Stable Perfluoroalkyl Carbanion Salts

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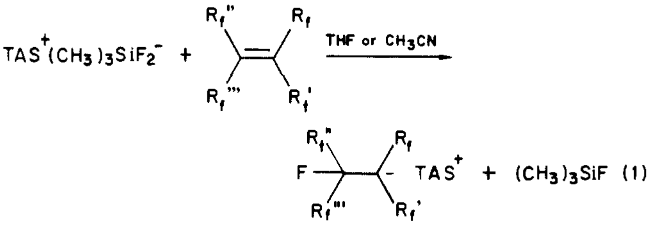
Abstract: The synthesis and properties of tris(dimethylamino)sulfonium (TAS) salts of perfluoro tertiary carbanions are described. Many of these unique salts are isolable and stable up to their melting points, and they dissolve in organic solvents to provide high concentrations of perfluoro carbanions. Several reactions of $TAS^+CF_3CF_2CF_2C^-(CF_3)_2$, which exemplify the synthetic utility of these new salts, are reported.

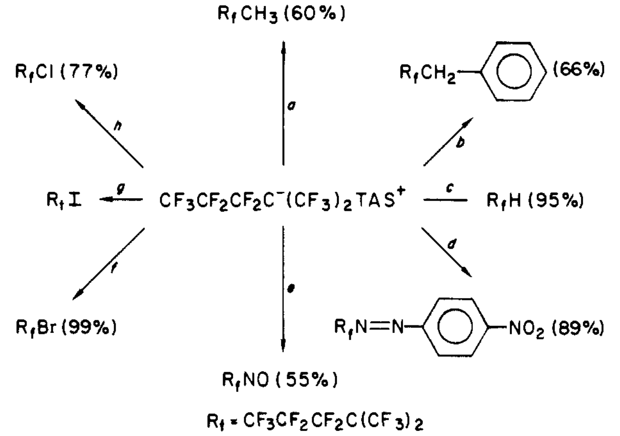
Perfluoroalkyl carbanions are important reactive intermediates in fluorocarbon chemistry.[1] They commonly are generated from fluoro olefins and fluoride ion or by deprotonation of monohydroperfluoroalkanes. Although many are sufficiently long-lived to be trapped by electrophiles, few have been detected spectroscopically,[2-4] and except for some special zwitterions,[5] no perfluoroalkyl carbanion salts have been isolated. We report the synthesis and characterization of the first insolable perfluoroalkyl carbanion salts.[7]

Tris(dimethylamino)sulfonium (TAS) trimethyldifluorosiliconate (**1**)[8] reacts with fluorinated olefins to give TAS perfluoro tertiary carbanions (eq 1).[9] The carbanion salts are obtained by simply removing the solvent and the $(CH_3)_3SiF$ byproduct. Representative examples of isolable salts are listed in Table I.



The TAS carbanion salts are distinguished by their ease of preparation and their remarkable stability. The crystalline salts are stable up to their melting points. By contrast, attempts to isolate the Cs^+ salts of **9**[2] and other perfluoro tertiary carbanions[2,4] gave only CsF and fluoro olefins. The carbanions **5** or **8** could not even be detected by ^{19}F NMR in mixtures of CsF with $C_2F_5(CF_3)C{=}C(CF_3)C_2F_5$ or perfluorobicyclopentylidene in DMF.[2]

Scheme I



[a] CH_3OSO_2F, C_6H_5CN, 0 °C. [b] $C_6H_5CH_2Br$, CH_3CN, 25 °C. [c] CF_3CO_2H, tetraglyme, −30 °C. [d] $4\text{-}NO_2C_6H_4N_2^+PF_6$, 0–25 °C. [e] NOF, C_6H_5CN, 0 °C. [f] Br_2, C_6H_5CN, 0 °C. [g] *N*-Iodosuccinimide, THF, −30 °C; iodide unstable at 25 °C (crude yield ~50%), identified by NMR and converted to C_6H_5SR ((TAS)SC_6H_5, THF, −78 to 25 °C, 30% yield).[i] [h] Cl_2, C_6H_5CN, 0 °C. [i] Reactions of tris(dimethylamino)sulfonium mercaptides with perfluoroalkyl iodides have been described: Laganis, E. D. Paper presented at the Winter Fluorine Conference, Orlando, FL, Feb 1985.

