# Difluorodioxirane: An Unusual Cyclic Peroxide

**Elfi Kraka,*,† Zoran Konkoli,† Dieter Cremer,† Joseph Fowler,‡ and Henry F. Schaefer III‡**

*Contribution from the Department of Theoretical Chemistry, University of Göteborg, Kemigården 3, S-41296 Göteborg, Sweden, and Center of Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602*

*Received June 12, 1996. Revised Manuscript Received August 23, 1996*[⊗]

**Abstract:** The surprisingly high stability of the dioxirane $CF_2O_2$ (**2**), its unusual geometry, its infrared spectrum, and NMR chemical shifts are determined and analyzed on the basis of extended ab initio calculations including seven different methods and nine different basis sets. At the highest level of theory, the CCSD(T) approach has been used together with a cc-VTZ2P+f basis set, which leads to an accurate description of geometry and vibrational frequencies. Stabilizing CF,CF bond interactions add 19.5 kcal/mol and CF,CO bond interactions 12 kcal/mol to the stability of the dioxirane ring. The latter effect reduces ring strain from 32.8 (dioxirane) to 20.5 kcal/mol (**2**) where 17 kcal/mol are due to CO bond strengthening and 4.6 kcal/mol to OO bond weakening. Changes in CO and OO bond strength are caused by a transfer of negative charge from the $CF_2$ group to the antisymmetric Walsh MO of the ring. The calculated $\Delta H_f°(298)$ value of **2** is $-102 \pm 1.5$ kcal/mol, which indicates that **2** is thermodynamically rather stable. Calculated $^{13}C$ (133 ppm) and $^{17}O$ NMR chemical shifts (403 ppm) are unusually positive for an organic cyclic peroxide, but should facilitate the identification of **2** in the presence of its isomers $F_2COO$ and FC(=O)OF, which possess $\Delta H_f°(298)$ values of −60 and −104 kcal/mol, respectively.

## Introduction

Dioxiranes are effective oxygen carriers for regio- and stereoselective epoxidations.[1] They can be formed by thermal or photochemical isomerization of carbonyl oxides during the ozonolysis of alkenes or the oxidation of carbenes.[2,3] The parent dioxirane **1** was first detected in the gas-phase ozonolysis of ethylene by Lovas and Suenram, who used microwave spectroscopy to obtain the $r_s$-geometry of **1**.[4] Subsequent experimental[5] and, in particular, theoretical investigations[6−8] led to a detailed characterization of **1** as a rather labile cyclic peroxide, which can only be stabilized by appropriate substitution. Murray and Jeyaraman[9] were able to generate dialkyldioxiranes from caroate (monoperoxosulfuric acid)−ketone mixtures where this work was based on experiments by Montgomery, Edwards, Curci, and others[10] to use mixtures of ketones and peracids as synthetically useful oxidation agents. Further evidence on dioxiranes was collected by Bucher and Sander,[11] who synthesized and characterized a series of spiro-conjugated dioxiranes using matrix isolation techniques.

Recently, Russo and DesMarteau[12] succeeded in synthesizing diflourodioxirane (**2**) as the first dioxirane that is stable in the gas phase at room temperature. Dioxirane **2** had been proposed as an unstable intermediate in the decomposition of $CF_3OOCF_3$ based on two difficult-to-assign absorptions at 1592 and 1025 $cm^{-1}$.[13] Agopovich and Gillies[14] assumed that **2** is the intermediate in the ozonolysis of fluorinated ethylenes responsible for epoxidation products. A detailed examination of the reaction of $^3CF_2$ with $O_2$ by McKee and co-workers placed significant attention on the possible generation of **2**.[15] On the basis of ab initio calculations, Cremer and co-workers predicted that **2** should possess considerable stability.[16]

The successful generation of **2**[12] is based on the reaction of its isomer FC(=O)OF with ClF, $Cl_2$, or $F_2$ in the presence of

† University of Göteborg.
‡ University of Georgia.
[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1996.

(1) (a) Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187. (b) Murray, R. W. In *Molecular Structure and Energetics. Unconventional Chemical Bonding*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1988; Vol. 6, p 311. (c) Kafafi, S. A.; Martinez, R. I.; Herron, J. T. In *Molecular Structure and Energetics. Unconventional Chemical Bonding*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1988; Vol. 6, p 283. (d) Adam, W.; Curci, R.; Edwards, J. O. *Acc. Chem. Res.* **1989**, *22*, 205.

(2) Bailey, P. S. *Ozonation in Organic Chemistry*; Academic Press: New York; 1978, Vol. 1; 1982, Vol. 2.

(3) For reviews see (a) Sander, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 344. (b) Bunnelle, W. H. *Chem. Rev.* **1991**, *91*, 335 and references to ealier work cited therein.

(4) (a) Lovas, F. J.; Suenram, R. D. *Chem. Phys. Lett.* **1977**, *51*, 453. (b) Suenram, R. D.; Lovas, F. J. *J. Am. Chem. Soc.* **1978**, *100*, 5117.

(5) (a) Martinez, I. R.; Huie, R. E.; Herron, J. T. *Chem. Phys. Lett.* **1978**, *51*, 457. (b) Adam, W.; Curi, R.; Nunez, M. E. G.; Mello, R. *J. Am. Chem. Soc.* **1991**, *113*, 7654. (c) Sodeau, J. R.; Whyte, L. J. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3725.

(6) (a) Cremer, D. *J. Am. Chem. Soc.* **1979**, *101*, 7189. (b) Francisco, J. S.; Williams, I. H. *Chem. Phys.* **1985**, *95*, 71. (c) Gauss, J.; Cremer, D. *Chem. Phys. Lett.* **1987**, *133*, 420. (d) Gauss, J.; Cremer, D. *Chem. Phys. Lett.* **1989**, *163*, 549. (e) Cremer, D.; Schmidt, T.; Sander, W.; Bischof, P. *J. Org. Chem.* **1989**, *54*, 2515. (f) Bach, R. D.; Andrés, J. L.; Owensby, A. L.; Schlegel, H. B.; McDouall, J. J. W. *J. Am. Chem. Soc.* **1992**, *114*, 7207.

(7) Cremer, D.; Gauss, J.; Kraka, E.; Stanton, J. F.; Bartlett, R. J. *Chem. Phys. Lett.* **1993**, *209*, 547.

(8) Kim, S.-J.; Schaefer, H. F., III; Kraka, E.; Cremer, D. *Mol. Phys.* In press.

(9) (a) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847. For earlier work, see: (b) Murray, R. W.; Ramachandran, V. *Photochem. Photobiol.* **1979**, *30*, 187. (c) Jeyaraman, R.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 2462.

(10) (a) Montgomery, R. E. *J. Am. Chem. Soc.* **1974**, *96*, 7820. (b) Edwards, J. O.; Pater, R. H.; Curci, R.; DiFuria, F. *Photochem. Photobiol.* **1979**, *30*, 63. (c) Curci, R.; Fiorentino, M.; Troisi, L.; Edwards, J. O.; Pater, J. H. *J. Org. Chem.* **1980**, *45*, 4758. (d) Gallopo, A. R.; Edwards, J. O. *J. Org. Chem.* **1981**, *46*, 1684. (e) Cicala, G.; Curci, R.; Fiorentino, M.; Laricciuta, O. *J. Org. Chem.* **1982**, *47*, 2670.

(11) Bucher, G.; Sander, W. *Chem. Ber.* **1992**, *125*, 1851.

(12) Russo, A.; DesMarteau, D. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 905.

(13) Christe, K. O.; Pilipovich, D. *J. Am. Chem. Soc.* **1971**, *93*, 51.

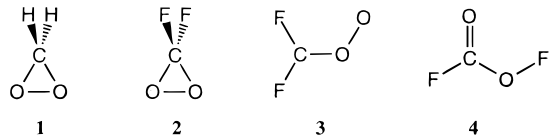
(14) Agopovich, J. W.; Gilles, C. W. *J. Am. Chem. Soc.* **1983**, *105*, 5047.

(15) (a) Rahman, M.; McKee, M. L.; Shelvin, P. B.; Sztyrbicka, R. *J. Am. Chem. Soc.* **1988**, *110*, 4002. (b) Rahman, M.; McKee, M. L.; Shevlin, P. B. In *Fluorine-Containing Molecules, Structure, Reactivity, Synthesis, and Applications*; Liebman, J. F., Greenberg, A., Dolbier, W. R., Jr., Eds.; VCH Publishers: New York, 1988; p 1.

