methylation (5-Me-dCMP). We are continuing to improve the method by optimizing sample preparation to enrich modified nucleotides.

### *Experimental Section*

DNA hydrolysis: DNA (10 μg) was diluted in water (5.2 μL) and hydrolyzed by incubation for 3 h at 37 °C with an enzyme mixture (4.0 μL; micrococcal nuclease: 150 mU μL$^{-1}$ and spleen phosphodiesterase: 2.5 mU μL$^{-1}$) and buffer (0.80 μL; 250 mM HEPES, 100 mM $CaCl_2$, pH 6.0).

Fluorescence derivatization: 1.8 M EDC (30 μL; in 800 mM HEPES buffer, pH 6.5), 25 mM BODIPY FL EDA (30 μL; in 800 mM HEPES buffer, pH 6.5), and 800 mM HEPES buffer (20 μL) at pH 6.5, were added to the hydrolysate and incubated for 25 h at 25 °C in the dark.

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# Structure of Bis(pentafluorophenyl)xenon, $Xe(C_6F_5)_2$**

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*Dedicated to Professor Peter Sartori on the occasion of his 70th birthday*

Recently, we synthesized the first homoleptic organoxenon(II) compound with two Xe–C bonds, $Xe(C_6F_5)_2$ (**1**), through the fluoride-initiated reaction of $(CH_3)_3SiC_6F_5$ and $XeF_2$.[1] An alternative route to **1** is the reaction of $C_6F_5XeF$ and $[Cd(C_6F_5)_2]$.[2] Compound **1** is obtained as a white solid which explosively decomposes above −20 °C. However, as single crystals could not be grown, **1** was characterized exclusively in solution by $^{129}$Xe, $^{19}$F, and $^{13}$C NMR spectroscopy.

The development of apparatus and methods has now advanced to the stage where it is possible to solve and refine even structures of complicated organic and organometallic compounds on the basis of X-ray powder data.[3] Since **1** is obtained as an almost single-phase microcrystalline powder, we were encouraged to determine the crystal structure from X-ray powder data despite of the extreme thermal instability of **1**.

Compound **1** was synthesized from $(CH_3)_3SiC_6F_5$ and $XeF_2$[1] and investigated at −223 °C (see Experimental Section).[4] The powder diffractogram was indexed in a monoclinic unit cell,[5] and the volume of the unit cell was in good agreement with the calculated volume for four formula units. On the basis of the systematic absences, the only space group that came into consideration was $P2_1/n$. Le Bail extraction[6–8] within this space group and a subsequent structure determination using direct methods[9] led to a position which was assigned to the Xe atom. As the positions of the $C_6F_5$ rings could not be determined by using difference Fourier syntheses, we applied the method of "simulated annealing".[10] Two "rigid bodies" were defined for the perfluorinated phenyl rings and placed on two arbitrary positions together with the position obtained for the Xe atom and used as starting parameters. After a few cycles, a reasonable structural solution was found which was refined by the Rietveld method.[11] On account of the limited quality of data as well as a large number of parameters, the $C_6F_5$ rings were refined as rigid bodies (C–C 1.38, C–F 1.35 Å) and isotropic temperature factors of identical elements were constrained. A stable refinement resulted which quickly converged.[12]

The resulting molecular structure of **1** is shown in Figure 1. Both Xe–C distances (Xe–C11 2.394(9) Å, Xe–C21 2.35(1) Å) are almost identical within the double standard

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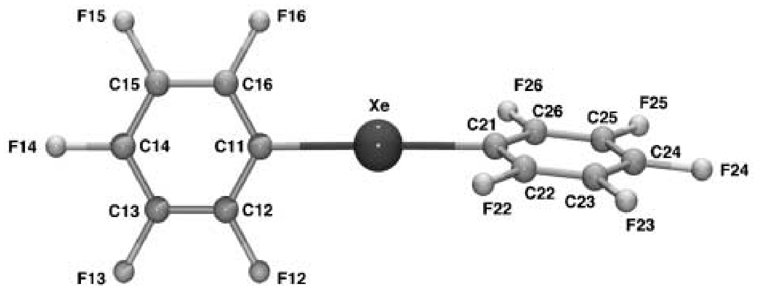

Figure 1. Molecular structure of **1** in the solid state; selected distances [Å] and angles [°]: Xe-C11 2.394(9), Xe-C21 2.35(1); C11-Xe-C21 178(3)°.