In solution, perfluoro carbanions normally exist in dynamic equilibrium with their corresponding fluoro olefins and fluoride ion, although their equilibrium concentrations often are vanishingly small. Even when they are present in significant concentrations, it usually is difficult to slow F exchange enough to observe the effectively static perfluoro carbanions on the ^{19}F NMR time scale.[1,2] For the few cases where spectra of static ions are reported,[3,4] temperatures ordinarily below −50 °C are required. The TAS perfluoro carbanions also undergo exchange processes in solution that are temperature (and solvent) dependent, but exchange can be slow at 25 °C. For example, TAS **3** in DMF-d_7 or Me_2SO-d_6 at 25 °C exhibits well-resolved F–F couplings between the geminal CF_3, the CF_2, and the terminal CF_3 nuclei (Figure 1). (Equally well-resolved spectra of ions **4–9** are obtained in DMF or Me_2SO.) In THF at 25 °C, however, the signals for **3** appear as broadened, unresolved singlets. The F exchange in THF can be sufficiently slowed to regain the coupling patterns either by lowering the temperature to ca. −15 °C or by adding small amounts of **1** (5–10 mol %). Magnetization transfer experiments are being done to measure the rates of exchange from the various β-sites of the perfluoro carbanions.

In no case have we been able to observe persistent secondary perfluoro carbanions. For example, adding $CF_3CF{=}CF_2$ to a large excess of **1** in various solvents gives **4**, but no spectroscopically detectable amounts of $TAS^+(CF_3)_2CF^-$. Similarly, perfluoro-

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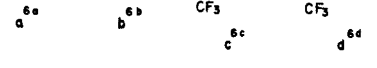
(1) (a) B. E. Smart, *The Chemistry of Functional Groups Supplement D: The Chemistry of Halides, Pseudo-Halides and Azides*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1983; Part 1, Chapter 14. (b) Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley: New York, 1973; Chapter 7. (c) Young, J. A. *Fluorine Chem. Rev.* **1967**, *1*, 359. (d) Dyatkin, B. L.; Delyagina, N. I.; Sterlin, S. R. *Russ. Chem. Rev.* (*Engl. Transl.*) **1976**, *45*, 607.

(2) Chambers, R. D.; Matthews, R. S.; Taylor, G.; Powell, R. L. *J. Chem. Soc., Perkin Trans. 1* **1980**, 435.

(3) Delyagina, N. I.; Igumnov, S. M.; Snegirev, V. F.; Knunyants, I. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, 1836.

(4) Ter-Gabriēlyan, V. G.; Gambaryan, N. P.; Lur'e, É. P.; Knunyants, I. L. *Dokl. Akad. Nauk SSSR* **1980**, *254*, 459.

(5) The zwitterions (ylides) **a–d** have been isolated and fully characterized.



a[6a] b[6b] c[6c] d[6d]

(6) (a) Howells, M. A.; Howells, R. D.; Baenzinger, N. C.; Burton, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 5366. (b) Baenzinger, N. C.; Foster, B. A.; Howells, M. A.; Howells, R. D.; VanderValk, P. D.; Burton, D. J. *Acta Crystallogr., Sect. B.* **1977**, *33*, 2339. (c) Burton, D. J.; Shinya, S.; Howells, R. D. *J. Am. Chem. Soc.* **1979**, *101*, 3689. (d) Burton, D. J.; Inouye, Y. *Tetrahedron Lett.* **1979**, 3397.

(7) (a) Presented in part at the 7th Winter Fluorine Conference, Orlando, FL, Feb 1985. (b) Middleton, W. J. (to Du Pont) US Patent 4535184.

(8) (a) Middleton, W. J. (to Du Pont) US Patent 3940402. (b) Middleton, W. J. *Org. Synth.* **1985**, *64*, 221. (c) Farnham, W. B.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4608.

(9) The TAS cation also uniquely stabilizes perfluorinated alkoxides: Farnham, W. B.; Smart, B. E.; Middleton, W. J.; Calabrese, J. C.; Dixon, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 4565.

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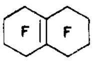
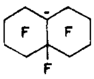
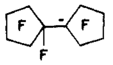
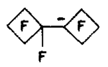
Table I. Isolable TAS Perfluoro Carbanions

olefin precursor	TAS carbanion	mp, °C
$(CF_3)_2C{=}CF_2$	$(CF_3)_3C^-$ (**2**)	170 dec
$(CF_3)_2C{=}CFCF_3$	$CF_3CF_2C^-(CF_3)_2$ (**3**)	166–168 dec
$(CF_3)_2C{=}CFCF_2CF_3$[a]	$CF_3(CF_2)_2C^-(CF_3)_2$ (**4**)	60 dec
$C_2F_5(CF_3)C{=}C(CF_3)C_2F_5$	$C_2F_5(CF_3)CFC^-(CF_3)C_2F_5$ (**5**)	~130 dec
$(CF_3)_2C{=}C(C_2F_5)_2$	$(CF_3)_2CFC^-(C_2F_5)_2$ (**6**)	oil
	 (**7**)	149–150 dec
[b]	 (**8**)	65–69
[c]	 (**9**)	oil

[a] Hexafluoropropene also gives **4**, see text. [b] Perfluorobicyclopentylidene also gives **8**. [c] Perfluorobicyclobutylidene also gives **9**.

