

Fluorinated heterocycles with bridged and spiro substituents

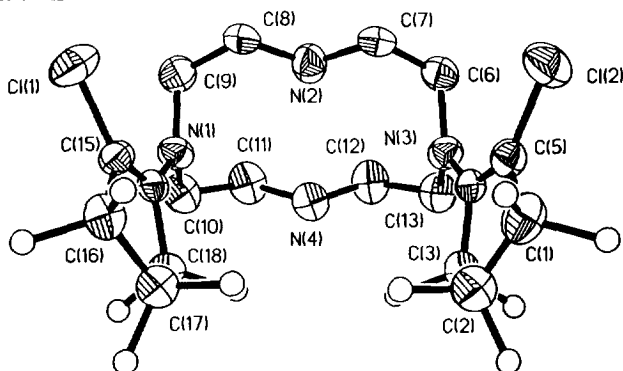
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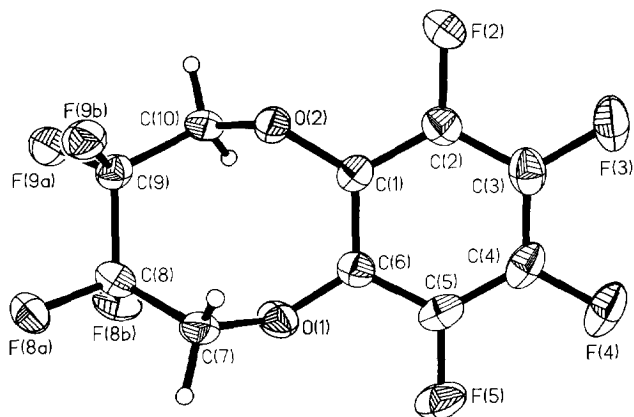
Our interest in the synthesis of fluorinated heterocycles began several years ago when we prepared the 32-membered polyfluorinated heterocycle $[\text{C}(\text{O})\text{N}(\text{CH}_3)\text{SO}_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_4\text{O}(\text{CF}_2)_2\text{SO}_2(\text{CH}_3)\text{NC}(\text{O})]_2$ [1]. Just prior to our discovery of this macrocycle, another group of researchers [2] published the synthesis of a neutral polyfluorinated heterocycle that forms a stable complex with the fluoride ion. It was also reported that perfluorinated crown ethers form observable complexes with molecular oxygen [3]. These were the first indications that fluorinated heterocycles could be expected to exhibit significant host/guest chemistry, and has led us to expand our synthetic efforts in this area. These non-bonding interactions are important to our understanding of a diverse range of chemistry from the functional design of fluorinated blood substitutes to chemical sensors, to chemical interactions that take place on low energy surfaces, and to the preparation of complexing agents that are specific hosts for a single metal or organic molecule in the presence of others.

To study these interactions, we have prepared a variety of cyclic compounds. The focus of the study described here is the preparation of nitrogen and/or oxygen-containing polyfluorinated heterocycles. Heterocycles containing nitrogen are readily obtained, for example the polyfluorinated heterocycle shown below is formed from the reaction between 1,2-dichloroperfluorocyclopentene and the macrocyclic amine aza-12-crown-4:



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Advantage has been taken of the ease with which difunctional siloxanes react with perfluorinated aromatic rings to prepare oxygen-containing heterocycles as shown:



A number of smaller heterocycles containing bridged and spirocyclic groups have also been obtained, and their structures have been confirmed by single-crystal X-ray analysis. The mechanism of formation of these small heterocycles has been studied. We are actively examining the host/guest chemistry of this interesting class of molecules with organic and inorganic substrates.

References

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- [3] R.J. Lagow, presented at the *N. Ishikawa Memorial Symp.*, Tokyo, Japan, 1991.