74.33, 120.96, 139.25, 140.59, 186.27.

Preparation of 1 from 2-Amino-2-deoxy-D-(+)-glucose Hydrochloride (6). The general procedure was followed by using 2-amino-2-deoxy-D-(+)-glucose hydrochloride (2.97 g, 13.77 mmol). After the final addition of sodium methoxide stirring was continued for 2 days at room temperature. Typical workup (vide supra) gave 0.60 g (19%) of 1.

Preparation of 1 from 1-Amino-1-deoxy-D-fructose Acetate (7). The general procedure was followed by using 1-amino-1-deoxy-D-fructose acetate (3.30 g, 13.77 mmol). After the final addition of sodium methoxide stirring was continued for 3 days at room temerature. Typical workup (vide supra) gave 1.46 g (46%) of 1.

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Registry No. 1, 94944-70-4; 2, 19479-65-3; 6, 66-84-2; 7, 6333-49-9.

Synthesis and Structure Determination of 3,3,4,4-Tetrafluoro-*N*-methyl-2-(*cis*,*s*-*trans*-methyl-*NNO*-azoxy)-*s*-*cis*-1-cyclobutene-1-amine[1]

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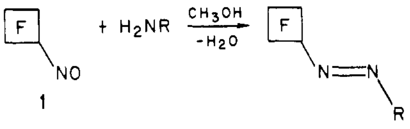
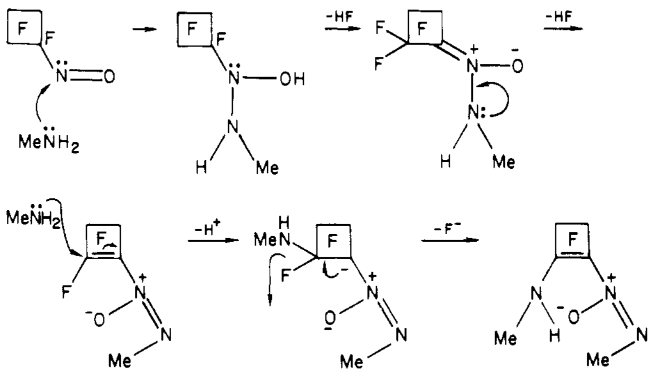
The reactions of nitroso compounds with primary amines normally result in the formation of azo compounds, with concomitant elimination of water.[4,5] Recently there has been renewed interest in the reaction of CF_3NO with aromatic amines as a route to the introduction of trifluoromethyl groups into these molecules via azo intermediates.[6-9] In this context, we studied the reactions of heptafluoronitrosocyclobutane (1) or nonafluoronitrosocyclopentane (2) with several primary amines. The expected condensation reactions occurred to form the azo products.[10] Corresponding reactions occur with 2. However, when methylamine is used instead of the aromatic amines the reaction takes a quite different and intriguing path. Although $CF_3N{=}NCH_3$ is the high-yield product from the reaction of CH_3NH_2 with CF_3NO,[11] no azo compound is obtained from the reaction of methylamine with 1. Instead, a sublimable, crystalline product with the empirical formula $C_6H_7F_4N_3O$ is formed. A firm structural assignment from spectroscopic data was difficult. The correct structure was determined by X-ray methods, showing that the compound is 3 which may result via the mechanism in Scheme I.



1

R = C_6H_5, C_6F_4H, $C_6H_4NH_2$

Scheme I



The elimination of HF, leading to an azoxy compound, is preferred to the loss of H_2O which would result in the formation of an azo material. The electron shift to form the stable conjugated azoxybutene system aids the attack of the methylamine at the more positive carbon, followed by further loss of HF to give the isolated product.

Although electrophilic fluorinated nitrosoalkanes have been reacted with dozens of aliphatic, alicyclic, and aromatic compounds that contain the nucleophilic NH_2 group, no evidence has been found for the formation of azoxy compounds in addition to the expected azo materials.[11] It should be noted that the analogous azoxy product was formed when 2 was reacted with methylamine. The existence of the latter was demonstrated by comparing the ^1H and ^{19}F NMR, UV, IR, MS, and elemental analysis data with those of 3 whose structure is reported in this paper.

