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Synthesis and Structure of Perfluorocongressane

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Perfluorocongressane was synthesized using elemental fluorine and characterized by mass spectra, ^{19}F NMR, and X-ray crystallography.

The direct fluorination of inorganic,[1] organometallic[2] and organic[3] compounds, employing the LaMar method,[4] has impacted the synthesis of structurally unusual fluorinated compounds over the past 25 years. Recently, a new direct fluorination technology, the Exfluor−Lagow method,[5] has been invented by Exfluor Research Corp. of Austin, TX. The system of perfluoroadamantane and its derivatives was first accomplished using the LaMar process, and the yield of perfluorinated products is usually less than 10%.[6] In 1992, perfluorocongressane was first made by aerosol direct fluorination in 8% yield.[7] We report in this paper the crystal structure of perfluorocongressane which was synthesized by using a combination of the LaMar and the Exfluor−Lagow methods in 45% yield.

Results and Discussion

Crystals of perfluorocongressane suitable for single crystal structure determination[11] were obtained by recrystallization from diethyl ether. Check reflections of moderate intensity were remeasured periodically to monitor instrument and crystal stability. The structure was solved by direct methods using SHELXS-90[8] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for all atoms using SHELXL-93.[9] The data were corrected for extinction.

A graphical representation of the molecule is given in Figure 1. The molecule lies on a three-fold rotary inversion axis with C(1) and F(1) positioned on that axis. Congressane and perfluorocongressane exhibit the same molecular symmetry and thus it is not surprising that perfluorocongressane also lies on a three-fold rotary inversion axis.[10] The carbon−carbon distances found in either of the compounds are close to the ideal distance of 1.541 Å, and the angles within the carbon framework of both molecules are close to the angle expected for tetrahedral geometry. The carbon−fluorine bond distances found are between 1.34 and 1.36 Å, which are the expected carbon−fluorine bond distances.

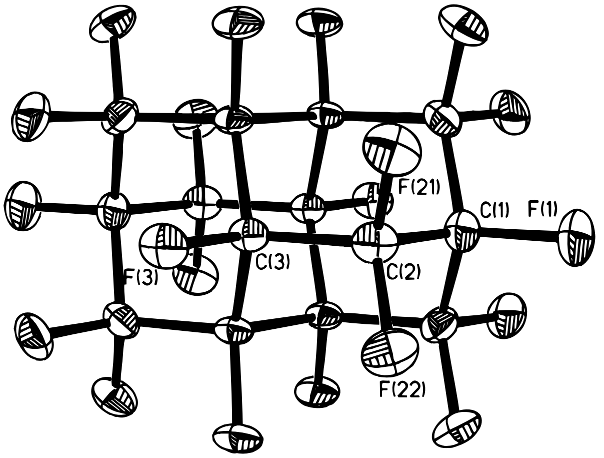

Figure 1. X-ray crystal structure of perfluorocongressane.

In general, yields of perfluorinated polycyclic compounds are determined by two factors: fluorination conditions and the number of bridgehead protons. During the early stages (stages 1−3; Table 1) of the direct fluorination reaction, the reaction energy was dissipated more rapidly than in the LaMar method. Thus, the destruction of the congressane molecules can be avoided and the yield of perfluorocongressane improves.

Stages 4 and 5 require a higher reaction temperature to replace the bridgehead protons, which substantially decreases the solubility of fluorine gas in 1,1,2-trichlorotrifluoroethane with the higher reaction temperature. Therefore yield of perfluorocongressane was limited to 25% which is based on GC integration.

Bridgehead protons are less reactive toward fluorine. There are eight bridgehead protons in one congressane molecule, which necessitates stronger reaction conditions. Therefore we applied the LaMar method at 60 °C (stage 6) to replace the bridgehead protons with fluorine. After the sixth stage the yield of perfluorocongressane was increased from 25% to 45%. The combination of the Exfluor−Lagow and the LaMar methods has proven to be a powerful tool for synthesizing previously inaccessible perfluorinated compounds. Perfluorocongressane is currently under investigation for unusual solid lubricant properties.

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Table 1. Direct Fluorination Condition

stage	He[a]	F_2[a]	temp (°C)	time (h)
1	400	0	−20	0.5
2	400	80	−20	6
3	10	10	0	12
4	10	10	ambient (35−37)	24
5	0	10	ambient (35−37)	24
6	0	10	60	24

[a] mL/min.

Experimental Section

Congressane was purchased from Aldrich Chemical Co. (Milwaukee, WI). The data for the X-ray structure determination were collected on a SIEMENS P4 diffractometer at reduced temperature using a SIEMENS LT2 low-temperature delivery system.

Fluorination Procedures. A solution fluorination reactor contains 100 g of NaF and 500 mL of 1,1,2-trichlorotrifluoroethane which was cooled to −20 °C and flushed with helium for 30 min (stage 1; Table 1). It was then charged with helium−fluorine gas mixture. A 5 g amount congressane was dissolved in 300 mL of 1,1,2-trichlorotrifluoroethane and added to fluorination reactor. The reaction temperature was kept at −20 °C for 6 h (stage 2). During the next 60 h the relative fluorine concentration and the reaction temperature were slowly raised (stages 3−5).

Filtration of the solution and removal of 1,1,2-trichlorotrifluoroethane by simple distillation left colorless solid. The solid was redissolved in a small amount of 1,1,2-trichlorotrifluoroethane and transferred into a nickel boat and fluorinated by the LaMar method at 60 °C (stage 6; Table 1).

Purification and Characterization. Purification of the product was achieved by performing preparative GC on a OV-210 column (10 ft × 0.25 in), helium flow rate was 45 mL/min. The column temperature was 160 °C and retention time was 6.3 min. Pure product was obtained this way as a colorless solid.

Chemical ionization mass spectral analysis (positive mode): *m/e* 548 ($C_{14}F_{20}$, M^+) and 529 ($C_{14}F_{19}$, $M^+ - F$). Elemental compositions were studied by high resolution mass spectroscopy in chemical ionization positive mode. Results were consistent with $C_{14}F_{20}$ (calcd 547.9681; found 547.9671) and $C_{14}F_{19}$ (calcd 528.9697; found 528.9702). The ^{19}F NMR ($CDCl_3$ and diethyl ether) spectrum consists of three peaks at −117.32, −209.58, and −223.40 ppm (−117.32, −209.68, and −223.68, ppm, lit.[7]) which was referenced to internal $CFCl_3$ with higher field designated as negative. Melting point is 126−128 °C (sublimes).

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