(16) Cremer, D.; Schmidt, T.; Gauss, J.; Radhakrishnan, T. P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 427.

S0002-7863(96)01983-X CCC: $12.00 

CsF. Russo and DesMarteau[12] proposed a suitable mechanism for this reaction and confirmed that **2** is a powerful oxidant. They reported eight infrared



**1** **2** **3** **4**

(IR) vibrational frequencies and four Raman peaks to identify **2** with the help of ab initio data. Subsequent spectroscopic work on the mid-IR FT spectrum of **2** carried out by Bürger and co-workers[17] led to a confirmation of the dioxirane structure of **2**, reassignment of two of the vibrational frequencies reported by Russo and DesMarteau, the determination of ground state rotational constants, and derivation of a first $r_0$-geometry of **2**. This geometry was later refined by measuring the IR spectrum of the $^{16}O^{18}O$ isotopomer of **2**.[18] The most detailed spectroscopic investigation of **2** was recently published by Christen, Oberhammer, Willner, and co-workers,[19] who recorded gas electron diffraction intensities and infrared spectra of **2** and its $^{16}O^{18}O$ isotopomer at cryogenic temperatures to obtain harmonic force field and $r_z$-geometry.

Since **2** is an unusual molecule that has attracted and still attracts experimentalists to determine its properties, there is considerable need for theoretical verification of measured (geometry, vibrational frequencies, rotational constants, $^{19}F$ NMR spectrum) and reliable prediction of unmeasured properties (heat of formation, reaction enthalpies, dipole moment, charge distribution, $^{13}C$ and $^{17}O$ NMR spectrum). All previous ab initio investigations have been carried out at the Hartree−Fock (HF) or second-order Møller−Plesset perturbation theory (MP2) level of theory employing rather modest basis sets.[15,17−19] It is well-known that for molecules such as $F_2O$, FOOF, $CF_4$, etc. these methods are insufficient to lead to reliable data.[20] Multiple substitution of C by highly electronegative atoms leads to molecules which represent both with regard to basis set description and correlation coverage difficult calculational problems that cannot be handled at the relatively low levels of theory used in previous investigations.

Here, we report a state-of-the-art investigation of **2** that is aimed at describing the properties of **2** in a reliable way:

(1) Using Coupled Cluster theory at the CCSD(T) level in combination with a TZ2P basis set augmented by f-functions, the $r_e$-geometry of **2** is determined and compared with recently measured $r_z$- and $r_0$-geometries.

(2) The heat of formation $\Delta H_f°(298)$ is the best measure of the stability of **2**. We will show that its determination is an extremely difficult calculational problem, which requires the calculation of up to 30 reference molecules. However, once a reliable value of $\Delta H_f°(298,\mathbf{2})$ has been determined it is possible to quantify the various energy contributions that add to the stability of **2**.

(3) The stability of **2** is compared with that of its isomers difluorocarbonyl oxide (**3**) and FC(═O)OF (**4**). Reasons for the extraordinary stability of **2** will be given on the basis of its electronic structure.

(4) Little is known about the reactivity of **2** and, therefore, we will examine whether **2** can undergo those reactions that are typical of dioxiranes. In particular, we will investigate a possible formation of **2** and its subsequent decomposition in the course of the ozonolysis that has been the subject of many speculations.[2,14]

(5) All previous spectroscopic investigations of **2** focused on its vibrational spectra.[12,17−20] Accordingly, there is a need to verify the results of the spectroscopic investigations and by doing so obtain a reliable description of the electronic structure of **2** that is based on both theory and experiment.

(6) So far, neither dipole moment nor $^{13}C$ and $^{17}O$ NMR chemical shifts of **2** have been measured. They will be calculated in this work and compared with those of related molecules.

Besides chemical relevant questions, we will also use the present investigation to demonstrate the necessity of using f-functions and including three-electron correlation effects in calculations of molecules composed of electronegative atoms. To our knowledge, such an extensive investigation of these effects has not yet been reported for a medium-seized molecule with five heavy atoms.

## Theoretical Approach

The basis sets used in this study are of double-ζ plus polarization (DZP), triple-ζ plus double polarization (TZ2P), and TZ2P+f quality. The DZP basis set is the standard Huzinaga−Dunning[21,22] double-ζ (DZ) (9s5p1d)[4s2p1d] contracted Gaussian basis set where spherical d-type polarization functions with orbital exponents $\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.85$, and $\alpha_d(F) = 1.0$ are used. One of the TZ2P basis sets corresponds to the Huzinaga−Dunning[21,23] (10s6p2d)[5s3p2d] set augmented by two sets of spherical d-type polarization functions with $\alpha_d(C) = 1.5, 0.375$, $\alpha_d(O) = 1.7, 0.425$, and $\alpha_d(F) = 2.00, 0.50$. The spherical f-type polarization functions added to this basis have exponents $\alpha_f(C) = 0.8$ and $\alpha_f(O) = 1.40$. Since CCSD(T) calculations with this basis were not feasible, we employed for our final calculations Dunning's correlation corrected cc-VTZ2P+f,d basis, which is composed of a (10s5p2d)[4s3p2d] contraction (α(C): 1.097, 0.318 (d), 0.761 (f); α(O): 2.314, 0.645 (d), 1.428 (f); α(F): 3.107, 0.855 (d), 1.917 (f); α(H): 1.407, 0.388 (p), 1.057 (d))[24] and has proven to lead to rather reliable results[7] although it is slightly smaller than the TZ2P+f basis used. In addition, we used for density functional theory (DFT) calculations Pople's 6-311+G(3d,3p) and 6-311+G(3df,3pd) basis sets,[25] which include, besides the VTZ basis diffuse s,p-functions, three sets of spherical d-type functions and a set of spherical f-type functions for all heavy atoms. In total, seven different basis sets (DZP, TZ2P, cc-VTZ2P, 6-311+G(3d,3p), TZ2P+f, cc-VTZ2P+f, 6-311+G(3df,3pd)) of increasing size and flexibility were used.

Six different levels of ab initio theory were employed ranging from HF, MP2,[26] MP4 (fourth-order MP including S, D, T, and Q excitations),[27] CISD (configuration interaction with S and D excitations),[28] CCSD (projected Coupled Cluster with S and D),[29] and CCSD(T) (CCSD with perturbative inclusion of T excitations).[30] The CISD

(17) Bürger, H.; Weinrath, P.; Argüello, G. A.; Jülicher, B.; Willner, H.; DesMarteau, D. D.; Russo, A. *J. Mol. Spectrosc.* **1994**, *168*, 607.
(18) Bürger, H.; Weinrath, P.; Argüello, G. A.; Willner, H.; Jülicher, B. *J. Mol. Spectrosc.* **1995**, *171*, 589.
(19) Casper, B.; Christen, D.; Mack, H.-G.; Oberhammer, H.; Argiiello, G. A.; Jülicher, B.; Kronberg, M.; Willner, H. *J. Phys. Chem.* **1996**, *100*, 3983.
(20) (a) Rohlfing, C. M.; Hay, P. J. *J. Chem. Phys.* **1987**, *86*, 4518. (b) Raghavachari, K.; Trucks, G. W. *Chem. Phys. Lett.* **1989**, *162*, 511. (c) Scuseria, G. *J. Chem. Phys.* **1991**, *94*, 442.
(21) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.
(22) Dunning, T. H., Jr. *J. Chem. Phys.* **1971**, *53*, 2823.
(23) Dunning, T. H., Jr. *J. Chem. Phys.* **1971**, *55*, 716.
(24) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
(25) Krishnan, R.; Frisch, M.; Pople, J. A. *Chem. Phys.* **1980**, *72*, 4244.
(26) MP2: (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.
(27) MP4: (a) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91. (b) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.
(28) CISD: (a) Brooks, B. R.; Laidig, W. D.; Saxe, P.; Goddard, J. D.; Yamaguchi, Y.; Schaefer, H. F., III *J. Chem. Phys.* **1980**, *72*, 4652. (b) Rice, J. E.; Amos, R. D.; Handy, N. C.; Lee, T. J.; Schaefer, H. F., III *J. Chem. Phys.* **1986**, *85*, 963.
(29) CCSD: (a) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910. (b) Gauss, J.; Stanton, J. F.; Bartlett, R. J. *J. Chem. Phys.* **1991**, *95*, 2623.