deviation. The Xe–C bonds are 0.3 Å longer than the corresponding bond in the $XeC_6F_5^+$ ion in $[Xe(C_6F_5)][AsF_6]$.[13] The C11-Xe-C21 unit is as expected almost linear (angle 178(3)°). The two $C_6F_5$ rings are twisted by 72.5° with respect to each other. This torsion angle is comparable with that of the isoelectronic $[I(C_6F_5)_2]^-$ ion (69.54°).[14]

Figure 2 depicts the molecular packing of **1**. Arrangement of molecules in layers parallel to the (100) plane is perceptible; symmetrically equivalent phenyl rings are arranged parallel to each other. Short distances are found pairwise between the rings (3.57 and 3.73 Å, cf. graphite: 3.40 Å)[15] which can be interpreted in terms of weak interactions. The next closest distances between the rings exceed 5.36 Å. Four intramolecular (3.30(1) – 3.394(8) Å) and five intermolecular (3.36(1) – 3.536(9) Å) fluorine contacts are found in the coordination sphere of xenon being shorter than the sum of van der Waals radii of xenon and fluorine (3.63 Å).[16]

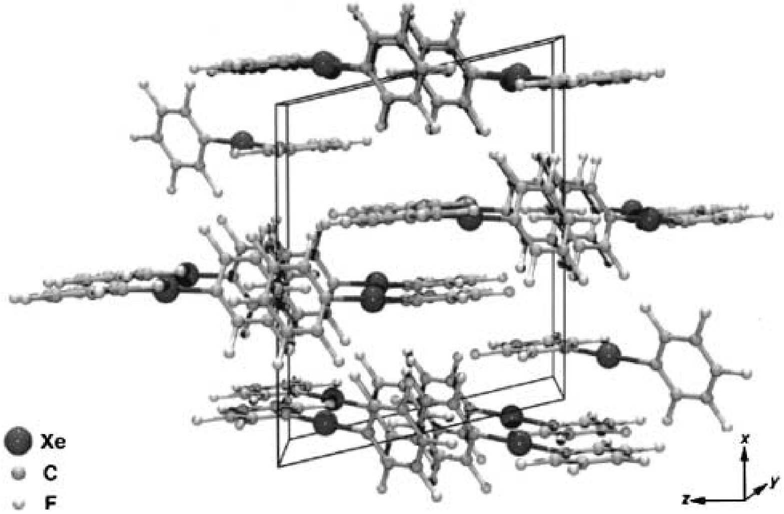

Figure 2. Molecular packing in the crystal structure of **1**.

The experimental results are supported by electron-correlated ab initio calculations (MP2[17]) and density functional thoery (DFT) calculations (B3LYP[18]), which were performed with quasi-relativistic pseudopotential basis sets (LANL2DZ,[19] CEP-121G,[20] SDD[21]) as well as the correlation-consistent cc-pVQZ basis set[22] for fluorine and carbon and the optimized Stuttgart – Dresden – Bonn[23] relativistic effective core potential (ECP46MWB[21]) for xenon (Table 1). Geometry optimizations and normal vibration analyses were carried out using Gaussian 98.[24] All calculated structures represent real minima of the potential hypersurface and do not give evidence for any imaginary frequencies.

Calculated bond lengths and angles of **1** at the DFT level are in better agreement with experimental results than those of prior calculations at the Hartree – Fock level.[2] Best results for Xe–C bond lengths were achieved with calculations at the B3LYP level using basis sets CEP-121G, LANL2DZ, and SDD. Also conformity of calculated and measured angles appears extraordinary.[25] Results at the MP2 level exhibit values that are too high, those at the HF level values that are too low. The well-known bad conformity of experimental values and HF calculations for non-metal fluorine derivatives exhibits the necessity to take electron correlation into account to achieve sufficient agreements.[26, 27] The results using the combination HF/cc-pVQZ for geometry optimization correspond extensively with those of DFT calculations (B3LYP/SDD). The inclusion of polarized d, f, and g orbitals hardly influences the results at all.

The great deviation of the calculated dihedral angle C16-C11-C21-C26 from an angle of 90° may be attributed to intramolecular packing effects. To obtain further information on intramolecular interactions between Xe and F, the potential hypersurface was investigated as a funciton of the torsion angle by relaxed-potential energy-surface scans[28] using B3LYP/SDD calculations. The rotational barrier of the $C_6F_5$ rings is about 1.2 kJ mol$^{-1}$. The potential graph exhibits two saddle points at 40° and 60°. As a result, evidence for interactions of orbitals of the *ortho*-fluorine atoms and of the xenon atoms can be assumed.

