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NEW AMINES AND HYDRAZINES WITH PENTAFLUOROCHALCOGEN SUBSTITUENTS

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The novel hydrazine $(SF_5)_2N\text{-}N(SF_5)_2$ has been prepared in up to 65% yield from the UV photolysis of $(SF_5)_2NCl$. The compound is a colorless, crystalline solid (mp 44.5-46.0°C) which has been characterized by its IR, NMR, and mass spectra. In CCl_3F solvent in the vicinity of room temperature, $(SF_5)_2N\text{-}N(SF_5)_2$ undergoes reversible N-N bond homolysis to give $(SF_5)_2N\cdot$ radicals which were identified by ESR spectroscopy. The spectrum of the radical (g = 2.0033)

$$(SF_5)_2N\text{-}N(SF_5)_2 \rightleftarrows 2\ (SF_5)_2N\cdot \qquad (1)$$

consists of an eleven line pattern (overlapping triplet of nonets; $a(^{14}N)$ = 13.5 G, $a(^{19}F)$ = 13.5 G) with an intensity ratio of 1:9:37:92:154:182:154:92:37:9:1 thus indicating eight equivalent (basal) fluorines. The results of a number of studies which are currently underway on the hydrazine and the equilibrium shown in equation 1 will be presented. These include a structural investigation by X-ray diffraction and/or electron diffraction, a relaxation time study by fluorine-19 NMR, a thermodynamic and kinetic study, and INDO and ab initio calculations on $(SF_5)_2N$ radical. The first derivative chemistry of $(SF_5)_2N\text{-}N(SF_5)_2$ will also be discussed.

The compound $Hg[N(CF_3)SF_5]_2$ can be obtained from the direct reaction of $SF_5N{=}CCl_2$ with excess HgF_2 at 160°C. Reactions of this mercurial with halogens or interhalogens give the series of tertiary amines $SF_5N(X)CF_3$. In contrast to the above reaction of $(SF_5)_2NCl$, the photolysis of $SF_5N(Cl)CF_3$ gives the amine $(SF_5)_2NCF$ in 50% yield and only traces of the hydrazine $SF_5(CF_3)N\text{-}N(CF_3)SF_5$. Crystal structure analysis of $Hg[N(CF_3)TeF_5]_2$ reveals a linear N-Hg-N arrangement as well as an almost planar framework around each nitrogen (<TeNC = 118.5°). In order to determine the relative group electronegativities of $SF_5(CF_3)N\text{-}$ and $TeF_5(CF_3)N\text{-}$, the methyl amine derivatives were prepared from the reactions of the respective mercurial with methyl iodide. The proton NMR chemical shifts of these derivatives will be compared to those of other methyl derivatives containing highly electronegative groups or elements.