energies were corrected for unlinked quadruple excitations by using Davidson's method and corrected CISD results are denoted by CISD+Q.[31] In addition, DFT was applied utilizing Becke's three-parameter functional Becke3LYP (B3LYP).[32,33] This was done in view of the surprisingly accurate B3LYP results in the case of carbonyl oxides and dioxiranes as described by Cremer and co-workers.[34]

While in the case of the CISD, CCSD, and CCSD(T) (DZP or TZ2P) calculations the frozen core approximation was used (5 core and the corresponding 5 virtual MOs were excluded from the calculation of the correlation energy), full correlation calculations were carried out at the MP2, MP4, and CCSD(T)/cc-VTZ2P levels of theory and are denoted by "method(full)/basis set". Analytical derivatives were used for all geometry optimizations and the calculation of harmonic vibrational frequencies $\omega$ and IR intensities at the HF, MP2, and DFT levels of theory, while vibrational frequencies at higher levels of theory were determined by the method of finite differences in connection with analytical gradients.[35] At the MP4/cc-VTZ2P+f, CCSD(T)/TZ2P+f, and CCSD(T)/cc-VTZ2P+f levels of theory, just $a_1$ vibrational modes were investigated because of cost reasons. However, the effects of f-functions on calculated frequencies were carefully studied at MP2, CISD, and CCSD so that it was possible to derive the missing TZ2P+f frequencies from the corresponding TZ2P values with an accuracy of a few wavenumbers. In our recent investigation on dioxirane, we have shown that reliable values can be obtained in this way.[8]

Sum-over-states density functional perturbation theory (SOS-DFPT)[36] based on the "individual gauge for localized orbitals" (IGLO) scheme of Kutzelnigg and Schindler[37] was employed to calculate $^{13}C$, $^{17}O$, and $^{19}F$ NMR chemical shifts for **2** and some related peroxides. A combination of the Becke exchange[38] and the PW91 correlation functionals[39] rather than B3LYP was used since the former is known to lead to somewhat better shift values.[40] As an appropriate basis the (11s7p2d/6s2p) [7s6p2d/4s2p] set of Kutzelnigg and co-workers was employed, which is of VQZ+2P quality and has especially been designed for NMR chemical shift calculations with the IGLO method.[41] SOS-DFPT calculations were based on an accurate calculation of the Coulomb part and numerical integration of the exchange-correlation potential.[40] The well-known deficiencies of DFT methods to lead to occupied orbitals with relatively high energies and, accordingly, to an overestimation of paramagnetic contributions to chemical shifts was compensated by adding appropriate level shift factors to orbital energy differences as was first suggested by Malkin and co-workers[42] and studied in detail by Olsson and Cremer.[40] $^{13}C$ chemical shifts are given relative to TMS, $^{17}O$ shifts relative to gaseous $H_2O$, and $^{19}F$ shifts relative to $CFCl_3$. Experimental $^{17}O$ shifts measured relative to liquid water have been converted according to $\delta_{gas} = \delta_{liq} + 36.1$ ppm while $^{19}F$ shifts have been calculated relative to FH and converted to the $CFCl_3$ scale by the relationship $\delta_{CFCl_3} = \delta_{FH} - 214.4$ ppm.

Calculated vibrational modes were investigated using the adiabatic mode analysis of Konkoli and co-workers.[43] This approach is based on a decomposition of normal modes in terms of adiabatically relaxed internal parameter modes that are not contaminated by any other mode of the molecule. As has been shown previously the adiabatic mode analysis is superior to the potential energy distribution (PED) analysis and provides reliable internal frequencies that can directly be assigned to the internal parameters of a molecule. Both internal coordinates and symmetry coordinates have been used to determine the adiabatic modes of **1** and **2**. For all molecules considered, zero point energy (ZPE) and thermal corrections have been determined to evaluate reaction enthalpies at 298 K.

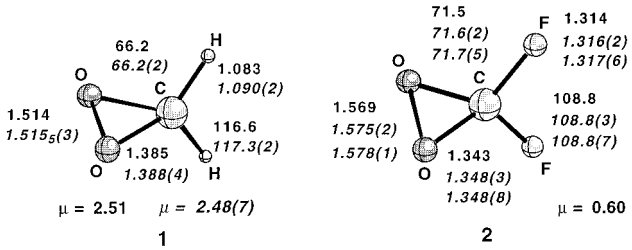



**Figure 1.** Comparison of experimental (numbers in italics) and calculated CCSD(T)(full)/cc-VTZ2P+f,d geometries of dioxiranes **1** and **2**. Bond lengths in Å and angles in deg. Uncertainties of the $r_S$-values of **1** [4] and the $r_O$- (first entry) or $r_Z$-values (second entry) of **2**[18,19] are given in parentheses.

Calculations were carried out with COLOGNE96,[44] PSI-2,[45] ACES,[46] and GAUSSIAN94[47] ab initio packages.

## Results and Discussion

In Table 1, calculated energies and geometries are listed and compared with the available experimental data while calculated dipole moments and rotational constants can be found in Table 2. Drawings of the geometries of **1** and **2** are shown in Figure 1, while a selection of calculated geometries of reference molecules **3**−**33** is presented in Figure 2. The calculated energies, ZPE values, and thermal corrections of all reference molecules are given in the Supporting Information. In Table 3, reaction energies and enthalpies are listed that have been used to determine the $\Delta H_f°(298)$ value of **2**. Enthalpies $\Delta\Delta H_f°(298)$ of decomposition, rearrangement, and bimolecular reactions typical of dioxiranes are shown in Figure 3. Table 4 gives a summary of calculated vibrational frequencies and infrared intensities. The agreement between calculated and measured frequencies is analyzed in Table 5 and graphically confirmed in Figure 4. Tables 6 and 7 complete the vibrational analysis by listing isotopic shifts, adiabatic mode contributions, and adiabatic frequencies. Finally, in Figure 5 calculated NMR chemical shifts of **2** and related peroxides are given.

**Geometry**. Both $r_z$- and $r_0$-geometry of **2**[17−19] are characterized by a rather long OO bond of 1.575−1.578 Å (Table 1), which is 0.06 Å longer than the corresponding bond of **1** (1.515, Figure 1). The CO bonds of **2** (1.348 Å) are slightly shortened with regard to the CO bonds of **1** (1.388 Å) while the measured CF bonds are 1.317 Å.

(30) CCSD(T): (a) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479. (b) Watts, J. D.; Gauss, J.; Bartlett, R. J. *Chem. Phys. Lett.* **1992**, *200*, 1.

(31) Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61.

(32) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(33) (a) Stevens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623. (b) Bauschlicher, C. W., Jr.; Partridge, H. *Chem. Phys. Lett.* **1995**, *240*, 533.

(34) Gutbrod, R.; Schindler, R. N.; Kraka, E.; Cremer, D. *Chem. Phys. Lett.* **1996**, *252*, 221.

(35) For reviews see (a) Yamaguchi, Y.; Osamura, Y.; Goddard, J. D.; Schaefer, H. F., III *A New Dimension to Quantum Chemistry: Analytical Derivative Methods in Ab Initio Molecular Electronic Structure Theory*; Oxford University Press: New York, 1994. (b) Gauss, J.; Cremer, D. *Adv. Quantum Chem.* **1992**, *23*, 205.

(36) Malkin, V. G.; Malkina, O. L.; Salahub, D. R. *Chem. Phys. Lett.* **1993**, *204*, 80.

(37) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919.

(38) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098.

(39) Perdew, J. P.; Wang, Y. *Phys. Rev.* **1992**, *B45*, 13244.

(40) (a) Olsson, L.; Cremer, D. *J. Chem. Phys.* In press. (b) Olsson, L.; Cremer, D. *J. Phys. Chem.* In press.

(41) Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR, Basic Principle and Progress*; Diehl, P., Ed.; Springer: Berlin, 1991; Vol. 23, p 165.

(42) Malkin, V. G.; Malkina, O. L.; Casida, M. E.; Salahub, D. R. *J. Am. Chem. Soc.* **1994**, *116*, 5898.

(43) Konkoli, Z.; Cremer, D. *J. Chem. Phys.* Submitted for publication.

