that were formed in the oxidation of **6a**, except **8**, were detected. The compositions of the reaction mixture at each temperature during the oxidation of **6b** are also given in Table I. The initial intermediate in this reaction (**9**) was an unsymmetrical species (C1 and C4 were not equivalent) and reached a peak concentration of 69% at 0 °C and subsequently continued to disappear.

The identity of **9** was determined from two observations; it was the first compound formed in the oxidation of **6b** and the second detected during the oxidation of **6a**. Also, α-disulfoxide **8** was not formed during the oxidation of **6b**. It is clear that oxidation of **6b** at the sulfenyl sulfur atom and from the expected direction (exo) would give an α-disulfoxide that is not symmetric about the C8–C6 axis, thus C1 and C4 should have different chemical shifts. The chemical shifts for **9**[17] indicated that it was nonsymmetric, thus it can be assigned as the unsymmetrical α-disulfoxide (Scheme I).

It is expected that the S–S bond of **6a** and **6b** would be relatively weak due to the strained bicyclic system and the expected repulsion between the two parallel sulfur–oxygen bonds. A concerted-type rearrangement of α-disulfoxide **8** is not likely as the sulfinyl oxygen is not able to reach an empty orbital on the adjacent sulfur atom due to the rigidity of the system. It is expected that homolysis of the S–S bond would occur to give two sulfinyl radicals **14**[20] that can recombine by several possible routes. One of these routes must involve a rotation about one C–S bond and head-to-head recombination to give the unsymmetrical α-disulfoxide **9**. *This was verified by the appearance of* **9** *as the second intermediate in the oxidation of* **6a**.[21]

The final product of the oxidation in both cases was thiosulfonate **13**.[22] The identities of the remaining intermediates, **10**, **11**, and **12**, are deduced by a careful analysis of the possible pathways that intermediates **8** and **9** may follow in order to produce thiosulfonate **13** (Scheme I). It is known from the NMR spectra that **10** and **12** were unsymmetrical species and **11** was symmetric; they were also stable enough to exist at room temperature and above but could not be isolated. Intermediates **10** and **12** are therefore best assigned as the two possible *O,S*-sulfenyl sulfinates and can easily be pictured to form from a head-to-tail recombination of the two sulfinyl radicals.[23] Species **11** logically is assigned as a sulfinic anhydride; however, the disappearance of this species without evidence for a decomposition product argues that **11** is likely the symmetric endo α-disulfoxide (Scheme I). The formation of final product **13** can clearly be pictured to proceed via rearrangement of *O,S*-sulfenyl sulfinates **10** and **12**.[5,13-15]

The electrophilic oxidation of bridged bicyclic thiosulfinates has thus provided the most stable α-disulfoxides to date. In addition, these results give a thorough picture of this important oxidative process.

Acknowledgment. We thank the F.C.A.R. (Québec) and the Natural Sciences and Engineering Research Council of Canada for financial support.

Supplementary Material Available: Analytical and NMR data for compounds **6a**, **6b**, and **15** as well as ^{13}C and ^{1}H NMR spectra from low-temperature experiments (5 pages). Ordering information is given on any current masthead page.

(20) Sulfinyl radicals were proposed as intermediates in the disproportionation of aryl arenethiosulfinates (Koch, P.; Ciuffarin, E.; Fava, A. *J. Am. Chem. Soc.* **1970**, *92*, 5971) and in the rearrangement of α-disulfoxides to thiosulfonates in the oxidation of diaryl thiosulfinates (ref 5a and references therein).

(21) α-Disulfoxide **9** could also be formed by a direct attack of the oxidizing agent on the endo side of the sulfur–sulfur bond of **6a**; however, approach from this face has been shown to be unfavorable (ref 16); thus, this mechanism should not account for the formation of a significant amount of **9** from **6a**.

(22) The structure was confirmed by esterification of the unsubstituted bridged bicyclic thiosulfonate (**13**; R = H) and a comparison of the NMR data with that of **13** (R = $C(O)(CH_2)_4CH_3$); see supplementary material for analytical data on **13** (R = H).

(23) A concerted rearrangement of **9** (Scheme I) could also lead to compounds **10** and **12**.

