Table II. Calculated and Experimental Absorption and VCD Intensities

scaled (one parameter)				scaled (six parameters)				experiment				
$\bar{\nu}^a$	D^c	R^d	$10^4(4R/D)^e$	$\bar{\nu}^a$	D^c	R^d	$10^4(4R/D)^e$	$\bar{\nu}^{a,b}$	$\epsilon_{max}{}^f$	$10^3\Delta\epsilon_{max}{}^f$	$10^4\Delta\epsilon_{max}/\epsilon_{max}{}^e$	assignment
							TDCCP-d_0					
3081	0.42	−0.12	−1.2	3112	0.42	−0.23	−2.3	3120	9.2	−0.5	−0.5	B, CH_2 as str
3032	0.88	2.63	−4.5	3062	0.88	2.70	−4.3	3055	32	1.6	0.5	B, CH as str
3031	0.29	−3.96		3061	0.28	−3.95						A, CH s str
2994	3.28	0.17	0.2	3024	3.25	0.16	0.2	3030	4.6 (sh)	+		A, CH_2 s str
2362	9.46	−0.89	0.3	2247	9.86	−0.76	0.3	2255	135	6.3	0.5	B, CN as str
2362	84.09	7.45		2247	87.97	7.53						A, CN s str
1475	5.00	7.60	6.1	1460	4.98	7.67	6.2	1445	7.3	5.7	7.8	A, CH_2 def
1402	0.14	−1.49	−43.2	1388	0.20	−1.70	−34.3	1380	2.2	−5.4	−25	A, CH bend + CH_2 bend
							TDCCP-d_2					
1466	4.69	2.80	2.4	1450	4.72	2.79	2.4	1442	7.8	1.9	2.4	A, CH_2 def
1337	0.26	−0.40	−6.2	1327	0.30	−0.40	−5.3	1325	0.61	−1.2	−20	A, CH_2 bend

[a] In cm^{-1}. [b] From ref 17. [c] In 10^{-40} esu^2 cm^2. [d] In 10^{-44} esu^2 cm^2; origin at center of (+)-ve charge. [e] $\Delta\epsilon/\epsilon = 4R/D$. [f] Estimated from ref 17; ϵ_{max} values are likely to be inaccurate.

The equilibrium geometry and the vibrational force field at that geometry for TDCCP were obtained with GAUSSIAN 82.[9] This force field, transformed to internal coordinates, was then scaled to fit the experimental absorption and Raman frequencies for TDCCP-d_0 of Schrumpf and Dunker,[18] following the protocol of Pulay and co-workers.[19,20] Scaling with one parameter leads to a RMS deviation from experiment of 37 cm^{-1}. Scaling with six parameters reduces this to 13 cm^{-1}, without major change in the nature of any normal coordinates. All calculated frequencies, together with the experimental frequencies, are given in Table I. $P^{\lambda}_{\alpha\beta}$ and $I^{\lambda}_{\alpha\beta}$ were calculated by using CADPAC and transformed to D_i and R_i values for both scaled force fields and for both d_0 and d_2 isotopomers. These, and the anisotropy ratios derived therefrom, are given in Table II for those transitions for which VCD data exist. All ab initio calculations were carried out with the 6-31G** basis set[9] (125 basis functions) and the San Diego CRAY XMP supercomputer.

The relative absorption intensities of the C≡N stretch, CH_2 scissor, and CH/CH_2 bend modes are correctly predicted, as also are the absolute signs and relative intensities of their VCD. The effects of *trans*-1,2-dideuteriation on the frequencies, absorption intensities, VCD absolute signs, and VCD intensities of the CH_2 scissor and CH/CH_2 bend modes are also correctly reproduced. The weak absorption and VCD of the CH_2 symmetric and antisymmetric stretching modes of TDCCP-d_0 are qualitatively reproduced. However, the absorption intensity of the (essentially degenerate) CH stretch modes is considerably underestimated, and the net VCD is incorrect in sign. Our predictions are qualitatively identical for the two force fields, indicating that they are unlikely to be affected by any small adjustments to the force field that might result from minor revision in the vibrational assignment arrived at here.