Table 1. Experimental and calculated structural parameters [Å, °] and energies [kJ mol$^{-1}$] of **1**.

| | Exp. | HF/LANL2DZ | B3LYP/CEP-121G[a] | B3LYP/LANL2DZ | B3LYP/SDD | MP2/LANL2DZ | MP2/SDD |
|---|---|---|---|---|---|---|---|
| Xe-C11 | 2.394 | 2.344[2] | 2.394 | 2.401 | 2.336 | 2.443 | 2.338 |
| Xe-C21 | 2.35 | | | | | | |
| Xe-$F_{intramol.}$ | 3.364[b] | 3.369 | 3.427 | 3.422 | 3.377 | 3.485 | 3.397 |
| C12-C11-C16 | 120 | 117.4[2] | 118.1 | 118.5 | 118.1 | 117.8 | 118.2 |
| C11-Xe-C21 | 178 | 180.0 | 180.0 | 180.0 | 180.0 | 180.0 | 180.0 |
| C11-C12-F12 | 120 | 119.4 | 119.7 | 119.9 | 119.6 | 119.8 | 119.4 |
| *E* | – | 326.7 | 301.6 | 306.0 | 305.7 | 298.9 | 297.5 |
| ZPE[c] | – | 274.4 | 244.5 | 249.7 | 249.5 | 241.7 | 240.9 |

[a] Consideration of 3df polarisation functions (CEP-121G(3df)) led to the following results: Xe–C11, Xe–C21 2.367, Xe–$F_{intramol.}$ 3.385, C12-C11-C16 118.8, C11-C12-F12 120.3, $E = 325.2$ kJ mol$^{-1}$. [b] The mean was determined from the four shortest Xe–F contacts. [c] Zero-point energies.

## Experimental Section

**1**: Microcrystalline **1**[1] was slowly precipitated from CH$_2$Cl$_2$, purified, and dried in dynamic vacuum at −40 °C (10$^{-3}$ bar). Under an argon atmosphere, the residue was spread smoothly on a polymer foil at −100 °C using a spatula precooled to −196 °C. To prevent a loss of substance, the sample carrier was coated with perfluorinated silicon grease (Voltaleff). Samples prepared in this manner were additionally dried in vacuo at −40 °C and then transferred to the sample chamber of the X-ray powder diffractometer (Huber G645) at −100 °C, which was cooled to −223 °C for collecting diffraction data.

**Caution!** Pure Xe(C$_6$F$_5$)$_2$ is thermally unstable and may vigorously explode on contact. Protection glasses and Kevlar gloves were worn throughout all manipulations.

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[12] Structure refinement of **1**: crystal system: monoclinic, space group $P2_1/n$ (no. 14), $a = 13.635(3)$, $b = 8.248(2)$, $c = 11.511(3)$ Å, $\beta = 102.625(3)^\circ$, $\rho_{calcd} = 2.447$ g cm$^{-3}$, $Z = 4$, 762 reflections, 34 structural and profile parameters were refined overall, $wR_P = 0.1843$, $R_P = 0.1393$, $R_F = 0.0691$. Rietveld refinement was performed with the GSAS software package.[11] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-169453. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[28] Relaxed potential energy surface scans were carried out starting with the geometry-optimized structure within 90 single steps varying by 1°. Structures deriving from these calculations were optimized in geometry (SCF = tight). Use of a combination of B3LYP/LANL2DZ methods did not converge for calculations starting from 40°.

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# As[P(NMe$_2$)$_3$]$_2^+$ as Simultaneous As$^I$ and P$^I$ Source: Synthesis and Density Function Calculations of Planar Tetracoordinate Arsonium and Phosphonium Ions**

Matthias Driess,* Holger Ackermann, Joachim Aust, Klaus Merz, and Christoph von Wüllen

*Dedicated to Professor Rolf Gleiter*
*on the occasion of his 65th birthday*

Recently we reported on the unusual organometallic phosphonium ion P[Zr(H)Cp$_2$]$_4^+$ (Cp = $\eta$-C$_5$H$_5$) in the BPh$_4$

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