A 32-Membered Fluorinated Multifunctional Heterocycle

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Received August 8, 1991

The synthesis and characterization of fluorinated heterocycles have been subjects of intense study in this laboratory[1-3] and others.[4-7] Many of these materials are small rings (seven members or less) containing nitrogen, oxygen, and/or sulfur and are used in applications such as blood substitutes,[7] inert fluids,[1] and antistatic coatings.[8] Small heterocycles containing one or two fluorine atoms or a trifluoromethyl group are common biologically active materials.[4,9,10] In addition, a variety of metalloheterocycles have been synthesized and studied extensively for their potential use in the preparation of conducting polymers.[11-13]

Most recently, a great deal of interest in the synthesis of macroheterocycles (rings containing more than seven members) has been kindled. While the use of crown ethers for metal ion extraction is well-known, current synthetic efforts are directed toward heterocycles which are metal ion specific, e.g., a 16-membered heterocycle containing oxygen and sulfur which is specific for Ag^+,[14] a 15-membered macrocyclic ether containing amide and amine functional groups which reportedly shows selectivity as a chelating agent for Pb^{2+},[15] and a 16-membered heterocycle containing four nitrogen heteroatoms which is specific for nickel.[16] Larger multifunctional heterocycles containing as many as 36 atoms are being designed for selective molecular recognition. These macrocycles demonstrate the ability, for example, to act as biological mimics of ionophore antibiotics,[17] as synthetic analogues of enzyme receptors,[18] and as selective complexing agents for organic picrates.[19] A series of excellent reviews are available covering the synthesis and chemistry of fluorinated and nonfluorinated heterocycles, three of which are referenced here.[20-22]

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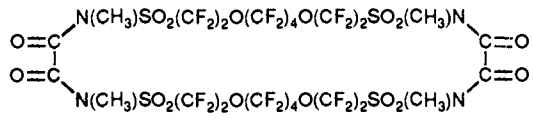
0002-7863/91/1513-9000$02.50/0

Although interest in fluorinated heterocycles is increasing,[4] reports of the synthesis and characterization of per- or polyfluorinated macrocycles are limited. The synthesis of perfluorinated 18-crown-6 has been achieved; however, its potential for formation of neutral complexes is expected to be poor.[23,24] A number of large perfluoroalkyl heterocycles (16-membered rings or smaller) containing the sulfamide functional group have been prepared and characterized.[25] The first successful host/guest relationship between a large polyfluorinated heterocyclic ether (an 18-membered ring) and fluoride ion has only recently been established by X-ray crystal structure analysis.[26]

We now report the synthesis and structure of a unique, polyfluorinated, 32-membered multifunctional heterocyclic ring, **1**. The ring contains four *N*-methyl sulfonamide, two α,β-diketone, and four ether functional groups. The starting material, I(C-



1

$F_2)_2O(CF_2)_2SO_2F$ (**2**), was prepared by the literature method.[27] Refluxing **2** in the presence of zinc in $CH_2Cl_2/(CH_3CO)_2O$ (1/1) for 8 h gave an 85% yield of $FO_2S(CF_2)_2O(CF_2)_4O(CF_2)_2SO_2F$ (**3**). The bis(*N*-methyl sulfonamide) $HN(CH_3)SO_2(CF_2)_2O(C-F_2)_4O(CF_2)_2SO_2(CH_3)NH$ (**4**) was obtained in 90% yield from the reaction of **3** with CH_3NH_2 at −40 °C over a period of 4 h.[28] Compound **4** was quantitatively converted to the bis(*N*-methyl sodium sulfonamide) **5** by reaction at 25 °C with sodium in anhydrous ethanol. The heterocycle **1** (mp 108 °C) is isolated in 60% yield when **5** (0.38 mmol in 5 mL of CH_3CN) is added dropwise to a solution of oxalyl chloride[29] (0.76 mmol in 3 mL of CH_3CN) with vigorous stirring at 0 °C, followed by the addition of 10 mL of water and filtration. The white solid thus obtained is recrystallized twice from a mixture of acetone and hexane (1/2) to give pure **1**. The ^{19}F NMR (ϕ −81.40, −82.99, −112.24, −125.56) and ^1H NMR (δ 3.48, 3.35) spectra and the elemental analytical data (Calcd: C, 21.43; F, 45.24; N, 4.16; S, 9.52. Found: C, 21.47; F, 45.1; N, 4.15; S, 9.62) are consistent with the structure of **1**.

The X-ray crystal structure of **1** (obtained with a $P2_1$ Syntex diffractometer system using the Nicolet SHELXTL (Version 5.1) structure solution package) is shown in Figure 1, along with selected bond lengths and angles. The crystal class is monoclinic with lattice constants of a = 11.836 (4) Å, b = 13.856 (5) Å, c = 14.658 (7) Å, β = 102.38 (3)°, and V = 2348 (2) Å^3 based on 25 reflections in the range $15 < 2\theta < 18$. A total of 3081 unique reflections were obtained with 1472 having $F > 3\sigma(F)$. Refinement of 251 parameters yielded R = 0.1073, R_w = 0.0683, and GOF = 1.717.

