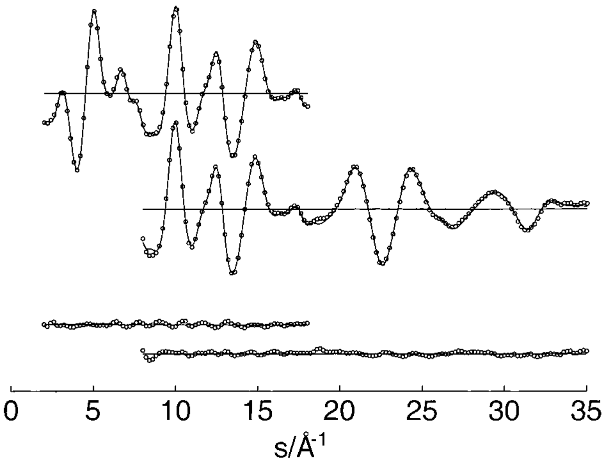

Figure 1. Experimental (dots) and calculated (full line) molecular intensities for long (above) and short (below) nozzle-to-plate distances.

The radial distribution function (Figure 2), which was obtained by Fourier transformation of the molecular intensities, is reproduced very well with a planar ring structure and D_{3h} overall symmetry. In the least-squares refinement, the molecule was constrained to this symmetry. Furthermore, local C_{3v} symmetry was assumed for the CF_3 groups with a possible tilt angle between the C_3 axis and the P−C bond direction. Vibrational amplitudes with similar values were collected in groups and amplitudes, which either caused high correlations with geometric parameters or were poorly determined in the GED experiment, were constrained to calculated values. With these assumptions seven geometric parameters and 12 vibrational amplitudes were refined simultaneously. Only two correlation coefficients had values larger than |0.6|: PC/FCF = −0.75, CPC/tilt(CF_3) = −0.65. The geometric parameters for the D_{3h} symmetry are included in Table 1, and the structure is shown in Figure 3. The vibrational amplitudes are given as Supporting Information. A slight improvement of the fit of the experimental intensities is obtained if the molecule is allowed to deviate from D_{3h} symmetry. If a flap angle between the N−P−N plane and the plane of the three nitrogen atoms (oop(P)) is introduced, the agreement factor decreases from $R = 6.0\%$ for D_{3h} symmetry to $R = 5.5\%$ for the slightly nonplanar ring with C_{3v} symmetry and oop(P) = 4.8(7)°. All geometric parameters are unchanged in this refinement with the exception of the endocyclic angles, which decrease by less than 0.2°. The GED intensities are insensitive toward out-of-plane distortions of the nitrogen atoms. This minor deviation from planarity is considered to be due to

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10.1021/ic000504y CCC: $19.00 © 2000 American Chemical Society
Published on Web 10/21/2000

Table 1. Experimental and Calculated Geometric Parameters for $[(CF_3)_2PN]_3$

	X-ray [a]	GED[b]	HF/3-21G*[c]	HF/6-31G*[c]	B3LYP/ 6-31G*[c]
P−N	1.581(4)	1.583(3)	1.573	1.583	1.607
P−C	1.852(4)	1.870(2)	1.810	1.862	1.886
C−F	1.316(2)	1.333(1)	1.346	1.315	1.341
N−P−N	119.9(2)	119.5(7)	114.5	117.1	119.1
P−N−P	120.1(3)	120.5(7)	125.5	122.9	120.9
C−P−C	102.8(3)	105.5(12)	104.8	103.8	103.3
F−C−F	107.5(6)	108.6(7)	109.1	108.7	108.6
tilt(CF_3)[d]	2.3 (6)	0.6(15)	2.1	2.0	1.5

[a] Mean values from ref 1. [b] r_a values with 3σ uncertainties. [c] Mean values for C−F bond lengths and F−C−F bond angles. [d] Tilt angle between C_3 axis and P−C bond direction away from the opposite CF_3 group.

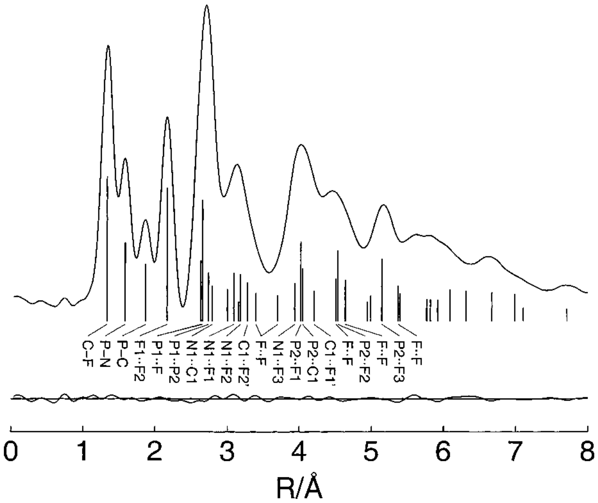

Figure 2. Experimental radial distribution function and difference curve. The positions of important interatomic distances are shown by vertical bars.

