temperature in a nitrogen-filled glovebox. It was not easily apparent how the two sets of results could be so different; however, if **2a** is allowed to stand in water at room temperature, the color of the solid changes from dark orange to yellow and its spectral properties change also. The new compound, **5**, shows carbonyl absorptions at 1940 and 1610 cm^{-1} (Nujol mull), reacts with methyl alcohol to give ester **4**, and reacts with excess acid to give cation **1**. We suggest that **5** may be the anhydride, [CpFe(CO)(PPh$_3$)C(O)]$_2$O, a member of a currently unknown class of organometallic compounds, and that it was **5** and not **2a** which was studied earlier. Efforts are in progress to characterize compound **5**. The lithium salt, **2b**, is more stable to further reaction with water, but slowly degrades after standing overnight; compound **5** does not appear to be formed from **2b**.

Efforts are in progress to probe further for differences in the chemical behavior of metallocarboxylates **2a** and **2b** and their sodium and calcium analogues.

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Theory of Vibrational Circular Dichroism: *trans*-1(*S*),2(*S*)-Dicyanocyclopropane

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Vibrational circular dichroism (VCD) reflects the stereochemistry of a chiral molecule and, in principle, provides a tool for its elucidation. More than a decade since the earliest observations[1-3] the measurement of VCD is now nearly routine.[4,5] However, until recently, the absence of a convincing theory of VCD has impeded the analysis and application of VCD spectra.[5]

Recently, an a priori theoretical formalism of vibrational rotational strengths has been derived by Stephens, allowing for the first time direct calculation of VCD spectra from molecular wave functions.[6] Stephens' equation for the rotational strength, R_i, of the fundamental transition in the *i*th normal mode requires the computation of two molecular tensors: $P^{\lambda}_{\alpha\beta}$ and $I^{\lambda}_{\alpha\beta}$ at the molecular equilibrium geometry, $\mathbf{R}_o$. $P^{\lambda}_{\alpha\beta}$ is the familiar atomic polar tensor (APT)[7]

$$P^{\lambda}_{\alpha\beta} = [\partial(\mu^{G}_{\text{el}})_{\beta}/\partial X_{\lambda\alpha}]\mathbf{R}_o \qquad (\alpha, \beta = x, y, z)$$

where μ^{G}_{el} is the adiabatic electric dipole moment of the ground electronic state G and $X_{\lambda\alpha}$ is a Cartesian displacement coordinate from $\mathbf{R}_o$ of nucleus λ. $I^{\lambda}_{\alpha\beta}$ is a new tensor given by

$$I^{\lambda}_{\alpha\beta} = \left\langle \left(\frac{\partial\psi_G(\mathbf{R})}{\partial X_{\lambda\alpha}}\right)_{\mathbf{R}_o} \middle| \left(\frac{\partial\psi_G(\mathbf{R}_o,H_\beta)}{\partial H_\beta}\right)_{H_\beta=0} \right\rangle$$

where $\psi_G(\mathbf{R})$ is the adiabatic electronic wave function of G, and $\psi_G(\mathbf{R}_o,H_\beta)$ is the wave function of G at $\mathbf{R}_o$ in the presence of a magnetic field perturbation. $P^{\lambda}_{\alpha\beta}$ alone determines dipole strengths, D_i, and absorption spectra of vibrational transitions.

Table I. Calculated and Experimental Vibrational Frequencies[a] of TDCCP-d_0

symmetry[b]	expt[c]	unscaled	scaled (one param)	scaled (six params)
B	3119	3419	3081	3112
B	3052	3364	3032	3062
A	3052	3362	3031	3061
A	3035	3322	2994	3024
A	2247	2621	2362	2247
B	2247	2621	2362	2247
A	1443	1636	1475	1460
A	1385	1556	1402	1388
B	1297	1447	1304	1288
A	1190	1312	1183	1176
B	1131	1260	1136	1122
B	1104	1226	1105	1090
A	1075	1223	1103	1089
A	1048	1191	1074	1064
B	992	1091	984	978
B	908	1041	938	915
A	871	995	897	893
A	809	887	799	797
B	778	852	768	763
B	553	613	553	542
B	530	587	529	535
A	518	575	519	513
A	497	546	492	498
B	270	290	262	252
A	237	252	227	232
B	129	169	152	154
A	88	128	115	107
RMS Deviation from Experiment[a]				
		182	37	13

[a] In cm^{-1}. [b] Calculated. [c] Reference 18.