(44) Kraka, E.; Gauss, J.; Reichel, F.; Olsson, L.; Konkoli, Z.; He, Z.; Cremer, D. COLOGNE 96, Göteborg, 1996.

(45) PSI 2.08: Jansen, C. L.; Seidl, E. T.; Scuseria, G. E.; Hamiltion, T. P.; Yamaguchi, Y.; Remington, R. B.; Xie, Y.; Vacek, G.; Sherrill, C. D.; Crawford, T. D.; Fermann, J. T.; Allen, W. D.; Brooks, B. R.; Fitzgerald, G. B.; Fox, D. J.; Graw, J. F.; Handy, N. C.; Laidig, W. D.; Lee, T. J.; Pitzer, R. M.; Rice, J. E.; Saxe, P.; Scheiner, A. C.; Schaefer, H. F., III; PSITECH Inc.: Watkinsville, GA, 1994.

(46) Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *ACES II*, Quantum Theory Project, University of Florida, 1992.

(47) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian 94, Gaussian Inc.: Pittsburgh, PA, 1994.

**Table 1.** Absolute Energies and Geometrical Parameters of Difluorodioxirane (**2**) at Various Levels of Theory[a]

| method/basis set | energy | *R*(CF) | *R*(CO) | *R*(OO) | *θ*(FCF) |
|---|---|---|---|---|---|
| Becke3YLP/6-311+G(3d) | −388.248190 | 1.324 | 1.345 | 1.550 | 108.8 |
| Becke3YLP/6-311+G(3df) | −388.261277 | 1.320 | 1.344 | 1.542 | 108.9 |
| HF/DZP | −386.440814 | 1.294 | 1.321 | 1.479 | 109.6 |
| HF/TZ2P | −386.489650 | 1.291 | 1.318 | 1.481 | 109.6 |
| HF/TZ2P+f | −386.505761 | 1.289 | 1.315 | 1.472 | 109.5 |
| MP2(full)/cc-VTZ2P | −387.563276 | 1.320 | 1.350 | 1.575 | 108.7 |
| MP2(full)/cc-VTZ2P+f | −387.677866 | 1.313 | 1.344 | 1.555 | 108.8 |
| MP4(SDTQ)(full)/cc-VTZ2P | −387.612190 | 1.325 | 1.353 | 1.603 | 108.5 |
| MP4(SDTQ)(full)/cc-VTZ2P+f | −387.729197 | 1.318 | 1.348 | 1.580 | 108.7 |
| CISD/DZP | −387.139318 | 1.310 | 1.338 | 1.518 | 109.2 |
| CISD+Q/DZP | −387.237953 | | | | |
| CISD/TZ2P | −387.336558 | 1.303 | 1.330 | 1.513 | 109.3 |
| CISD+Q/TZ2P | −387.454557 | | | | |
| CISD/TZ2P+f | −387.431755 | 1.298 | 1.324 | 1.494 | 109.3 |
| CISD+Q/TZ2P+f | −387.561097 | | | | |
| CISD/cc-VTZ2P+f | −387.422292 | 1.294 | 1.323 | 1.488 | 109.5 |
| CISD+Q/cc-VTZ2P+f | −387.550844 | | | | |
| CCSD/DZP | −387.263191 | 1.325 | 1.352 | 1.573 | 108.8 |
| CCSD/TZ2P | -387.487882 | 1.319 | 1.346 | 1.572 | 108.8 |
| CCSD/TZ2P+f | -387.597722 | 1.313 | 1.339 | 1.548 | 108.9 |
| CCSD/cc-VTZ2P+f | -387.585988 | 1.307 | 1.338 | 1.538 | 109.2 |
| CCSD(T)/DZP | -387.289039 | 1.329 | 1.357 | 1.604 | 108.5 |
| CCSD(T)/TZ2P | -387.528534 | 1.326 | 1.353 | 1.610 | 108.6 |
| CCSD(T)(full)/cc-VTZ2P | -387.608601 | 1.321 | 1.348 | 1.592 | 108.7 |
| CCSD(T)/TZ2P+f | -387.641489 | 1.320 | 1.346 | 1.583 | 108.7 |
| CCSD(T)(full)/cc-VTZ2P+f | -387.717711 | 1.314 | 1.343 | 1.569 | 108.8 |
| $r_0$-structure (IR, ref 17)) | | (1.315) | 1.349 | 1.576 | 109.05 |
| $r_0$-structure (IR, ref 18) | | 1.316(2) | 1.348(3) | 1.575(2) | 108.8(3) |
| $r_z$-structure (ED + IR, ref 19) | | 1.317(6) | 1.348(8) | 1.578(1) | 108.8(7) |

[a] Energies in hartrees, bond lengths in Å, bond angles in deg. Experimental geometries are based on infrared (IR) and electron diffraction (ED) measurements published in refs 17−19. The CF distance in parentheses is assumed. Otherwise, numbers in parentheses give uncertainties.

HF theory underestimates all bond lengths showing the typical dependence on the basis set, namely that with increasing basis set size bond lengths become shorter. At all levels of theory, this trend is reproduced, i.e. with the largest basis set used in this work the shortest OO, CO, and CF bond lengths are obtained. Since correlation corrections lead to an increase in bond lengths, an accurate account of the geometry of **2** requires a method including a large amount of correlation effects (lengthening of bonds) and a large basis set (reduction of bond lengths).

Normally, left−right pair correlation effects generated by the corresponding D excitations lead to bond lengthening. This is also found for **2**, where effects are strongest for the OO bond. For example, the second most important configuration in the CISD wave function corresponds to a D excitation from the symmetric to the antibonding Walsh orbital of the dioxirane ring. However, pair correlation alone is insufficient to lead to an accurate geometry of **2**.

The data of Table 1 reveal that all methods that include just orbital relaxation effects (S excitations) and pair correlations fail to predict the geometry of **2** correctly. For example, CISD/DZP leads to bond lengths that are somewhat shorter than $r_0(r_z)$-values and, as a consequence, improvement of the basis results in increasing deviations from $r_0(r_z)$-values. CCSD includes besides S and D excitations also higher correlation effects due to disconnected cluster effects. Accordingly, CCSD/DZP bond lengths are close to experimental values, however, they deviate more and more from experimental values with increasing basis set. Although the same is true at the MP2 level of theory, the reason for the fortuitous accuracy of the MP2/cc-VTZ2P geometry is the well-known exaggeration of pair correlation effects rather than the inclusion of higher correlation effects. The addition of f-functions to the basis leads to an underestimation of the OO bond length by 0.02 Å at the MP2 level.

Recently, Cremer and co-workers[34] showed that DFT with the B3LYP functional leads to surprisingly accurate geometries in the case of carbonyl oxides and dioxiranes due to the fact that DFT covers a relatively large amount of (unspecified) correlation effects. This is also reflected in the B3LYP geometries listed in Table 1. However, DFT fails to reproduce the OO bond length correctly, which is predicted (1.550 Å) 0.028 Å too short compared to the experimental $r_0$-value of 1.575 ($r_z$-value of 1.578) Å. Upon addition of f-functions, this difference even increases to 0.033 (0.036) Å, which clearly indicates that **2** represents a rather difficult correlation problem comparable to those encountered for other F-containing molecules such as FOOF, FOF, or FNNF.[20]

A reasonable geometry of **2** is obtained at the MP4 level of theory provided f-functions are included into the basis set (CF: 1.318; CO: 1.348; OO: 1.580 Å, Table 1). Clearly, connected T excitations describing three-electron correlation effects and a TZ2P basis set augmented by f-functions are needed to predict a reliable geometry of **2**. This is also confirmed by the CCSD(T) results listed in Table 1. The two calculations with f-functions lead to reasonable geometries where the inclusion/exclusion of core correlation effects seems to have little effect on the geometry. The correlation consistent basis set of Dunning is more flexible and leads to a 5 mhartree larger coverage of correlation effects, which might be responsible for the somewhat shorter bond lengths.

Three-electron correlation effects either at the MP4 or CCSD(T) level of theory are essential for the description of the geometry of **2**. In a recent paper, Cremer and Zhi He[48] have pointed out that electron clustering in the valence shell as it occurs for electronegative atoms such as O or F requires efficient correlation mechanisms that involve at least three electrons and

(48) Cremer, D.; He, Z., *J. Phys. Chem.* **1996**, *100*, 6173.