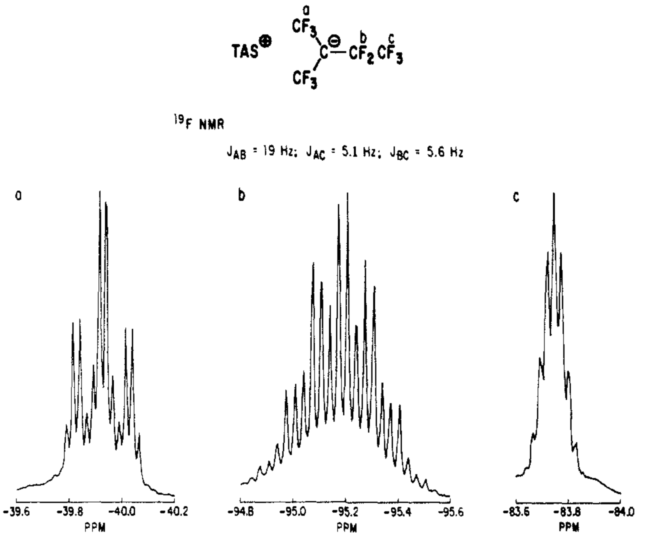


Figure 1. ^{19}F NMR spectrum of tris(dimethylamino)sulfonium 1,1,1,3,3,4,4,4-octafluoro-2-(trifluoromethyl)-2-butanide (Me_2SO, 25 °C).

cyclopentene and perfluorocyclobutene afford only **8** and **9**, and $(CF_3)_2CFCF{=}CF_2$ gives **4**, not $(CF_3)_2CF\bar{C}FCF_3$. Perfluoro-1-heptene is isomerized by **1** to *trans*-perfluoro-2-heptene, but no long-lived carbanions are produced. These results reflect the relative instability of α-fluorinated carbanions.[1a–c]

There also appears to be steric constraints on the stability of perfluorinated tertiary carbanions. For example, adding **1** to the hexafluoropropylene trimer $CF_3CF{=}C[CF(CF_3)_2]_2$ (**10**)[10] at 25 °C does not give any spectroscopically detectable amounts of the bulky anions **10a** or **10b** but instead gives anion **4**.

$$\underset{\textbf{10a}}{[(CF_3)_2CF]_2\bar{C}C_2F_5} \qquad \underset{\textbf{10b}}{(CF_3)_2\bar{C}CF(C_2F_5)CF(CF_3)_2}$$

The formation of **4** can be rationalized by the process in eq 2. The key step involves C–C bond cleavage of **10b** *at 25 °C*.[11]

$$\textbf{10} \underset{-F^-}{\overset{F^-}{\rightleftharpoons}} (CF_3)_2C{=}C(C_2F_5)CF(CF_3)_2 \underset{-F^-}{\overset{F^-}{\rightleftharpoons}} [\textbf{10b}] \rightleftharpoons$$
$$(CF_3)_2C{=}CFC_2F_5 + [(CF_3)_2\bar{C}F] \rightarrow \textbf{4} + CF_3CF{=}CF_2 \quad (2)$$

Interestingly, **1** with $(CF_3)_2C{=}C(C_2F_5)_2$ gives stable carbanion **6** but none of its isomer $(CF_3)_2\bar{C}CF(C_2F_5)_2$. The fact that **6** is stable but neither its isomer nor **10a**, which differs from **6** only by a CF_3 group in place of F at C_2, is long-lived indicates that tertiary carbanion stability is controlled by a rather delicate balance of steric and electronic factors.

The TAS perfluoro tertiary carbanion salts can be routinely handled and used as stock reagents if precautions are taken to rigorously exclude moisture.[12] Several reactions of **4** that exemplify synthetic utility are outlined in Scheme I.

The availability of stable perfluorocarbanion salts provides the opportunity to conduct physical organic studies that heretofore were very difficult or impossible to undertake. It is now possible to determine reliably the reactivities, nucleophilicities, and electrochemical oxidation potentials of perfluoro-*tert*-carbanions, and to measure accurately the thermodynamic acidities of their conjugate acids.[13] These studies are in progress.

Experimental Section

Fluorine chemical shifts are reported in parts per million (ppm) from $CFCl_3$ and ^1H and ^{13}C chemical shifts in ppm from $(CH_3)_4Si$. Solvents with minimum water concentration are required for preparation and manipulation of the carbanion salts reported here. Tetrahydrofuran (THF), dimethoxyethane, and diethyl ether were distilled from sodium benzophenone and then stored over activated molecular sieves. Acetonitrile, dimethyl sulfoxide (Me_2SO), and dimethylformamide (DMF) were distilled from calcium hydride and stored over activated sieves. All reactions were carried out in an atmosphere of dry nitrogen, and most manipulations of the carbanions salts were performed in a Vacuum Atmospheres drybox.

