

The First Cyclic Perfluoropolyketone: The Synthesis and Solid State Conformation of Perfluoro(hexamethylcyclohexane-1,3,5-trione)

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A novel perfluorinated cyclic polyketone **1** was synthesized by liquid-phase direct fluorination; its crystal structure and solid state conformation were determined by X-ray crystallography.

Perfluoroketones are useful intermediates for several classes of compounds.^{1,2} They can be prepared by several indirect methods, such as rearrangement of perfluoroepoxides over SbF_5 or KF , halogen exchange reactions between chlorinated ketones and hydrogen fluoride using a Cr^{III} catalyst, sulfuric acid hydrolysis of alkyl perfluorocycloalkyl ethers, reactions of perfluoroalkyl carboxylates with perfluoroalkyl lithium or perfluorinated Grignard reagents and fluoride-induced substitution of perfluoroacyl fluorides with perfluoroalkenes.¹ Because starting materials are difficult to prepare or the yields of these reactions are low, these methods are seldom used to prepare novel perfluoroketones. Other direct methods such as CoF_3 and KCoF_4 have been used to fluorinate ketones but the major reaction of the fluorination was cleavage of the C–CO bond.³ Elemental fluorine also has been used to fluorinate monoketones by using several special methods and reactors, such as jet reactor,⁴ aerosol direct fluorination⁵ and cryogenically controlled direct fluorination,⁶ but these methods often give lower yields or cleavage of the C–CO bond. The target of the present synthesis was the polyketone **1** which was obtained in 72% yield.

We report here the first example of liquid-phase direct fluorination of a cyclic polyketone and the crystal structure of its perfluorinated analogue **1**. The liquid-phase direct fluorination of hexamethylcyclohexane-1,3,5-trione was carried out by slowly injecting a trichlorotrifluoroethane solution of the compound into a reactor containing trichlorotrifluoroethane saturated with fluorine and sodium fluoride. The reactor design of the liquid-phase direct fluorination was described previously.⁷ The fluorination conditions are shown in Table 1. After fluorination, the solvent was distilled off and the residue was distilled under high vacuum to give pure corresponding perfluoro(hexamethylcyclohexane-1,3,5-trione) **1** in 72% isolated yield. Its melting point is 40 °C.

The byproducts were lower molecular weight fluorinated alcohols produced by hydrolysis. Straight chain products were absent from the byproducts indicating that cleavage of the C–CO bond did not occur in this reaction. Sodium fluoride as a hydrogen fluoride scavenger is essential for the reaction since addition of hydrogen fluoride to fluorinated ketones followed by fluorination, gives hypofluorites.⁸

The ^{19}F NMR signal of **1** is a singlet at $\delta(\text{CDCl}_3, \text{CFCl}_3) -59.5$. The carbonyl absorption in its IR spectrum is shifted to

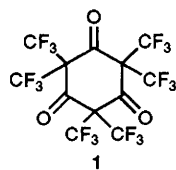


Table 1 Fluorination conditions for **1**

Temp./°C	He/ml min ⁻¹	F ₂ /ml min ⁻¹	Time/h
-28	500	0	0.5
-28	500	60	5 ^a
0	80	10	12
25	80	10	24

^a Slowly adding sample into reactor during this time.

5.7 μm from the value of 5.9 μm for the hydrocarbon analogue.⁹ Single crystals of **1** were obtained by sublimation and its molecular structure (Fig. 1) was determined by X-ray structure analysis.[†]

The molecule is unusually flat, as can be seen from the sum of the six ring torsion angles $31^\circ + 18^\circ + 14^\circ + 32^\circ + 18^\circ + 12^\circ = 125^\circ$. By comparison, the sum of the torsional angles in the cyclohexane ring and for hexamethylcyclohexane-1,3,5-trione are 336° and 192° , respectively.⁹ In comparison to the boat conformation of hexamethylcyclohexane-1,3,5-trione,⁹ the conformation of **1** is a twisted boat. The three axial trifluoromethyl groups, which are larger than methyl groups, create steric bulk and possibly strained and hindered rotation. The atoms C(1), C(3), C(4), and C(6) are 0.08 Å out of the best plane through these atoms. The atoms C(2) and C(5) are 0.3 Å out of this plane in the same direction. The shortest intramolecular $\text{CF}_3\cdots\text{CF}_3$ contact of **1** is 3.7 Å [C(11)---C(32)].