Experimental Section

All reagents were used as received from commercial suppliers. Methylamine was obtained from Matheson. Heptafluoronitrosocyclobutane and nonafluoronitrosocyclopentane were prepared by literature methods.[10]

Gases and volatile liquids were handled in a conventional Pyrex glass vacuum system equipped with a Heise Bourdon tube gauge and a Televac thermocouple gauge. Starting materials were measured quantitatively by PVT techniques. Spectrometers used were IR, Perkin-Elmer 599; ^{19}F and ^1H NMR, JEOL FX-90Q FT at 84.26 and 90 MHz, or Varian EM-360L at 54.6 MHz; MS, Hitachi Perkin-Elmer RMU-6E at 17 eV; UV, Beckman Acta MVII, scanning from 250 to 800 nm, using $CHCl_3$ solutions contained in 1-cm cuvettes. For the NMR studies, $CDCl_3$ and/or $CFCl_3$ were used as solvents and as internal or external references; ^{19}F chemical shifts upfield from that of $CFCl_3$ were assigned negative values. for IR, KBr disks were employed. Elemental analyses were by Beller Mikroanalytisches Laboratorium, Göttingen, FRG.

1 (6 mmol) and methylamine (8 mmol) were added to methanol (10 mL, liquid N_2 temperature) in a 250-mL round-bottomed flask equipped with a 19/26 inner ground glass joint to which was attached a Kontes Teflon-brand stopcock. The flask was then

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[1] Cis and trans are based upon Cahn-Ingold-Prelog priorities for fluorine and nitrogen.

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0022-3263/85/1950-1136$01.50/0

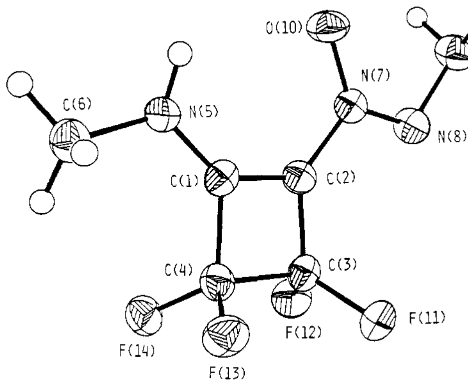

Figure 1. Thermal ellipsoid plot of the molecule, indicating atom numbering. Ellipsoids are drawn at 50% probability, H atoms with fixed radius.

warmed gradually (1 h) to −78 °C and then over a period of 24 h to room temperature. All volatile compounds were removed under vacuum, leaving a pale orange solid residue. The stopcock was then replaced with a water-cooled sublimation finger. A yellow-white solid sublimed under vacuum (10 μm) at 40 °C over a period of 4–6 h, for a yield of 10–12%. The pure, white compound **3** was obtained by successive recrystallizations from hexane.

Properties of $CH_3N{=}N(O)C{=}C(NHCH_3)CF_2CF_2$: mp 88.0–88.8 °C; IR 3355 (s), 1723 (vs), 1498 (s), 1440 (m), 1422 (m), 1382 (s), 1347 (s), 1275 (m), 1250 (s), 1149 (s), 1086 (m), 1063 (s), 1025 (w), 949 (vs), 908 (mw), 850 (mw), 778 (m), 736 (m), 700 (mw), 670 (mw), 661 (mw), 593 (mw), 496 (s), 362 (mw), 350 (w), 318 (w) cm^{-1}; ^{19}F NMR two singlets in a 1:1 ratio at ϕ −108 and −115; ^1H NMR δ 3.05 (d, 3 H), 3.3 (s, 3 H), 6.2 (br s, 1 H) [based on decoupling experiments and bands are assigned to CH_3NH, $CH_3N{=}N$ and NH, respectively]; UV λ_{max} = 325 nm (br), ϵ_{max} = 105 cm^{-1} mol^{-1} L (assigned to the $n \rightarrow \pi^*$ transition); mass spectrum, *m/e* 213 ($C_6F_4H_7N_3O^+$). Anal. Calcd for $C_6F_4H_7N_3O$: N, 19.72; F, 35.66. Found: N, 19.51; F, 36.0.

X-ray Data and Structure Determination. A preliminary data set was measured by C.B.S. and D.P.S. Because of the relatively high sublimation rate of the compound, the crystal was sealed in a capillary. From these initial data the positions of all non-hydrogen atoms were determined with the program MULTAN,[12] and the structure was partially refined. However, it became clear that low-temperature data would be helpful, and the final data set was then collected (by H.H.). The data were measured with a Syntex $P2_1$ diffractometer equipped with a locally modified LT-1 low-temperature device. The data collection techniques used have been described elsewhere.[13] Because of the low-temperature technique used, data collection could be safely carried out without a capillary or other protection of the crystal.