These results further support the conclusion arrived at in our earlier calculations[8] that the sign and relative magnitudes of VCD intensities calculated with SCF wave functions and basis sets of medium size are in reasonable agreement with experiment. In the case of overlapping transitions whose VCD is opposite in sign and comparable in magnitude, predictions are less reliable. We believe that, for chiral molecules whose size permits ab initio calculations using basis sets of adequate sophistication, VCD should be capable of application to the elucidation of molecular stereochemistry. The development of efficient procedures for the calculation of vibrational rotational strengths, illustrated here, greatly increases the practical limits to the size of molecule and basis set that are accessible and the range of potential applications of VCD.

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N-Fluoroperfluoroalkylsulfonimides. Remarkable New Fluorination Reagents

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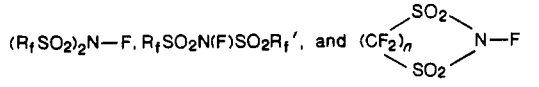
Nuclear-fluorinated aromatic compounds were first synthesized in the 1870's by the use of aromatic diazo compounds.[1] This methodology continues to be the most widely used today for the practical synthesis of fluoroaromatics, but the method has many limitations. Selectively fluorinated organics have grown in importance, driven by the useful biological activity of many known compounds and the expanding search for new examples with useful activity.[2] Considerable effort has been made to develop new reagents and methodology for selective fluorinations. For aromatic compounds, there have been interesting successes in small-scale reactions in the laboratory, but critical examination of these reports would not encourage very many chemists to attempt to utilize these methods.[3] In general, the reagents are not commerically available and are difficult to prepare. Even those that are commerically available (e.g., CF_3OF, F_2) require special equipment and experience to handle safely. It is an accurate generalization to say that essentially all these methods pose extraordinary hazards for the nonspecialist.

We wish to report a new class of reagents with potentially wide applicability in selective fluorinations of organic compounds and which appear to be particularly attractive for direct aromatic fluorinations. These new reagents are *N*-fluorosulfonimides of the type

$(R_fSO_2)_2N{-}F$, $R_fSO_2N(F)SO_2R_f'$, and 

They are easily prepared in high yield and have excellent stability

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and desirable physical properties. They require elemental fluorine for their synthesis, but, once obtained, they are easily handled by conventional techniques and thus can be readily utilized by anyone with reasonable skills.

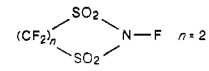
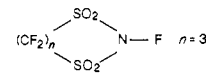
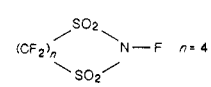
Indications that *N*-fluoro compounds can possess useful reactivity in fluorinations of organic compounds have existed for sometime, with one of the earliest reports being the reactions of *N*-fluoroperfluoropiperidine.[4] An interesting and little noted report in 1977 describes the use of N_2F_2 in fluorinations.[5] If one compares the activity of N_2F_2 with that of N_2F^+,[6] it becomes fairly obvious that the reactivity of any neutral *N*-fluoro compound will be enhanced by decreasing the electron density on nitrogen. The use of electron-withdrawing groups which can also stabilize the resulting anion formed by the loss of fluorine from nitrogen will further enhance the reactivity. These concepts have been utilized in recent reports on fluorinations with *N*-fluoro-2-pyridone[7] and *N*-fluoro-*N*-alkylsulfonamides.[8] In our work with xenon compounds, we recognized the unusual character of the nitrogen in the sulfonimides $(FSO_2)_2NH$ and $(CF_3SO_2)_2NH$, wherein stable N-bonded xenon species were obtained.[9,10] *N*-Fluoro derivatives of these acids exhibit unprecedented reactivity for fluorine bonded to nitrogen in a neutral molecule.