Tris(dimethylamino)sulfonium (TAS) 1,1,1,3,3,3-Hexafluoro-2-(trifluoromethyl)-2-propanide (2). 1,1,3,3,3-Pentafluoro-2-(trifluoromethyl)propene (14.8 g, 0.074 mol) (**Caution**: **Toxic**[14]) was slowly distilled into a stirred solution of 20.3 g (0.074 mol) of **1** in 75 mL of dry THF cooled to 0 °C. The reaction mixture was warmed to 25 °C and then evaporated to dryness under reduced pressure to give 26.6 g (94%) of tris(dimethylamino)sulfonium 1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)-2-propanide (**2**) as a white solid: mp 170 °C (from THF/ether at −35 °C); ^{19}F NMR (CD_3CN) δ −45.0 (s); ^1H NMR (CD_3CN) δ 2.88 (s); ^{13}C NMR (CD_3CN) δ 38.75 (q of q, J_{CH} = 141, 3.6 Hz, CH_3), 43.97 (dec, J_{CF} = 40 Hz, C^-), 132.27 (q, J_{CF} = 264 Hz, CF_3); UV λ_{max} (CH_3CN) 288 (ϵ 105), 207 nm (ϵ 12 800). Anal. Calcd for $C_{10}H_{18}F_9N_3S$: C, 31.33; H, 4.73; N, 10.96. Found: C, 31.89; H, 4.85; N, 11.05.

A similar procedure was used to prepare the following carbanion salts from the appropriate perfluoro olefin.

Tris(dimethylamino)sulfonium 1,1,1,3,3,4,4,4-octafluoro-2-(trifluoromethyl)-2-butanide (**3**) was prepared from **1** and 1,1,1,3,4,4,4-heptafluoro-2-(trifluoromethyl)-2-butene or 1,1,2,3,4,4,4-heptafluoro-3-(trifluoromethyl)-1-butene[15] in THF: mp 166–168 °C (from THF/ether); ^{19}F NMR (THF-d_8, 25 °C) δ −41.5 (br s, 6F), −84.2 (br s, 3F), −94.3 (br s, 2F); ^{19}F NMR (THF-d_8 plus 5 mol % **1**, 25 °C) δ −41.37 (t of q,

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(10) von Halasz, S. P.; Kluge, F.; Martini, T. *Chem. Ber.* **1973**, *106*, 2950.

(11) A similar mechanism has been posulated to account for the fragmentation products, $(CF_3)_2CFH$ and $(CF_3)_2C{=}CFC_2F_5$, produced from the reaction of **10** with KHF_2 in dimethylformamide at 100 °C: Brunskill, W.; Flowers, W. T.; Gregory, R.; Haszeldine, R. N. *J. Chem. Soc.,Chem. Commun.* **1970**, *1444*.

(12) The TAS salts are very water sensitive and their hydrolysis is not straightforward. For example, quenching **4** in water gives nearly equivalent amounts of $CF_3(CF_2)_2C(CF_3)_2H$ and $CF_3CF_2C(O)C(CF_3)_2H$.

(13) The pK_a of $(CF_3)_3CH$, for instance, remains in doubt: (a) Sleigh, J. H.; Stephens, R.; Tatlow, J. C. *J. Chem. Soc., Chem. Commun.* **1979**, 921. (b) Sleigh, J. H.; Stephens, R.; Tatlow, J. C. *J. Fluorine Chem.* **1980**, *15*, 411. (c) Streitwieser, A., Jr.; Holtz, D.; Ziegler, G. R.; Stoffer, J. O.; Brokaw, M. L; Guibe, F. *J. Am. Chem. Soc.* **1976**, *98*, 5229.

(14) Clayton, J. W., Jr. *Fluorine Chem. Rev.* **1967**, *1*, 197.

(15) Haszeldine, R. N.; Mir, I.-ud-D.; Tipping, A. E. *J. Chem. Soc., Perkin Trans 1* **1979**, 565.

6F, J = 19.0, 5.1 Hz), −84.20 (m, 3F), −94.22 (sept. of q, 2F, J = 19.0, 5.6 Hz). Anal. Calcd for $C_{11}H_{18}F_{11}N_3S$: C, 30.49; H, 4.19; N, 9.70. Found: C, 30.95; H, 4.71; N, 10.62.

Tris(dimethylamino)sulfonium 1,1,1,3,3,4,4,5,5,5-decafluoro-2-(trifluoromethyl)-2-pentanide (**4**) was prepared from **1** and 1,1,1,1,3,4,4,5,5,5-nonafluoro-2-(trifluoromethyl)-2-pentene[16] in acetonitrile: mp 60 °C (triturated with ether); ^{19}F NMR (THF-d_8, 25 °C) δ −41.3 (br s, 6F), −80.1 (br s, 3F), −91.7 (br s, 2F), −125.2 (br s, 2F); ^{19}F NMR (Me_2SO-d_6, 25 °C) δ −40.22 (t of t, 6F, J = 20, 6 Hz), −79.35 (t, 3F, J = 10 Hz), −91.47 (m, 2 F), −125.00 (m, 2 F); UV λ_{max} (CH_3CN) 337 (ϵ 67), 240 (ϵ 7620), 220 nm (ϵ 7180). Anal. Calcd for $C_{12}H_{18}F_{13}N_3S$: C, 29.82; H, 3.75; F, 51.10; N, 8.69. Found: C, 29.43; H, 3.87; F, 50.70, N, 8.77.