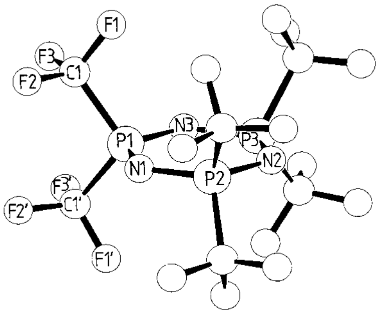

Figure 3. Molecular model of $[(CF_3)_2PN]_3$ with atom numbering.

vibrational effects. The HF/3-21G* approximation predicts a rather rigid ring structure with out-of-plane vibrations between 118 and 355 cm^{-1}. The lowest vibrational frequencies are CF_3 torsions (26−37 cm^{-1}) and rocking, twisting, and wagging motions of the $(CF_3)_2P$ moiety (61−115 cm^{-1}).

Discussion

In Table 1 the geometric parameters derived by X-ray crystallography, GED, and quantum chemical calculations are compared. Within experimental uncertainties the structure of the cyclotriphosphazene ring (P−N, N−P−N, and P−N−P) is identical in the solid and gaseous phase. The values for the P−C and C−F bond lengths derived by X-ray diffraction are shorter by about 0.02 Å than the gas-phase values. Qualitatively, these differences can be rationalized by vibrational effects that cause systematic differences between bond lengths determined in the solid and gaseous state. X-ray crystallography determines distances between mean atomic positions, whereas GED determines mean interatomic distances. Large amplitude vibrations such as the rocking, twisting, and wagging motions of the $(CF_3)_2P$ moiety and the CF_3 torsional motions make the solid-state values for the P−C and C−F bond lengths shorter than the gas-phase values.

Table 2. Geometric Parameters of Cyclotriphosphazene Rings in $[R_2PN]_3$, R = F, CF'

compound	P−N	N−P−N	P−N−P
$[F_2PN]_3$ (crystal)[a]	1.569(2)	119.1(2)	121.2(2)
$[(CF_3)_2PN]_3$ (crystal)[a]	1.581(4)	119.9(2)	120.1(3)
$[(CF_3)_2PN]_3$ (gas)[b]	1.583(3)	119.5(7)	120.5(7)
$[(CH_3)_2PN]_3$ (crystal)[c]	1.594(2)	116.8(1)	122.6(1)

[a] Reference 1. [b] This work. [c] Reference 7, uncorrected values.

Comparison between the results of the three quantum chemical methods with the experimental gas-phase structure shows considerable variance. Neglecting systematic differences between the experimental r_a and the calculated r_e values, the HF approximation with small basis sets (HF/3-21G*) underestimates the P−C bond length by 0.06 Å. The predicted endocyclic N−P−N angle is 9° smaller than P−N−P, whereas the experimental values are very similar and differ only by 1°. The HF/6-31G* method reproduces all bond lengths to within ±0.02 Å, but the difference between the calculated endocyclic bond angles is still 6°. These angles are reproduced best with the B3LYP/6-31G* calculations where the two angles agree with the experimental values within their uncertainties. This method, however, overestimates all bond lengths slightly, especially the P−N bond. Thus, none of these three standard computational methods reproduces the experimental structure satisfactorily.

Ring parameters of cyclotriphosphazenes $[R_2PN]_3$ with R = F, CF_3, and CH_3 are listed in Table 2. The rings in these three compounds are essentially planar. The P−N bond lengthens with decreasing electronegativity of the substituent from 1.569(2) Å in $[F_2PN]_3$ to 1.581(4) Å in **1** and to 1.594(2) Å in $[(CH_3)_2PN]_3$. Whereas the two endocyclic bond angles N−P−N and P−N−P differ by only 2° or 1° for R = F and CF_3, respectively, the phosphorus bond angle is about 6° smaller than the nitrogen bond angle in the methylated compound. Comparison of the X-ray data of **1** and $[(CH_3)_2PN]_3$ reveals that the P−C bond lengthens by about 0.06 Å upon CH_3/CF_3 substitution. Even stronger substitution effects in P(V) compounds have been observed previously between $(CH_3)_3PO$ (P−C = 1.809(2) Å[8]) and $(CF_3)_3PO$ (P−C = 1.895(3) Å[9]).

Acknowledgment. F.T. and H.O. thank the Fonds der Chemischen Industrie for financial support. R.P.S., R.L.K., and J.M.S. express appreciation to the National Science Foundation (Grant CHE-9720635), the Petroleum Research Fund, administered by the American Chemical Society, and the Idaho Space Grant Consortium. The starting material $P_3N_3Cl_6$ for the synthesis of $[(CF_3)_2PN]_3$ was a gift from Otsuka Chemical Co., Ltd.

Supporting Information Available: Table S1 with interatomic distances and experimental and calculated vibrational amplitudes. This material is available free of charge via the Internet at http://pubs.acs.org.

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