The observed bond angles and bond lengths are all as expected; however, a stereoview of this macroheterocycle provides some interesting observations. The gross symmetry of this molecule can best be described as a pair of bowls which are inverted with respect to each other. Each bowl is defined by 16 of the 32 atoms which make up the macrocyclic ring. The first bowl begins at N(1) and ends at S(1)′. The bottom of the bowl is confined by the methyl group bonded to N(2), the C(5) carbonyl, the di-

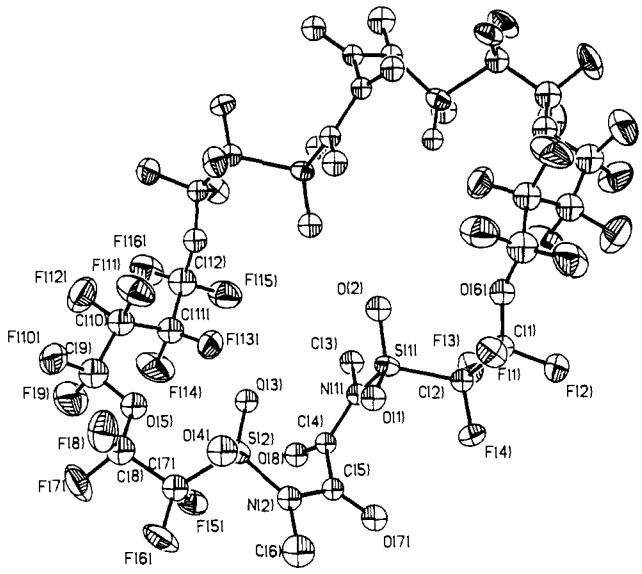


Figure 1. ORTEP diagram of **1** with hydrogen atoms removed. Selected bond lengths (Å): C(1)–C(2), 1.532 (17); C(1)–F(2), 1.341 (16); C(1)–O(6), 1.372 (16); S(1)–O(2), 1.400 (9); S(1)–C(2), 1.840 (13); S(1)–N(1), 1.646 (10); N(1)–C(3), 1.481 (15); N(1)–C(4), 1.398 (14); C(4)–O(8), 1.190 (15); C(4)–C(5), 1.576 (18). Selected bond angles (deg): C(2)–S(1)–N(1), 102.1 (5); O(1)–S(1)–O(2), 122.9 (5); O(1)–S(1)–C(2), 105.8 (5); O(1)–S(1)–N(1), 108.0 (5); C(3)–N(1)–S(1), 118.6 (7); C(4)–N(1)–S(1), 124.7 (8); C(3)–N(1)–C(4), 115.2 (9); N(1)–C(4)–O(8), 123.2 (11); C(5)–C(4)–N(1), 119.3 (10); C(5)–C(4)–O(8), 117.4 (10); C(4)–C(5)–N(2), 119.5 (11).

fluoromethylenes at C(11), C(12), C(1)′, and C(2)′, and the S(1)′ sulfone group. The remaining atoms form the sides and top of this bowl. For each bowl, a single oxygen of the sulfone is directed into the ring, as are one of the *N*-methyl moieties (N(2)) and the C(5) carbonyl group.

The crystal structures of such large, fluorinated multifunctional heterocycles have not been reported previously. We are continuing our exploration of the thermal and host/guest chemistry of this interesting and unusual molecule.

Acknowledgment. We thank the Air Force Office of Scientific Research (91-0189) and the National Science Foundation (CHE-9003509) for support of this work. We are also grateful to the National Science Foundation (Grant CHE-8408407) and the Boeing Company for the purchase of the X-ray diffractometer system and Dr. Roger Willet and Dr. Brian Scott for obtaining the crystal structure data.

Supplementary Material Available: Complete information on bond lengths and bond angles, atomic coordinates, and anisotropic and isotropic thermal parameters for **1** (4 pages); listing of observed and calculated structure factors for **1** (10 pages). Ordering information is given on any current masthead page.

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Backside Displacement in the Unimolecular Gas-Phase Decarboxylation of Alkyl Phenyl Carbonate Radical Cations

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Received June 24, 1991

Expulsion of carbon dioxide in the course of unimolecular rearrangements is well-known throughout organic and biological

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0002-7863/91/1513-9001$02.50/0