

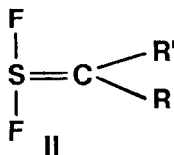
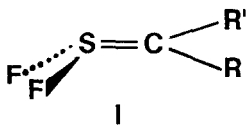
STRUCTURE AND STRUCTURAL DYNAMICS OF
 ALKYLIDENESULFUR DIFLUORIDES AND ALKYLIDENESULFUR
 DIFLUORIDE OXIDES: EXPERIMENT VERSUS THEORY

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Recently, Seppelt and co-workers reported the first examples of alkylidenesulfur difluorides [$\text{SF}_2=\text{C}(\text{CF}_3)_2$, $\text{SF}_2=\text{C}(\text{CF}_3)\text{SF}_5$] [1] and alkylidenesulfur difluoride oxides [$\text{O}=\text{SF}_2=\text{C}(\text{H})\text{C}(\text{O})\text{F}$] [2]. While these workers have predominantly studied the structures and structural dynamics of these compounds by NMR spectroscopy, we have assisted in their further study by computational methods. In the case of the alkylidenesulfur difluorides, the computational results are consistent with the experimental observation that the corresponding sulfenyl fluorides, $\text{R}_2\text{FC-SF}$, are the thermodynamically favored products. In addition, the lowest energy structure for $\text{SF}_2=\text{C}(\text{CF}_3)_2$ (I) is consistent with the appearance of two unique CF_3 resonances in the fluorine-19 NMR spectrum, and thus, with the appearance of cis and trans isomers for $\text{SF}_2=\text{C}(\text{CF}_3)\text{SF}_5$. However, another minimum energy structure II is found on the potential energy surface for each of the alkylidenesulfur difluorides calculated. For example, with $\text{SF}_2=\text{CF}_2$ the planar, T-shaped structure (II) is significantly lower in energy than is the structure corresponding to I, while with $\text{SF}_2=\text{C}(\text{H})\text{F}$ structures I and II are nearly equivalent in energy. Preliminary calculations on SFCF indicate a preference of an ylide structure over a triple bond structure.

The four possible conformations of $\text{O}=\text{SF}_2=\text{C}(\text{H})\text{C}(\text{O})\text{F}$, which would result from hindered rotation about the $\text{S}=\text{C}$ and $\text{C}-\text{C}$ bonds, have been calculated at the 3-21G(*) basis set level. Interconversion between these conformations has also been examined computationally by two separate mechanisms: (1) the barrier to rotation about the $\text{S}=\text{C}$ bond and (2) the barrier to inversion at the sulfur via edge inversion. The results of these calculations will be described and compared to the reported variable-temperature NMR data [2].



- 1 R. Damerius, K. Seppelt, and J. S. Thrasher, *Angew. Chem., Int. Ed. Engl.*, **28**, (1989).
- 2 T. Krügerke and K. Seppelt, *Chem. Ber.*, **121**, 1977 (1988).