Crystal data: formula $C_6H_7F_4N_3O$, M_r = 213.14, crystal selected from a sample recrystallized from hexane, triangular prism of length 1.0 mm, base 0.38 mm, and height 0.20 mm, mounted with the long direction near the diffractometer ϕ axis, monoclinic space group $P2_1/c$, cell dimensions at 140 K, a = 6.438 (2) Å, b = 13.185 (5) Å, c = 10.010 (2) Å, β = 92.55 (2) Å, V = 845.5 (5) Å^3, Z = 4, Mo Kα (graphite) λ = 0.71069 Å, μ = 1.91 cm^{-1}, d_{calcd} (140 K) = 1.67 mg m^{-3}, 2° ω scans at 58.6° min^{-1}, bg offsets ±1.5°, scan/bg time ratio = 1, max 2θ = 50°, 1500 unique reflections measured, 941 with $I > 3\sigma(I)$ used in refinement of 139 parameters.

All calculations were performed on a Data General Eclipse computer with the SHELXTL system. Scattering factors were from International Tables.[14] Refinement was started from the preliminary parameters, initially with isotropic temperature factors. With R at ≈0.09 an empirical absorption correction[15] was applied. Refinement was then concluded with anisotropic temperature factors for non-H atoms. The H atoms, located in a difference electron density map, were refined isotropically: the methyl groups with fixed, idealized geometry (C–H 1.00 Å, all angles 109.5°), and U's coupled to U(C), the remaining H(5) with no constraints imposed. The final R is 0.038, R_w is 0.036.

It is of interest to note that the total diffractometer time for this data set was about 6 h, including setup time.

Discussion

A view of the molecule with the atomic numbering is given in Figure 1. The derived structure clearly shows that the compound is **3**. Bond distances and angles are within normal ranges, but with some interesting features. The two ring C–C distances adjacent to C=C are of different lengths: 1.505 Å for C_1–C_4 and 1.436 Å for C_2–C_3. The bonding of N_7 to both N and O gives rise to a longer C–N bond (1.409 Å) than is found at N_5 (C_1–N_5 = 1.320 Å) and the relative strengths of the C(ring)–N bonds is reflected in the lengths of the adjacent C–C bonds. All C, N, and O atoms are essentially coplanar; the maximum deviation from the least-squares plane is 0.050 Å for N(5); H(5) is also in the same plane. The molecules are associated through N–H···O links to weakly hydrogen bonded, centrosymmetric dimers. the O(10′)–H(5) distance is 2.12 Å, N(5)–H(5)···O(10′) 2.907 Å, and the angle at H(5) 169°.

The azoxy derivative reported here has been obtained via a route which has not been used previously for other than the syntheses of azo compounds. The conditions employed are particularly mild, the reaction being run with slow warm up in methanol. While azoxy compounds are prepared easily by the condensation of nitroso compounds with hydroxylamines, the reported reactions of nitroso compounds with amines require oxidizing conditions in order to form azoxy derivatives. Recently cyclohexylamine and *n*-butylamine were reacted with *tert*-butyl hypochlorite in the presence of iodine and nitrosobenzene to give the two azoxy compounds, *N*-cyclohexyl-*N′*-phenyldiazine *N′*-oxide and *N*-*n*-butyl-*N′*-phenyldiazine *N′*-oxide, respectively, in high yield.[16] These reactions are presumed to have R′NHI or $R'NI_2$ as intermediates.

The ^{19}F NMR spectrum, with two singlets in a 1:1 ratio at ϕ −108 and −115 (vide supra), requires that both vicinal F–F coupling constants be very small, or zero. A small coupling constant is reconciled with the fact that all C, N, and O atoms are coplanar. A similar phenomenon has been observed for other compounds, e.g., $(CO_4Mn(CH_3)_2$-$AsMn(CO)_4(CH_3)_2AsC{=}CCF_2CF_2$, for which the ^{19}F NMR spectrum consists of a singlet at ϕ −107.[17] The structure has been determined by X-ray crystallography.

Since we have also been able to synthesize the azoxy derivative of nonfluoronitrosocyclopentane, we expect that the method described in this article will be applicable to the synthesis of many other fluorinated azoxy systems.

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Registry No. **1**, 2261-41-8; **2**, 91816-92-1; **2** (azoxy deriv), 95122-32-0; **3**, 95122-31-9; methanamine, 74-89-5.

Supplementary Material Available: Listings of positional and thermal parameters, distances, and angles for **3** (2 pages). Ordering information is given on any current masthead page. Structure factor tables may be obtained from H.H.

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