Tris(dimethylamino)sulfonium 1,1,1,2,2,4,5,5,6,6,6-undecafluoro-3,4-bis(trifluoromethyl)-3-hexanide (**5**) was prepared from **1** and 1,1,1,2,2,5,5,6,6,6-decafluoro-3,4-bis(trifluoromethyl)-3-heptene[17] in THF: mp ~130 °C; ^{19}F NMR (DMF-d_7) δ −36.72 (s, 3F), −74.85 (s, 3F), −78.80 (s, 3F), −82.75 (s, 3F), −88.8, −90.2 (ABm, 2F, J_{AB} = 245 Hz), −114.6, −118.9 (ABm, 2F, J_{AB} = 289 Hz), −170.3 (s, 1F). Anal. Calcd for $C_{14}H_{18}F_{17}N_3S$: C, 28.83; H, 3.11; N, 7.30. Found: C, 29.54; H, 3.97; N, 8.49. Attempts to recrystallize this carbanion salt were unsuccessful.

Tris(dimethylamino)sulfonium 1,1,1,2,4,4,5,5,5-nonafluoro-2-(trifluoromethyl)-3-(pentafluoroethyl)-3-pentanide (**6**) was prepared from **1** and 1,1,1,4,4,5,5,5-octafluoro-2-(trifluoromethyl)-3-(pentafluoroethyl)-2-pentene[18] in THF: viscous oil; ^{19}F NMR (DMF-d_7) δ −75.5 (m, 6 F), −82.0 (d, 6F, J = 15 Hz), −85.7 (m, 4F), −169.4 (m, 1F).

Tris(dimethylamino)sulfonium 2,2,3,3,4,4,5,5,6,7,7,8,8,9,9,10,10-hexadecafluorobicyclo[4.4.0^{1,6}]decan-1-ide (**7**) was prepared from **1** and perfluoro-1,2,3,4,5,6,7,8-octahydronaphthalene[19] in THF: mp 149–150 °C (from THF/ether/petroleum ether); ^{19}F NMR (DMF-d_7) δ −67.9, −105.6 (ABm, 4F, J_{AB} = 263 Hz), −112.3, −129.3 (ABm, 4F, J_{AB} = 257 Hz), −119.1, −139.8 (ABm, 4F, J_{AB} = 258 Hz), −122.2, −138.7 (ABm, 4F, J_{AB} = 270 Hz), −95.3 (m, 1 F). Anal. Calcd for $C_{16}H_{18}F_{17}N_3S$: C, 31.63; H, 2.99; F, 53.18; N, 6.92; S, 5.28. Found: C, 30.96; H, 3.38; F, 53.00; N, 7.97; S, 6.08.

Tris(dimethylamino)sulfonium 2,2,3,3,4,4,5,5-octafluoro-1-(nonafluorocyclopentyl)-1-cyclopentanide (**8**) was prepared from **1** and perfluorocyclopentene (2 equiv) or perfluorobicyclopentylidene[20] (1 equiv) in THF: mp 65–69 °C (from THF/ether/petroleum ether); ^{19}F NMR (DMF-d_7) δ −79.8 (d of m, 4F, J = 52 Hz), −108.7, −133.7 (ABm, 4F, J_{AB} = 258 Hz), −115.5 (m, 1F), −121.5, −127.9 (ABm, 4F, J_{AB} = 247 Hz), −127.4 (m, 4F). Anal. Calcd for $C_{16}H_{18}F_{17}N_3S$: C, 31.64; H, 2.99; F, 53.17. Found: C, 32.09, H, 3.40; F, 53.19.

Tris(dimethylamino)sulfonium 2,2,3,3,4,4-hexafluoro-1-(heptafluorocyclobutyl)-1-cyclobutanide (**9**) was prepared from **1** and hexafluorocyclobutene (2 equiv) or perfluorobicyclobutylidene[21] (1 equiv) in acetonitrile: viscous oil; ^{19}F NMR (DMF-d_7) −85.9 (d, 4F, $J \cong$ 50 Hz), −123.2, −126.8 (ABm, 4F, J_{AB} = 226 Hz), −123.6 (s, 2F), −127.4, −132.6 (ABm, 2F, J_{AB} = 224 Hz), −132 (br m, 1F).