In Table I some *N*-fluoro-*N*-perfluoroalkylsulfonimides are listed which we have prepared and characterized. Each has been prepared by the same methodology, utilizing the reaction of elemental fluorine with the parent sulfonimide at 22 °C. An example of an *N*-fluoro-*N*-alkylperfluoroalkylsulfonamide is also shown to illustrate that these compounds can be obtained but in much lower yields and only by low-temperature fluorination in solution.

For a typical preparation of $(CF_3SO_2)_2N$–F, 10.0 g of $(CF_3SO_2)_2N$–H[11] are placed in a 500-mL, 304-ss bomb. The vessel is evacuated and cooled to −196 °C. An ~10% molar excess of fluorine is then added, and the reactor is allowed to warm slowly (~2 h) from −196 to 22 °C as follows. Without removing the reactor from the liquid nitrogen filled dewar, the apparatus is turned on its side so that the reactor is turned ~95° from vertical. This discharges the liquid nitrogen allowing the slow warm-up to begin and causes the liquid fluorine in the reactor to flow away from the solid sulfonimide. This minimizes the contact of the sulfonimide with liquid fluorine during the initial warm-up period, which sometimes leads to uncontrolled reaction and low yields.[12] After the reactor has stood at 22 °C for 4–5 h, the reactor is cooled to −196 °C, and excess fluorine is removed by vacuum pumping through a soda-lime column. The remaining contents are then vacuum transferred at 22 °C to another vessel cooled to −196 °C, containing ~10 g of NaF. This vessel is then warmed to 22 °C and allowed to stand with occasional shaking for 1–2 h. The volatile materials are then pumped out slowly through a glass trap at −55 °C, yielding 10.13 g (95%) of pure $(CF_3SO_2)_2N$–F as a colorless liquid in the −55 °C trap. *Caution*: The safe handling of pure fluorine requires a thorough understanding of the hazards involved and should only be attempted by experienced personnel who are knowledgeable in the procedures for the safe handling of the element.

The *N*-fluoro derivatives in Table I are all stable for long periods at 22 °C and are preferably stored in a fluoropolymer plastic container. Prolonged storage in Pyrex at 22 °C results in a slow etching of the glass. Further details on the synthesis and characterization of these compounds will be published separately. Not all possible *N*-fluoroperfluoroalkylsulfonimides can be obtained, e.g., $(C_4F_9SO_2)_2NF$ could not be isolated under a variety of different reaction conditions.

Table I. *N*-Fluorosulfonimides

	yield (%)	VP (22 °C, Torr)	mp (°C)	δ NF[a]
$(CF_3SO_2)_2NF$	95	~30	−69.8	−33.7
$CF_3SO_2N(F)SO_2C_4F_9$	96	~3	−56	−32.4
$CF_3SO_2N(F)SO_2C_6F_{13}$	93	~1	−28	−32.4
$C_4F_9SO_2N(F)SO_2C_6F_{13}$	88	<0.2	60 (dec)	−31.1
	77	~13	59	−13.9
	61	~8	97	−27.2
	86	~7	54	−32.8
$CF_3SO_2N(F)CH_3$[b]	11	~38		−40.5

n = 2 *n* = 3 *n* = 4

[a] In $CDCl_3$ solvent with internal $CFCl_3$ reference. All other resonances were as expected for the alkyl groups. The compounds are fully characterized by NMR, IR, EI, and CI MS and physical properties. [b] The fluorination of the parent sulfonamide was carried out in $CFCl_3$ solvent at −75 °C in the presence of NaF(s) with use of 1% F_2 in N_2.