VCD spectra calculated with Stephens' equations have to date been compared to experiment for two small chiral molecules: propylene oxide and *trans*-1,2-dideuteriocyclobutane.[5,8] SCF wave functions at the 4-31G basis set level[9] were used. The derivatives determining $P^{\lambda}_{\alpha\beta}$ and $I^{\lambda}_{\alpha\beta}$ were obtained by finite difference procedures.[10] The results were in encouraging agreement with experiment. However, the use of finite difference procedures for the calculation of $P^{\lambda}_{\alpha\beta}$ and $I^{\lambda}_{\alpha\beta}$ is extremely cumbersome and only practical for very small molecules and basis sets. State-of-the-art calculations of $P^{\lambda}_{\alpha\beta}$ now employ vastly more efficient analytical derivative techniques.[11-15] We have therefore developed the methodology for the calculation of $I^{\lambda}_{\alpha\beta}$ as well as $P^{\lambda}_{\alpha\beta}$ using analytical derivative methods and implemented it in the Cambridge Analytical Derivatives Package (CADPAC) program.[16] This now permits the efficient prediction of VCD spectra for much larger molecules and basis sets than heretofore practicable.

We report here the first application of this new calculational technology. The VCD spectra of the d_0 and *trans-1,2-d_2* isotopomers of *trans*-1(*S*),2(*S*)-dicyanocyclopropane (TDCCP) are predicted by using SCF wave functions and the 6-31G** basis set[9] and compared to the experimental spectra of Heintz and Keiderling.[17]

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(1) Holzwarth, G.; Hsu, E. C.; Mosher, H. S.; Faulkner, T. R.; Moscowitz, A. *J. Am. Chem. Soc.* **1974**, *96*, 251.

(2) Nafie, L. A.; Cheng, J. C.; Stephens, P. J. *J. Am. Chem. Soc.* **1975**, *97*, 3842.

(3) Nafie, L. A.; Keiderling, T. A.; Stephens, P. J. *J. Am. Chem. Soc.* **1976**, *98*, 2715.

(4) Nafie, L. A. *Adv. Infrared Raman Spectrosc.* **1984**, *11*, 49.

(5) Stephens, P. J.; Lowe, M. A. *Ann. Rev. Phys. Chem.* **1985**, *36*, 213.

(6) Stephens, P. J. *J. Phys. Chem.* **1985**, *89*, 748.

(7) Person, W. B.; Newton, J. H. *J. Chem. Phys.* **1974**, *61*, 1040.

(8) Lowe, M. A.; Stephens, P. J.; Segal, G. A. *Chem. Phys. Lett.* **1986**, *123*, 108.

(9) Hehre, W. J.; Radom, L.; Schleyer, P. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: 1986.

(10) Lowe, M. A.; Segal, G. A.; Stephens, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 248.

(11) Amos, R. D.; *Chem. Phys. Lett.* **1984**, *108*, 185.

(12) Amos, R. D. *Chem. Phys. Lett.* **1985**, *114*, 10; **1985**, *122*, 180.

(13) Amos, R. D. *Chem. Phys.* **1986**, *104*, 145.

(14) Yamaguchi, Y.; Frisch, M.; Gaw, J.; Schaefer, H. F.; Binkley, J. S. *J. Chem. Phys.* **1986**, *84*, 2262.

(15) Amos, R. D. *Adv. Chem. Phys.* **1987**, *67*, 99.

(16) Amos, R. D.; Handy, N. C.; Jalkanen, K. J.; Stephens, P. J. *Chem. Phys. Lett.* **1987**, *133*, 21.

0002-7863/87/1509-7193$01.50/0

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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(17) Heintz, V. J.; Keiderling, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 2395.

(18) Schrumpf, G.; Dunker, H. *Spectrochim. Acta* **1985**, *41A*, 841.

(19) Fogarasi, G.; Pulay, P. *Ann. Rev. Phys. Chem.* **1984**, *35*, 191.

(20) Lowe, M. A.; Alper, J. S.; Kawiecki, R.; Stephens, P. J. *J. Phys. Chem.* **1986**, *90*, 41.

N-Fluoroperfluoroalkylsulfonimides. Remarkable New Fluorination Reagents

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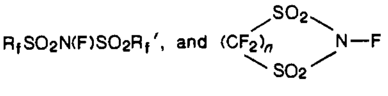
Nuclear-fluorinated aromatic compounds were first synthesized in the 1870's by the use of aromatic diazo compounds.[1] This methodology continues to be the most widely used today for the practical synthesis of fluoroaromatics, but the method has many limitations. Selectively fluorinated organics have 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 

$$(CF_2)_n\overset{SO_2}{\underset{SO_2}{\rangle}}N{-}F$$

They are easily prepared in high yield and have excellent stability

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(1) For an authoritative historical survey, see: Banks, R. E.; Tatlow, J. C. *J. Fluorine Chem.* **1986**, *33*, 71.

(2) *Biomedicinal Aspects of Fluorine Chemistry*; Filler, R., Kobayshi, Y., Eds.; Elsevier Biomedical Press: New York, 1982.

(3) For a selection of reviews, see: Sharts, C. M.; Sheppard, W. A. *Org. React.* **1974**, *21*, 125. Purrington, S. T.; Kagen, B. S.; Patrick, T. B. *Chem. Rev.* **1986**, *86*, 997. Gerstenberger, M. R. C.; Haas, A. *Agnew. Chem., Int. Ed. Engl.* **1981**, *20*, 647. Boguslavskoya, L. S. *Russian Chem. Rev.* **1984**, *54*, 1178.