Hexafluoropropylene Trimer 10 and 1. The trimer **10**[10] (4.4 g, 9.8 mmol) was pipetted into a stirred solution of 3.0 g (10.9 mmol) of **1** in 10 mL of benzonitrile at 25 °C. The stirring was stopped, whereupon the mixture separated into two layers. By ^{19}F NMR spectroscopy, the upper layer proved to be a solution of mostly **4** in benzonitrile, and the lower layer comprised a 1:2.2 mixture of **10** and its isomer $(CF_3)_2C{=}C(C_2F_5)CF(CF_3)_2$.[10]

1,1,1,2,2,3,3,5,5,5-Decafluoro-4-(trifluoromethyl)pentane. To a mixture of 3.75 mL of trifluoroacetic acid and 15 mL of tetraglyme at ca. −30 °C was added dropwise a solution of 11.6 g (0.024 mol) of **4** in tetraglyme. The mixture was warmed to 0 °C and stirred for 0.5 h, and the volatiles were transferred under vacuum. The volatile fraction, after treatment with sodium bicarbonate to remove excess trifluoroacetic acid, was again transferred under vacuum and finally distilled to afford 6.5 g (85%) of product: bp 60–61 °C [lit.[22] bp 60–61 °C]; ^{1}H NMR (THF-d_8) δ 5.58 (m); ^{1}H NMR ($CDCl_3$) δ 3.93 (m); ^{19}F NMR (THF-d_8) δ −61.5 (m, 6F), −80.4 (t, 3F, J_{FF} = 11.4 Hz), −111.2 (m, 2F), −125.3 (m, 2F).

4-Nitro-2′,2′,3′,3′,4′,4′,4′-heptafluoro-1′,1′-bis(trifluoromethyl)-benzene-1′-azobutane. *p*-Nitrobenzenediazonium hexafluorophosphate 33.6 g, 0.11 mol) was added in portions to a solution of 53.2 g (0.11 mol) of **4** in 75 mL of acetonitrile cooled to 0 °C. The reaction mixture was warmed to 25 °C, stirred for 1.5 h, and then poured into 800 mL of ice–water. The water was decanted from the semisolid residue, and the residue was triturated with ether to give 24.5 g (75%) of $TAS^+PF_6^-$. The ether wash was extracted with water, dried ($MgSO_4$), and evaporated to dryness to give 45.8 g (89%) of the azo compound as a bright orange oil: $n^{25}{}_D$ 1.4292; ^{19}F NMR ($CDCl_3$) δ −63.8 (m, 6F), −80.9 (t, 3F, J = 13 Hz), −110.5 (m, 2F), −124.2 (m, 2F); ^{1}H NMR ($CDCl_3$) δ 8.05, 8.48 (ABm, J_{AB} = 8 Hz). Anal. Calcd for $C_{12}H_4F_{13}N_3O_2$: C, 30.72; H, 0.86; F, 52.64; N, 8.96. Found: C, 30.84; H, 0.87; F, 52.51; N, 8.89.

1,1,1,2,2,3,3,5,5,5-Decafluoro-4-nitroso-4-(trifluoromethyl)pentane. Nitrosyl fluoride (20 g, 0.41 mol) was slowly distilled into a well-stirred mixture of 1 g of **1** and 120 g (0.4 mol) of 1,1,1,3,4,4,5,5,5-nonafluoro-2-(trifluoromethyl)-2-pentene[16] in 200 mL of benzonitrile cooled to 0 °C. The reaction mixture turned blue. After the addition was completed, the reaction mixture was warmed to room temperature and stirred 1.5 h. The lower blue layer then was separated and distilled to give 76.8 g (55%) of deep-blue liquid: bp 74–75 °C; ^{19}F NMR ($CDCl_3$) δ −63.5 (tt(quintet), 6F, J = 10, 10 Hz), −81.0 (t, 3F, J = 13 Hz), −109.7 (m, 2F), −124.7 (m, 2F); IR (neat) 1620 cm^{-1} (NO). Anal. Calcd for $C_6F_{13}NO$: C, 20.65; N, 4.01. Found: C, 20.41; N, 4.29.

A similar reaction between 0.078 mol of nitrosyl chloride and 0.072 mol of **4** in 100 mL of acetonitrile at 0 °C gave a 25% yield of the pure nitroso product.

2-Bromo-1,1,1,3,3,4,4,5,5,5-decafluoro-2-(trifluoromethyl)pentane. Bromine (13.11 g, 0.082 mol) was added dropwise to a solution of 41.08 g (0.085 mol) of **4** in 75 mL of benzonitrile cooled to 10 °C. The exothermic reaction was kept below 15 °C during the addition. After the addition was completed, the reaction mixture was warmed to room temperature and stirred for 0.5 h. The volatiles boiling below benzonitrile were distilled out at reduced pressure and redistilled on a spinning band column to give 27.64 g (99%) of colorless liquid: bp 99–101 °C [lit.[23] bp 97.5 °C (745 mm)]; ^{19}F NMR ($CDCl_3$) δ −65.2 (t of t, 6F, J = 12, 10 Hz), −81.1 (t, 3F, J = 13 Hz), −105.9 (m, 2F), −122.6 (m, 2F). Anal. Calcd for C_6BrF_{13}: C, 18.06; F, 61.91. Found: C, 17.90; F, 61.55.