Table II. Examples of Selective Fluorination with $(CF_3SO_2)_2NF$ at 22 °C

compound[a]	conditions[d]	products (%) δ ^{19}F[c]
nitrobenzene	neat, 12	no reaction
acetophenone	$CDCl_3$, 12	no reaction
chlorobenzene	$CDCl_3$, 24	no reaction
benzene	neat, 18	monofluorobenzene (50) −112.9[14] (50% conversion)
toluene	neat, 10	2-fluorotoluene (74) −117.7[14] 3-fluorotoluene (4) −114.1 4-fluorotoluene (22) −118.4 (80% conversion)
anisole	neat, 2	2-fluoroanisole (69) −135.4[14] 4-fluoroanisole (24) −122.6 polyfluoroanisole (7) −162.2 (100% conversion)
phenol[b]	$CDCl_3$, 12	2-fluorophenol (60) −140.7[14] 4-fluorophenol (40) −123.0
m-cresol[b]	$CDCl_3$, 12	2-fluoro-5-methylphenol (44) −145.3[15] 4-fluoro-3-methylphenol (56) −127.5
p-cresol[b]	$CDCl_3$, 12	2-fluoro-4-methylphenol (80) −140.8[15] other (20) −148.0, −162.2
m-xylene[b]	$CDCl_3$, 12	2-fluoro-5-methyltoluene 2-fluoro-3-methyltoluene (1:2 mixture) −122.4, −123.6[15]
naphthalene[b]	$CDCl_3$, 12	1-fluoronaphthalene (80) −123.8[14] 2-fluoronaphthalene (7) −115.3 other (13) −128.4
$NaC(CH_3)(CO_2Et)_2$	$CDCl_3$, 2, −10 °C	$F-C(CH_3)(CO_2Et)_2$ (96) −157.9[8]

[a] All aromatic compounds in 2:1 excess or larger with use of 1–2 mmol of $(CF_3SO_2)_2N$–F. [b] Conversions were high but not accurately determined. Yield is an NMR yield as a percent of fluorinated products. [c] $CFCl_3$ internal reference in $CDCl_3$ solvent. [d] Time is in hours.

All the *N*-fluorosulfonimides in Table I have the remarkable ability to directly replace hydrogen in an aromatic compound with fluorine at 22 °C.

$$>N\text{-}F + \text{aryl-}H \rightarrow \text{aryl-}F + H\text{-}N<$$

Benzene reacts slowly at 22 °C and as an aromatic ring is activated toward a classical electrophilic halogenation, its reaction rate increases. When excess aromatic is used, the yields can be very

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(12) Obviously, the contact of liquid fluorine could be avoided in a number of ways. This procedure is simple and effective for the scale indicated.

high and a pronounced preference for ortho fluorination is observed with substituted aromatics. In Table II, a partial list of screening reactions that have been carried out with $(CF_3SO_2)_2NF$ under nearly identical conditions are summarized. The reactions are readily monitored by ^{19}F NMR, by observing the growth of aryl-F with time, the disappearance of the *N*-fluorosulfonimide resonances, and the growth of the resonances of the parent sulfonimide. We have carried out reactions of the other sulfonimides with benzene, toluene, and other aromatics, and the observed results are very similar, except that $(CF_3SO_2)N-F$ is clearly the most reactive of the compounds in Table I.

In addition to their utility in direct aromatic fluorinations, these reagents are clearly useful in the fluorination of carbon anions. Reaction of $(CF_3SO_2)NF$ with sodium diethyl 1-methylmalonate in $CDCl_3$ at −10 °C gave a 96% isolated yield of diethyl 1-fluoro-1-methylmalonate along with the expected sodium salt of the imide, $NaN(SO_2CF_3)_2$. This is one of the highest yields that we are aware of for this type of reaction.[13] The only limitation we see for this use is the need for a solvent which will not itself react with the *N*-fluorosulfonimide.

The reactivity shown by these compounds is unique in our opinion. We have not demonstrated that these N-fluorosulfonimides can be used on a preparative scale to prepare a given monofluoro aromatic nor have we defined the scope of these reactions. Such work is in progress, and our earlier statement of potentially wide applicability in selective fluorinations continues to be warranted.

Acknowledgment. The financial support of this research by the National Science Foundation (CHE-8517336) is gratefully acknowledged. We also acknowledge the 3M Company for generous gifts of perfluoroalkanesulfonyl fluorides.