**Table 2.** Calculated and Experimental Dipole Moments and Rotational Constants of Difluorodioxirane (**2**)[a]

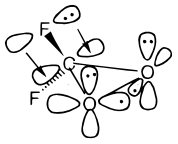
| method/basis | $\mu$ | A | B | C | $\sigma$[b] |
|---|---|---|---|---|---|
| Becke3YLP/6-311+G(3d) | 0.50 | 0.266 68 | 0.210 58 | 0.160 78 | 0.000 12 |
| Becke3YLP/6-311+G(3df) | 0.53 | 0.268 15 | 0.211 25 | 0.161 11 | 0.001 42 |
| HF/TZ2P+f | 0.72 | 0.283 59 | 0.222 39 | 0.167 59 | 0.011 39 |
| MP2(full)/cc-VTZ2P | 0.57 | 0.265 22 | 0.209 81 | 0.161 75 | 0.000 86 |
| MP2(full)/cc-VTZ2P+f | 0.61 | 0.268 82 | 0.211 81 | 0.162 68 | 0.001 31 |
| MP4(SDTQ)(full)/cc-VTZ2P | 0.54 | 0.261 31 | 0.208 14 | 0.161 44 | 0.002 83 |
| MP4(SDTQ)(full)/cc-VTZ2P+f | 0.59 | 0.265 28 | 0.210 31 | 0.162 48 | 0.000 44 |
| CISD/TZ2P+f | 0.68 | 0.280 28 | 0.217 96 | 0.165 65 | 0.008 17 |
| CISD/cc-VTZ2P+f | 0.73 | 0.281 74 | 0.218 91 | 0.166 20 | 0.009 15 |
| CCSD/TZ2P+f | 0.58 | 0.270 83 | 0.212 26 | 0.163 21 | 0.002 30 |
| CCSD/cc-VTZ2P+f | 0.65 | 0.273 00 | 0.213 75 | 0.164 05 | 0.003 80 |
| CCSD(T)/DZP | 0.58 | 0.261 35 | 0.206 08 | 0.160 33 | 0.003 88 |
| CCSD(T)/TZ2P | 0.50 | 0.261 50 | 0.207 28 | 0.161 60 | 0.003 00 |
| CCSD(T)(full)/cc-VTZ2P | 0.55 | 0.263 22 | 0.210 01 | 0.162 45 | 0.001 23 |
| CCSD(T)/TZ2P+f | 0.54 | 0.264 55 | 0.210 49 | 0.162 56 | 0.000 60 |
| CCSD(T)/cc-VTZ2P+f | 0.61 | 0.267 17 | 0.212 30 | 0.163 53 | 0.001 20 |
| CCSD(T)(full)/cc-VTZ2P+f | 0.60 | 0.267 22 | 0.212 11 | 0.163 41 | 0.001 12 |
| experiment[c] | | 0.265 755 41(28) | 0.210 956 53(14) | 0.162 667 91(15) | |

[a] Dipole moments in debye, rotational constants *A*, *B*, and *C* in $cm^{-1}$. [b] Mean deviation between experimental and calculated results. [c] From ref 17.

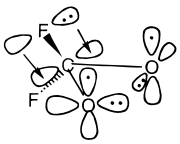
that can only be described when at least connected T are included in the calculation. Molecule **2** represents such a case and, therefore, calculations at lower levels of theory cannot provide the accuracy required to give a reliable description of its properties. Any accidental agreement with measured data observed, e.g. at the MP2/TZ2P level of theory, results from a cancellation of basis set and correlation errors as becomes obvious when a larger basis set is used.

Since $r_z$-($r_0$-) and $r_e$-geometries normally differ, it is difficult to predict which of the three calculations with T effects and f-functions leads to the most reliable $r_e$-geometry. According to calculated correlation energies, this should be the CCSD-(T)(full)/cc-VTZ2P+f geometry even though its bond lengths (1.314, 1.343, 1.569, Table 1) differ by 0.003 (0.002), 0.005 (0.005), and 0.009 (0.006) Å from experimental $r_z$($r_0$)-values. Normally, measured $r_z$-values should be closer to the $r_e$-geometry than the $r_0$-values. However, in the present case $B_z$ constants are smaller than $B_0$ constants indicating that the $r_0$-rather than the $r_Z$-geometry is closer to the $r_e$-geometry, which is confirmed by the data in Table 1. Therefore, measured rotational constants $A_0$, $B_0$, $C_0$[17,18] rather than $A_z$, $B_z$, $C_z$[19] are compared with calculated $A_e$, $B_e$, $C_e$ values in Table 2. Calculated mean deviations reveal that the best agreement between measured and calculated rotational constants is obtained at the MP4/cc-VTZ2P+f level followed by the three CCSD(T) calculations with TZ2P+f-type basis sets.

The differences in the $r_e$-geometries of **1** and **2** suggest a strong electronic effect of the F substituents. Although the lengthening of the OO bond is most obvious, another geometrical parameter provides a better insight into the electronic nature of **2**. The external ring angle of **1** (HCH: 116.6° [8]) decreases by 8° to 108.8° in **2**, which can be considered as a direct result of CF,CF bond interactions well-known for geminal F-substituted hydrocarbons. As a consequence, the internal ring angle at C is enlarged from 66.2 (**1**) to 71.7° (**2**, Figure 1). These changes can be translated into electronic effects with the help of the Cremer−Kraka electron density model of three-membered rings.[49] The $\pi$-donor capacity of the F atoms is enhanced and, as a consequence, the population of the antisymmetric Walsh MO is increased rather than decreased as one might expect in view of the larger electronegativity of a $CF_2$ group compared to that of a $CH_2$ group.[49] This leads to a lengthening of the OO bond, which does not necessarily mean that **2** partially obtains the character of a difluorobisoxymethylene biradical. On the contrary, such a biradical could only stabilize itself by adopting a $2\pi$ configuration, which is electronically destabilized due to enhanced 4e-repulsion effects.



ring: 4π



biradical: 2π

**Heat of Formation and Stability**. The heat of formation $\Delta H_f°(298)$ of **2** can be calculated with the help of suitable reactions using calculated reaction energies, ZPE, and thermal corrections as well as known $\Delta H_f°(298)$ values[52,53] of all other reaction partners. For reactions 1−7, we have calculated B3LYP/6-311+G(3df,3pd) and CCSD(T)/cc-VTZ2p+f,d reaction energies and corrected them by B3LYP/6-311+G(3df,3pd) ZPE and thermal corrections to obtain reaction enthalpies $\Delta\Delta H_f°(298)$. These values are listed in Table 3 together with

$$\mathbf{2} + 2CH_4 \rightarrow \mathbf{1} + 2\ CH_3F \quad (1)$$

$$\mathbf{2} \rightarrow CO_2 + F_2 \quad (2)$$

(49) See, e.g.: Cremer, D.; Kraka, E.; Szabo, K. J. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1995; Vol. 2, p 43.

(50) Cremer, D. *J. Am. Chem. Soc*. **1981**, *103*, 3619, 3627, 3633. Cremer, D. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 888.

(51) Cremer, D.; Kraka, E.; McKee, M. L.; Radhakrishnan, T. P. *Chem. Pys. Lett.* **1991**, *187*, 491.

(52) (a) Cox, J. D.; Pilcher, G. *Thermochemistry of Orhanic and Organometallic Compounds;* Academic Press: London, 1970. (b) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: New York, 1986. (c) *Handbook of Chemistry and Physics*, 64th ed.; West, R. C., Astle, M. J., Beyer, W. H., Eds; CRC Press: Boca Raton, FL, 1983. (d) Chase, M. W. *J. Phys. Chem. Ref. Data* **1996**, *25*, 551.