Note Added in Proof. After this paper was submitted, Chambers and co-workers reported the isolation of solid *cesium* salts of perfluoro carbanions **2** and **4** (Bayliff, A. E.; Bryce, M. R.; Chambers, R. D.; Matthews, R. S. *J. Chem. Soc., Chem. Commun.* **1985**, 1018). No data on the composition or stability of the isolated solids are given; however, the solids were shown to dissolve in tetraglyme, but not other solvents, to give high concentrations of **2** and **4** that undergo slow fluoride exchange on the ^{19}F NMR time scale at room temperature.

Registry No. 1, 59218-87-0; **2**, 100645-89-4; **3**, 102780-80-3; **4**, 100645-92-9; **5**, 102780-82-5; **6**, 102780-84-7; **7**, 102807-68-1; **8**, 102780-86-9; **9**, 100645-97-4; **10**, 30320-27-5; $(CF_3)_2C{=}CF_2$, 382-21-8; $(CF_3)_2C{=}CFCF_3$, 41004-33-5; $(CF_3)_2C{=}CFCF_2CF_3$, 1584-03-8; $C_2F_5(CF_3)C{=}C(CF_3)C_2F_5$, 25543-35-5; $(CF_3)_2C{=}C(C_2F_5)_2$, 58621-64-0; $MeC(CF_3)_2(CF_2)_2CF_3$, 100645-99-6; $CF_3(CF_2)_2C(CF_3)_2CH_2Ph$, 64356-97-4; $IC(CF_3)_2(CF_2)_2CF_3$, 102780-88-1; $ClC(CF_3)_2(CF_2)_2CF_3$, 67437-97-2; $PhSC(CF_3)_2(CF_2)_2CF_3$, 102780-89-2; $(CF_3)_2C{=}C(C_2F_5)CF(CF_3)_2$, 30320-26-4; 1,1,1,2,2,3,3,5,5,5-decafluoro-4-(trifluoromethyl)pentane, 30320-28-6; 4-nitro-2′,2′,3′,3′,4′,4′,4′-heptafluoro-1′,1′-bis(trifluoromethyl)benzene-1′-azobutane, 100646-01-3; *p*-nitrobenzenediazonium hexafluorophosphate, 1514-52-9; 1,1,1,2,2,3,3,5,5,5-decafluoro-4-nitroso-4-(trifluoromethyl)pentane, 67728-23-8; 1,1,1,3,4,4,5,5,5-nonafluoro-2-(trifluoromethyl)-2-pentane, 1584-03-8; 2-bromo-1,1,1,3,3,4,4,5,5,5-decafluoro-2-(trifluoromethyl)pentane, 22528-67-2; perfluoro-1,2,3,4,5,6,7,8-octahydronaphthalene, 54939-04-7; perfluorocyclopentene, 559-40-0; hexafluorocyclobutene, 697-11-0; hexafluoropropene, 116-15-4; perfluorobicyclopentylidene, 49851-76-5; perfluorobicyclobutylidene, 68252-05-1.

Supplementary Material Available: Experimental data for additional reactions of TAS perfluoro tertiary carbanion salts (4 pages). Ordering information given on any current masthead page.

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Planarization of Unsaturated Rings. A Cycloheptatriene with a Planar Seven-Membered Ring

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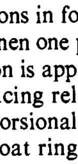
Abstract: Geometrical and structural requirements for the ring planarization of cyclopolyolefins are discussed. As an example, the crystal structure analysis and spectroscopic properties are described for a compound which involves a planar cycloheptatriene ring due to constraining a torsion angle around a C–C single bond at 0°. The constraint is introduced via fusion of a rigid norbornane moiety with the seven-membered ring. Implications for planarizing larger rings, in particular the eight-membered ring of *all-cis*-cyclooctatetraene, are pointed out.

A planar n-membered ring has $n - 3$ independent possibilities (normal coordinates) for nonplanar deformations, which may be represented as linear combinations of ring torsion angles. Thus a planar seven-membered ring may be subjected to nonplanar distortions in four different ways. If three torsion angles are fixed at 0°, then one possibility for nonplanar deformation remains. This situation is approximated in *all-cis*-cyclohepta-1,3,5-triene (**1**) by introducing relatively rigid double bonds. The remaining single (soft) torsional degree of freedom in **1** clearly corresponds to the boat–boat ring inversion. The geometrical flexibility properties of **1** may be instructively compared to those of cyclobutane (again one nonplanar deformation possibility corresponding to the ring inversion coordinate) into the four-membered ring of which a cycloheptatriene skeleton with ideally planar, rigid C—C═C—C segments can be inscribed (Figure 1a). Similar considerations are valid for *all-cis*-cycloocta-1,3,5,7-tetraene (**2**) (Figure 1b; see Discussion).[1]