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(15) These are known compounds (Misaki, S. *J. Fluorine Chem.* **1981**, *17*, 159. Koptyug, V. A.; Buraev, V. I.; Isaev, I. S. *Russian J. Org. Chem.* (*Engl. Transl.*) **1978**, *14*, 1782.), but we were unable to locate published ^{19}F NMR data for the compounds. The observed chemical shifts are very reasonable when compared to known values for a variety of monofluoro-substituted aromatics. The isomers claimed are, in any case, those expected for the directing groups present.

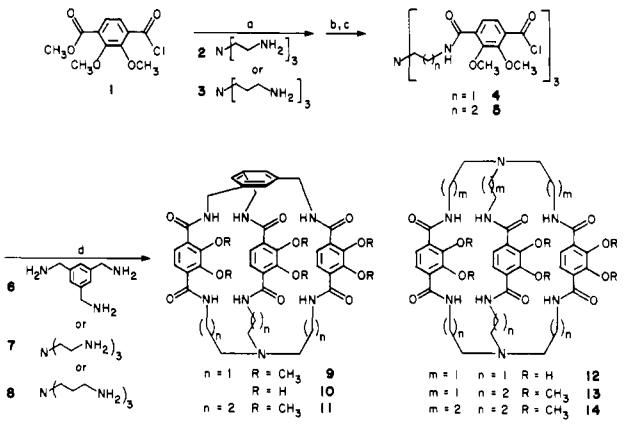

Figure 1. Synthetic scheme: a = amine **2** or **3**, Et_3N, THF, room temperature, 24 h, 80–88%; b = NaOH, CH_3OH, reflux for 2 h, 94–97%; c = $SOCl_2$, THF, DMF, room temperaure, 21 h, intermediate not isolated; d = a solution of amine **6**, **7**, or **8**, Et_3N, THF, and **4** or **5**, high dilution, room temperature, 24 h, 10–15%; e = BBr_3, $CHCl_3$, 0–25 °C, 48 h, 75%.

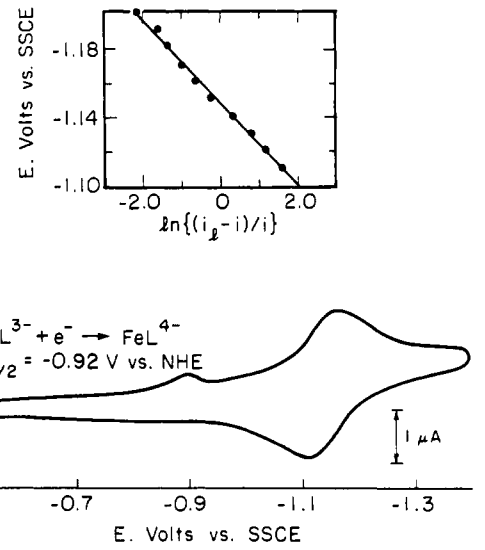

Figure 2. Electrochemistry of Fe(III) **10**. A one compartment cell with Hg as the working electrode, a Pt wire as the counter electrode, and a sodium chloride saturated calomel electrode (SSCE) as the reference electrode were used for all electrochemical studies. The solution was 0.2 mM in the ferric complex of **10**, 0.4 M in $NaClO_4$. The pH 12 was adjusted with KOH. (a) CV performed at a hanging Hg drop electrode and scan rate of 200 mV/s. (b) *E* versus ln $[(i_l - i)/i]$ was plotted by using the curent versus potential trace from NPP performed at 2.0 mV/s, pulse amplitude of 25 mV, and a flow rate of 0.7 mg/s.

Macrobicyclic Iron(III) Sequestering Agents[1]

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Macrobicyclic ligand designs first appeared in polyether complexing agents (such as the cryptands)[2] and later in polyamines (such as the sepulchrates).[3] These ligand topologies confer remarkable properties on their metal complexes. However, until the recent synthesis of compounds incorporating catechol binding subunits,[4,5] few other macrobicyclic ligands, particularly those designed to complex Fe(III) or other high valent transition metals, had been developed. Such new ligands, while incorporating the three catechol groups found in the siderophore enterobactin,[6] differ significantly in topology from earlier enterobactin analogues[7-12] and are related to phenolic cyclophane[13] macrocycles such as the

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