(53) (a) Montgomery, J. A.; Michels, H. H.; Francisco, J. S. *Chem. Phys. Lett*. **1994**, *220*, 391. (b) Schneider, W. F.; Wallington, T. J. *J. Phys. Chem*. **1994**, *98*, 7448. (c) Zachariah, M. R.; Westmoreland, P. R.; Burgess, D. R., Jr.; Tsang, W.; Melius, C. F. *J. Phys. Chem.* **1996**, *100*, 8737.

$$\mathbf{2} \rightarrow CO + F_2O \quad (3)$$

$$\mathbf{2} + H_2C{=}CH_2 \rightarrow \text{oxirane} + F_2C{=}O \quad (4)$$

$$\mathbf{2} \rightarrow O(^1D) + F_2C{=}O \quad (5)$$

$$\mathbf{2} + H_2C{=}O \rightarrow \mathbf{1} + F_2C{=}O \quad (6)$$

$$\mathbf{2} + \text{oxirane} \rightarrow \mathbf{1} + \text{2,2-difluorooxirane} \quad (7)$$

the average $\Delta H_f°(298)$ value obtained for **2** at the CCSD(T) and B3LYP levels of theory. Calculated $\Delta H_f°(298)$ values vary by 7−9 kcal/mol both at the DFT and CCSD(T) level of theory, where CCSD(T) values are on the average 4.4 kcal/mol more negative than DFT values.

The variation in calculated $\Delta H_f°(298)$ values clearly reflects the fact that the balanced description of **2** and other geminal F-substituted molecules in reactions such as 1−7 represents an extremely difficult calculational problem that is not completely solved even at the CCSD(T)/VTZ2P+f,d level of theory. For example, for reaction 3 the stability of **2** is overestimated relative to that of $F_2O$ because $F_2O$ is even more difficult to describe than **2**. Since CCSD(T) and DFT lead to variations in $\Delta H_f°(298)$, which are almost parallel to each other, it seems that the two methods suffer from the same deficiencies in the case of reactions 1−7, i.e. they cover correlation effects to a similar degree. However, test calculations with the TZ2P basis show that the use of f-functions leads to a considerable improvement of CCSD(T) based $\Delta H_f°(298)$ values and is responsible for the fact that these are more negative than the corresponding DFT-based $\Delta H_f°(298)$ values. We note that the absolute B3LYP energy of **2** decreases by just 8 kcal/mol while the corresponding CCSD(T) energy decreases by 73 kcal/mol when f-functions are added to the basis (Table 1).

In view of the large spread of calculated $\Delta H_f°(298)$ values one could tend to choose an average value to obtain a reasonable estimate for the heat of formation of **2**, namely −107.4 at CCSD(T) and −103.0 kcal/mol at B3LYP yielding an overall average of −105.2 kcal/mol. We have chosen an alternative way that is based on the following argument. If a formal reaction for calculating $\Delta H_f°(298)$ is constructed in such a way that the same structural units appear on both sides of the reaction equation, it is likely that calculational errors cancel each other out. In the ideal case, the difference between CCSD(T) and DFT reaction enthalpies should vanish and the reaction should be close to being thermoneutral since similar structural units are on both sides of the reaction. This is the case for reaction 6 (a cyclic peroxide, a $F_2CO$ group, and a ketone appear on both sides of the reaction, $\Delta\Delta H_f°(298,\text{CCSD(T)}) - \Delta\Delta H_f°(298,\text{B3LYP}) = -2.6$ kcal/mol) and even more for reaction 7 ($\Delta\Delta H_f°(298,\text{CCSD(T)}) - \Delta\Delta H_f°(298,\text{B3LYP}) = -2.2$ kcal/mol). Unfortunately, there is no reliable experimental value for $\Delta H_f°(298)$ of difluorooxirane and, therefore, reaction 7 could not be used for the determination of $\Delta H_f°(298,\mathbf{2})$.

Reaction 6 is suitable for the determination of $\Delta H_f°(298,\mathbf{2})$ because $\Delta H_f°(298)$ values for $H_2C{=}O$,[52] **1** [7], and $F_2C{=}O$[53] are well known from either experiment or theory. Recently, it was shown on the basis of high-level ab initio calculations that the experimental $\Delta H_f°(298)$ value of $F_2C{=}O$ (−153 kcal/mol[52]) is in error by 7−10 kcal/mol.[53] Values of −145.6 (CBS-QCI/APNO, isodesmic reaction),[53a] −145.3 (averaged G2 values, hydrogenation and isodesmic reactions),[53b] −143.6 (G2, isodesmic reaction),[53b] and −143.0 (BAC-MP4)[53c] were suggested. Our own calculations suggest a value of −143.0 kcal/mol, which differs from the JANAF value by 10 kcal/mol. Using the $\Delta\Delta H_f°(298,\text{CCSD(T)})$ and $\Delta\Delta H_f°(298,\text{B3LYP})$ values obtained for reaction 6 (Table 3), our best estimate for $\Delta H_f°(298,\mathbf{2})$ is $-102.0 \pm 1.5$ kcal/mol where the error bars are determined by the CCSD(T) and DFT heats of formation of −103.2 and −100.6 kcal/mol calculated with the help of reaction 6.

We have checked $\Delta H_f°(298,\mathbf{2})$ by determining $\Delta H_f°(298)$ of difluorooxirane with the help of the formal reaction 8

$$\text{difluorooxirane} + H_2C{=}O \rightarrow \text{oxirane} + F_2C{=}O \quad (8)$$

to be −114.9 kcal/mol and using this value in connection with reaction 7. We obtain $\Delta H_f°(298,\mathbf{2}) = -101.7$ kcal/mol (Table 3) in agreement with the value obtained from reaction 6.

Calculation of $\Delta\Delta H_f°(298)$ values for reactions 1−7 does not only lead to a reasonable estimate of $\Delta H_f°(298,\mathbf{2})$, but also helps to determine the various energy contributions that stabilize **2**. We note that geminal F-substitution in methane leads to stabilizing bond−bond interaction energies of 14 kcal/mol while the corresponding value for 2,2-difluoropropane is 15.8 kcal/mol (2,2-difluoropropane + propane → 2 × 2-fluoropropane) according to measured $\Delta H_f°(298)$ values.[52−54] In **2**, there are four C−F,C−O interactions besides the C−F,C−F interaction, which stabilize the dioxirane ring by delocalization of negative charge from the F atoms into the ring thus leading to CO bond strengthening. In turn, the C−O,C−F interactions also lead to a strengthening of the C−F bonds (reflected by CF bond lengths of 1.314 Å, which are clearly shorter than the CF bonds of the reference molecules: 1.34−1.35 Å, Figure 2) so that one has to distinguish between dioxirane stabilization by the $CF_2$ group and $CF_2$ stabilization by the dioxirane ring.

Actually, the first effect splits into two parts, of which the larger is stabilizing due to CO bond strengthening while the smaller is destabilizing due to charge transfer into the antisymmetric Walsh MO and subsequent OO bond weakening. There are at least four different electronic effects, which according to our calculations add to the stability of **2** in the following way: (1) C−F,C−F bond interactions (15.8 kcal/mol), (2) additional CF bond strengthening not found in $CH_3CF_2CH_3$ (3.7 kcal/mol), (3) CO bond strengthening (16.9 kcal/mol), and (4) OO bond weakening (−4.6 kcal/mol), where effects 3 and 4 determine the change in the ring strain energy upon geminal fluorination of **1**.

The magnitude of the total stabilization energy 1−4 has been estimated from the energy of formal reaction 1, which covers the change in both bond−bond interaction energies and strain energies when converting **2** into **1**. The CCSD(T)/cc-VTZP+f,d value for the reaction enthalpy at 298 K is 36.4 kcal/mol ($\Delta E(1) = 34.1$ kcal/mol, Table 3), which has to be corrected to 31.8 kcal/mol according to an error of −4.6 kcal/mol in the calculated $\Delta H_f°(298,\mathbf{2})$ based on reaction 1 (−106.6 compared to −102.0 kcal/mol, Table 3).

Homodesmotic ring strain energies of **1** and **2** can be determined with the help of formal reactions 9 and 10:

$$\mathbf{1} + HOOH + 2CH_3OH \rightarrow 2CH_3OOH + CH_2(OH)_2 \quad (9)$$

$$\mathbf{2} + HOOH + 2CHF_2OH \rightarrow 2CHF_2OOH + CF_2(OH)_2 \quad (10)$$

Utilizing heats of formations $\Delta H_f°(298)$ of 6.0 for **1**,[7] −32.6 for HOOH,[52] −48.0 for $CH_3OH$,[52] −93.5 for $CH_2(OH)_2$,[54] and −30.9 kcal/mol for $CH_3OOH$,[52] we calculate a homodesmotic ring strain enthalpy of 32.8 kcal/mol for **1** which is close to the average of the corresponding DFT and CCSD(T) values. In

(54) Cremer, D. *J. Comp. Chem.* **1982**, *3*, 165.