The average C–O bond length of **1**, 1.18 Å, is significantly shorter than the average C–O bond length (1.21 Å) of hexamethylcyclohexane-1,3,5-trione.⁹ This causes the carbonyl absorption in the IR spectrum of **1** to shift to a shorter wavelength. The three ring angles other than carbonyl angles in **1** are close to 115.8° , which is far from an ideal tetrahedral angle 109.28° and even larger than those of hexamethylcyclohexane-1,3,5-trione (107.2 , 111.6 and 112.4°).⁹

We are currently investigating liquid-phase direct fluorination of other polyketones.

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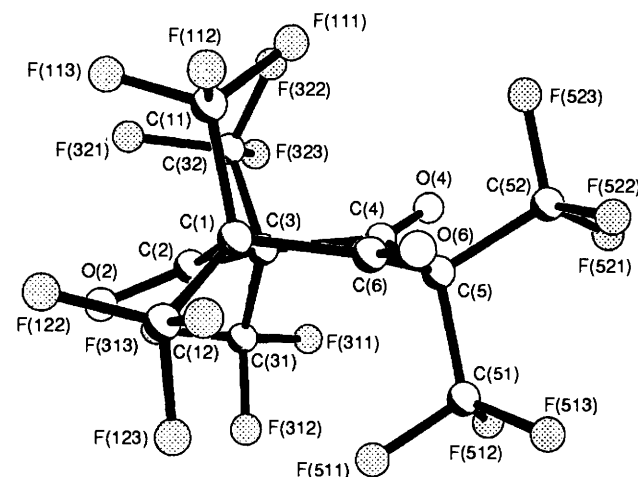


Fig. 1 Molecular structure of $\text{C}_{12}\text{F}_{18}\text{O}_3$ **1**; a twisted boat conformation. Selected bond lengths (Å): C(2)–O(2) 1.188(5), C(4)–O(4) 1.179(5), C(6)–O(6) 1.178(5); selected bond angles (°): C(2)–C(1)–C(6) $115.7(4)$, C(2)–C(3)–C(4) $115.8(4)$, C(6)–C(5)–C(4) $116.0(4)$; selected torsional angles (°): C(6)–C(1)–C(2)–C(3) $-30.8(6)$, C(1)–C(2)–C(3)–C(4) $17.9(6)$, C(2)–C(3)–C(4)–C(5) $14.4(6)$, C(3)–C(4)–C(5)–C(6) $-32.3(6)$, C(4)–C(5)–C(6)–C(1) $18.3(6)$, C(2)–C(1)–C(6)–C(5) $11.8(6)$.

Footnote

† *Crystal data* for **1**: C₁₂F₁₈O₃, crystal size 0.1 × 0.2 × 0.2 mm, *M* = 534.12 g mol⁻¹, monoclinic, space group *P*₂₁/*n* (No. 14, Internat. Tab.) *a* = 8.6493(1), *b* = 11.9106(1), *c* = 15.239(2) Å, β = 90.044(1)°, *V* = 1569.9(4) Å³ (from 25 reflections with 2θ range 6 to 27°), *Z* = 4, *D*_c = 2.260 g cm⁻³, *F*(000) 1032, μ = 0.296 mm⁻¹. 3212 data were collected on a Siemens *P*4 diffractometer [graphite monochromator, λ = 0.71073 Å (Mo-Kα), *T* = 173 K, 2θ range 5–50°, θ/2θ scans, program system XSCANS].¹⁰ Three standard reflections were measured periodically for intensity calibration. The number of unique reflections is 2762 (*R*_{int} = 0.0254). Intensity data were corrected for Lorentz and polarisation effects. The structure was solved by direct methods (SHELXTL PLUS)¹¹ and refined by full-matrix least-squares methods on *F*² using program system SHELXL-93.¹² The final *R* value was *wR*₂ = 0.067 for 2753 data and 298 parameters [*R*₁ = 0.0452 for 1209 data, *I* > 2σ(*I*)]. The final maximum shift/esd was -0.003 and the final ρ_(max)/ρ_(min) values (e Å⁻³) were +0.26 and -0.33, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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