The best structure of cycloheptatriene **1** is a boat conformation with mirror symmetry C_s (Appendix I). According to NMR measurements,[2] the ring inversion of this boat minimum requires an activation energy of 6.3 kcal mol^{-1} and probably proceeds across the planar C_{2v} symmetric form as a transition state. We have been wondering how a system could be structurally realized, the most favorable geometry of which has a planar cycloheptatriene ring. According to the introductory geometrical analysis, for this purpose a ring torsion angle around at least one C–C single bond in **1** is to be fixed at 0°.[3] The respective constraint may be imposed in two ways: (1) fusion of a small ring via a C–C single bond, as for instance in **3** and possibly also in **4** (this measure simultaneously supports planarization through facilitated angle openings in the seven-membered ring which are inevitably required for ring flattening[4]), and (2) fusion of a suitable polycyclic framework via single bonds with sufficiently rigid syn-planar partial conformations, as, for example, in **5**–**7**. Because of angle strain criteria, the known framework **7**[5] appears particularly favorable since also in this example angle openings in the seven-membered ring are relatively easy in view of the compressed C(1)–C(7)–C(4) angle of only 94° in norbornane. (The systems **3**–**6** are unknown.)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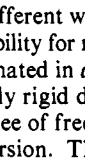
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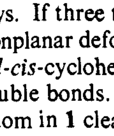
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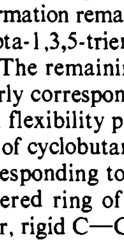
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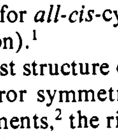
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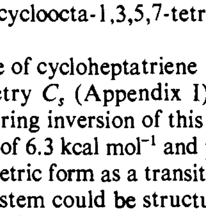

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The question arises as to whether the torsional rigidity of the norbornane skeleton in **7** indeed suffices to planarize the seven-membered ring and whether nonplanar double bond distortions are sufficiently resisted as supposed. A theoretical answer, e.g., with the help of force-field methods, is complicated by the special "homoaromatic" stabilization of the boat minimum of **1**.[6] Therefore, we have attempted an experimental solution of the present structural problem and report here the X-ray analysis of the dicarboxylic acid **8** at room temperature as well as some spectroscopic data. This derivative of **7** is readily available from a diester precursor,[5] and the two carboxylic groups ensure a sufficiently tight molecular packing via hydrogen-bonded chains.

Experimental Section

The *endo,exo*-dicarboxylic acid **8** was prepared by alkaline hydrolysis of the corresponding *endo,endo*- and/or *exo,exo*-dimethyl ester.[5] Apparently, a stereoisomerization occurs under the influence of the base, as evidenced by the subsequent crystal structure analysis.

X-ray Analysis. $C_{14}H_{14}O_4$, M_r 246.3, mp 177 °C, monoclinic crystals from ethyl acetate, space group Cc or $C2/c$ (centrosymmetric choice made), d_x = 1.323 g cm^{-3}, d_m = 1.33 g cm^{-3}, Z = 8, a = 26.146 (19) Å, b = 6.874 (5) Å, c = 13.683 (10) Å, β = 91.49 (7)°, 3580 independent intensities measured at room temperature on a four-circle diffractometer (λ_{Mo} = 0.71069 Å, θ_{max} = 30°), structure solved by direct methods, refinement including the 2920 reflections with $|F_o| > 3\sigma(F_o)$, R = 0.066, R_w = 0.066, all crystallographic calculations performed with the program system SHELX76.

We thank Dr. W. Gebert, Bochum, for the intensity measurements. The refined atomic coordinates and the averaged isotropic temperature factor coefficients are listed in Table I, while Figure 2 shows a stereoview of **8** with vibrational ellipsoids (35% probability), and relevant molecular geometry data, and the atomic numbering. Anisotropic temperature factor coefficients of the heavy atoms and a list of observed and calculated structure amplitudes are available as supplementary material.

Discussion

In the crystals of **8**, the cycloheptatriene ring is practically planar as witnessed by the torsion angles and the sum of the bond

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[1] Similarly, *cis,cis*-cycloocta-1,4-diene and *cis,cis*-cycloocta-1,5-diene may be compared with cyclohexane: Dunitz, J. D.; Waser, J. *J. Am. Chem. Soc.* **1972**, *94*, 5645. It is stressed that these comparisons are geometrical; they do not imply physically (energetically) similar flexibility properties.

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[3] For planarization of the seven-membered ring, the fixing of a ring torsion angle at 0° around a C(sp^2)—C(sp^2) single bond is less effective than that around a C(sp^3)—C(sp^2) single bond since in the C_s boat minimum of **1** the C═C—C═C torsion angles are considerably smaller in magnitude than the C═C—C—C torsion angles (Appendix I).

[4] The maximum possible average bond angle in a n-membered ring holds for planarity and obviously amounts to 180°(n – 2)/n, i.e., 900°/7 = 128.57°, in the planar seven-membered ring.

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