**Table 3.** Calculated Reaction Energies, $\Delta E$, and Enthalpies, $\Delta\Delta H_f°(298)$, Used for the Determination of $\Delta H_f°(298)$ of **2**[a]

| | reaction energies, $\Delta E$ | | reaction enthalpies, $\Delta\Delta H_f°(298)$ | | | $\Delta H_f°(298,\mathbf{2})$ | | |
|---|---|---|---|---|---|---|---|---|
| reaction no. | B3LYP | CCSD(T) | B3LYP | CCSD(T) | exp[b] | B3LYP | CCSD(T) | diff |
| 1 | 27.2 | 34.1 | 29.5 | 36.4 | 31.8 | −99.7 | −106.6 | −6.9 |
| 2 | 12.4 | 18.3 | 11.8 | 17.7 | 8.0 | −105.8 | −111.8 | −6.0 |
| 3 | 88.7 | 95.0 | 86.2 | 92.5 | 81.5 | −106.7 | −113.0 | −6.3 |
| 4 | −65.2 | −61.0 | −63.4 | −59.2 | −66.1 | −106.9 | −108.8 | −4.2 |
| 5 | 65.7 | 68.5 | 64.8 | 67.6 | 63.9 | −102.9 | −105.7 | −2.8 |
| 6 | −12.0 | −9.4 | −10.5 | −7.9 | −9.1 | −100.6 | −103.2 | −2.6 |
| 7 | 4.3 | 6.6 | 4.3 | 6.6 | 5.7 | −100.6 | −102.8 | −2.2 |
| av value, all reactions: $\Delta H_f°(298,\mathbf{2}) = -105.2$ | | | | | from | −103.0 | −107.4 | −4.5 |
| av value, reaction (6): $\Delta H_f°(298,\mathbf{2}) = -102.0 \pm 1.5$ | | | | | | | | |

[a] All energies (enthalpies) in kcal/mol. Reactions are given in the text. CCSD(T)/cc-VTZ+f,d single point calculations at B3LYP/6-311+G(3df,3pd) geometries apart from reaction 1, for which CCSD(T)/cc-VTZ+f,d geometries have been used. [b] Calculated from experimental $\Delta H_f°(298)$ values[52,53] and $\Delta H_f°(298,\mathbf{2}) = -102.0$ kcal/mol.

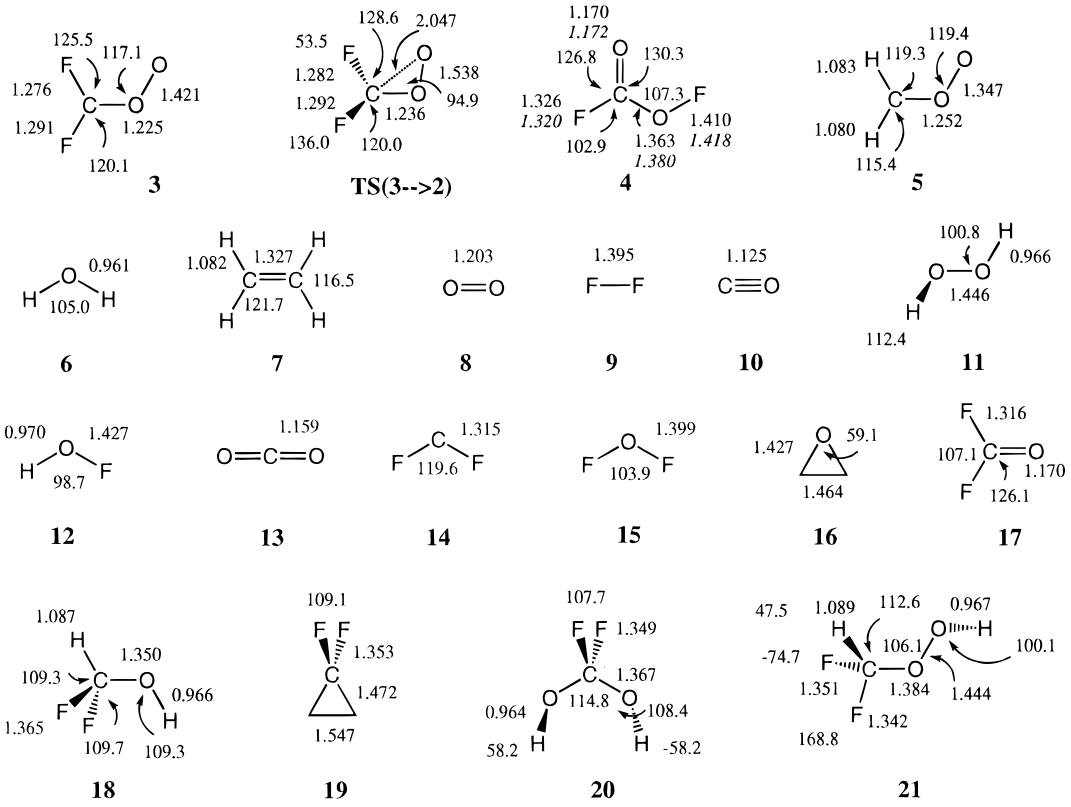



**Figure 2.** B3LYP/6-311+G(3df3pd) geometries of reference compounds **3**−**21**. Bond lengths in Å and angles in deg. Numbers in italics for **4** are from ref 60b.

view of the ring strain enthalpies of oxirane (27.5 kcal/mol[55]) and trioxirane (38.7 kcal/mol[49]), the calculated value suggests an increase of 5−6 kcal/mol with each additional O atom incorporated into the oxirane ring where this increase results from enhanced lone pair−lone pair repulsion.

To calculate the ring strain enthalpy of **2**, we have determined the unknown $\Delta H_f°(298)$ values of $CHF_2OH$ (−158.6), $CHF_2$-OOH (−133.1), and $CF_2(OH)_2$ (−206.18 kcal/mol) in the same way as described for **2**.[56] The homodesmotic strain enthalpy resulting from these $\Delta H_f°(298)$ values is 20.5 kcal/mol, suggesting a decrease in strain by 12.3 kcal/mol upon geminal fluorination of **1**. A decrease in ring strain upon fluorination of three-membered rings has been predicted by Cremer and Kraka[55b] and can be confirmed by calculating the ring strain enthalpies of difluorocyclopropane (23.6) or difluorooxirane (20.8 kcal/mol), which indicate strengthening of vicinal bonds by at least 3 and 6.7 kcal/mol, respectively, upon geminal fluorination of the corresponding parent compounds cyclopropane (ring strain: 26.5 kcal/mol) and oxirane (27.5 kcal/mol).[49,55]

The decrease in strain (12.3 kcal/mol) is dominated by effects 3 and 4, namely CO bond strengthening and OO bond weakening. To determine the energy contribution resulting from effect 4, we have investigated formal reactions 11 and 12

$$F_2C(OH)_2 + 2\ CH_4 \rightarrow H_2C(OH)_2 + 2CH_3F \qquad (11)$$

$$\mathbf{2} + H_2C(OH)_2 \rightarrow \mathbf{1} + F_2C(OH)_2 \qquad (12)$$

where (11) provides a basis to determine the bond−bond interaction energies of the acyclic counterpart of **2** and (12), which is a combination of reactions 1 and 11, is balanced with regard to C−F,C−F and C−O,C−F interaction energies and, therefore, should provide a measure for the OO bond weakening effect. For (11), we calculate a $\Delta\Delta H_f°(298)$ value of 36.4 kcal/

(55) (a) Cremer, D.; Kraka, E. The Concept of Molecular Strain: Basic Principles, Utility, and Limitations. In *Structure and Reactivity;* Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1988; p 65. (b) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800.

(56) Kraka, E.; Cremer, D. To be submitted for publication.

mol and, thereby, obtain for (12) $\Delta\Delta H_f°(298) = -4.6$ kcal/mol. This suggest that OO bond weakening contributes 4.6 kcal/mol and CO bond strengthening $12.3 - (-4.6) = -16.9 = 2 \times (-8.45)$ kcal/mol to the stability of **2** thus causing a decrease in the strain enthalpy by 12.3 kcal/mol (effects 3 + 4) when converting **1** into **2**. Considering that $\Delta\Delta H_f°$(298,reaction 1) = 31.8 kcal/mol covers the effects 1−4, the missing effect of C−F bond strengthening (effect 2) is calculated to be $31.8 - 15.8 - 12.3 = 3.7$ kcal/mol so that the total $CF_2$ contribution to the stability of **2** is $15.8 + 3.7 = 19.5$ kcal/mol (effects 1 + 2).

The large difference in the $\Delta H_f°(298)$ values of **2** (−02.0 kcal/mol) and **1** (6 kcal/mol[7]) can be understood with the help of the formal reaction

$$\mathbf{1} + F_2 \rightarrow \mathbf{2} + H_2 \qquad (13)$$

which has an estimated reaction enthalpy $\Delta\Delta H_f°(298)$ of −108.0 kcal/mol. Exchanging a $F_2$ molecule ($D_0 = 38$ kcal/mol[52c]) by a $H_2$ molecule (104 kcal/mol[52c]) in reaction 13 contributes −66 kcal/mol to $\Delta\Delta H_f°$(298,13). The change in bond−bond interaction and strain enthalpies adds −31.8 kcal/mol (reaction 1). The enthalpy contribution resulting from the replacement of two CH bonds by two CF bonds in reaction 13 can be calculated from the $\Delta\Delta H_f°(298)$ of reaction 14

$$F_2 + 2CH_4 \rightarrow H_2 + 2CH_3F \qquad (14)$$

which is −76.2 kcal/mol and, therefore, suggests an energy contribution of $-76.2 + 66 = -10.2$ for the CH/CF exchange. By adding all energy contributions $(-66 + (-31.8) + (-10.2))$, $\Delta\Delta H_f°(298) = -108.0$ kcal/mol of reaction 13 is reproduced.

We conclude that the stability of **2** is caused by (a) stabilizing CF,CF bond−bond interactions contributing 19.5 kcal/mol (effects 1 + 2), (b) a decrease of 12.3 kcal/mol in the ring strain from 32.8 (**1**) to 20.5 kcal/mol (**2**) (effects 3 + 4), which is predominantly due to CO bond strengthening, and (c) the larger strength of the CF bonds compared to those of the CH bonds, which adds 10 kcal/mol to the stability of **2**.

**Reactivity**. Dioxirane **2** is more stable than its carbonyl oxide isomer **3**. Carbonyl oxides are formed in the course of the ozonolysis although their intermediary could only be proven indirectly.[2] The isomerization barrier of carbonyl oxide (**5**) to yield dioxirane **1** is 19.2 kcal/mol and the corresponding reaction energy is −25.6 kcal/mol according to CCSD(T)/TZ2P calculations of Cremer and co-workers.[7] At the B3LYP/6-311+G(3df,2p) and even at the B3LYP/6-31G(d,p) level of theory, these values are reasonably reproduced (21.7 and −21.8 kcal/mol)[34] while MP methods lead to differences as large as 10 kcal/mol with regard to CCSD(T) results.[7] Therefore, we have used DFT to investigate the rearrangement **3** → **2**.

The B3LYP/6-311+G(3df,3pd) barrier for the carbonyl oxide−dioxirane isomerization **3** → **2** is just 11.2 kcal/mol, i.e. 8 kcal/mol smaller than that for the isomerization **5** → **1**. If one considers that carbonyl oxide is formed in the ozonolysis with an excess energy of 50 kcal/mol and more,[50] the reduction in the isomerization barrier may not mean very much as for the amount of dioxirane formed. Cremer and co-workers[51] have provided evidence that in the solution phase ozonolysis a dipole complex between carbonyl oxide and aldehyde is formed that directly leads to the formation of final ozonides rather than dioxiranes. Since carbonyl oxide **3** also possesses a relatively large dipole moment $\mu$ of 4.0 D, formation of a dipole complex is most likely as long as the reaction partners are generated and kept in a solvent cage. However, any conditions that lead to a generation of **3** outside a solvent cage will increase the probability of dioxirane formation, which in view of the relatively low barrier should be much higher in the case of **3** than of **5**.

CCSD(T)/cc-VTZ2P+f and B3LYP/6-311+G(3df) predict relative energies of 47 and 37 kcal/mol for **3**, indicating that a balanced description of the isomer pair **2**/**3** is very difficult. To get a more reliable energy difference, we have used the formal reaction 15

$$\mathbf{3} + H_2C{=}O \rightarrow \mathbf{5} + F_2C{=}O \qquad (15)$$

The CCSD(T) and B3LYP reaction enthalpies of (15) are −28.1 and −26.1 kcal/mol, which lead to $\Delta H_f°$(298,**3**) values of −58.7 and −60.7 kcal/mol suggesting an averaged value of −59.7 kcal/mol. Hence, **3** is 42 kcal/mol less stable than **2** and the formation of **3** from **2** can be excluded.

Cleavage of the OO bond of **2** and a subsequent F shift leads to the second isomer of **2**, FC(=O)OF (**4**), which was first synthesized in the 1960s.[57,58] Present interest in **4** results from the fact that the compound is the starting product for the synthesis of **2**[12] and some other interesting fluoroxy compounds such as chloroxyfluoroxydifluoromethane.[59] Although **4** was considered as being relatively unstable,[12,57−59] recent investigations by Argüello and co-workers[60] suggest that the molecule is more stable than originally assumed and that observed decomposition of **4** might result from the possible impurity FC(=O)-OOF. A detailed analysis of geometry, conformational behavior, and dissociation energies of **4** based on B3LYB/6-31+g(d) calculations has been performed by Mckee and Webb.[61]

According to the calculations presented in this work, **4** possesses about the same stability as **2** (Figure 3). Calculated values for $\Delta E$(B3LYP/6-311+G(3df)) = $E$(**4**) − $E$(**2**), $\Delta\Delta H_f°$-(298), and $\Delta\Delta G_f°(298) = \Delta\Delta H_f°(298) - T\Delta S(298)$ are −0.05, 0.3, and −0.8 kcal/mol while CCSD(T) predicts 6.1, 5.8, and 6.9 kcal/mol. Using the formal reactions 16 and 17

$$\mathbf{4} + H_2C{=}O \rightarrow HCOOH + F_2C{=}O \qquad (16)$$

$$\mathbf{4} + H_2O \rightarrow \mathbf{5} + F_2O \qquad (17)$$

an average $\Delta H_f°(298)$ of −103.6 kcal/mol is calculated for **4** suggesting that **4** is 1.6 kcal/mol more stable than **2**. In view of the fact that **1** rearranges to formic acid, HC(=O)OH, in a strongly exothermic reaction of −97 kcal/mol[7] (Figure 3), the similarity in the energies of **2** and **4** again documents that **2** is strongly stabilized.

The low $\Delta H_f°(298)$ value of **2** is responsible for the fact that all decomposition reactions shown in Figure 3 are endothermic. Decomposition into $CO_2$ and $F_2$ is endothermic by 8 kcal/mol compared to −100 kcal/mol calculated for the corresponding reaction of **1**.[7] Decomposition into CO and $F_2O$ or into triplet carbene $CF_2$ and triplet $O_2$ is endothermic by 81 and 108 kcal/mol, respectively (Figure 3). Similarly, the formation of $F_2C{=}O$ and $O(^1D)$ is endothermic (64 kcal/mol, Figure 3). Transfer of a $CF_2$ group to ethylene is endothermic by 30 kcal/mol compared to −7.5 kcal/mol calculated for the corresponding reaction of **1** with ethylene.[7] The only reaction of **2** being exotherm is the

(57) Ariva, A.; Aymonino, P. J.; Schumaker, H. J. *Z. Anorg. Chem.* **1962**, *316*, 327.
(58) Cauble, R. L.; Cady, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 5161.
(59) Russo, A.; DesMarteau, D. D. *Inorg. Chem.* **1995**, *34*, 6221.
(60) (a) Argüello, G. A.; Balzer-Jöllenbeck, G.; Jülicher, B.; Willner, H. *Inorg. Chem.* **1995**, *34*, 603. (b) Argüello, G. A.; Jülicher, B.; Ulic, S. E.; Willner, H.; Casper, B.; Mack, H.-G.; Oberhammer, H. *Inorg. Chem.* **1995**, *34*, 2089.
(61) McKee, M. L.; Webb, T. R., *J. Phys. Chem.* In press.

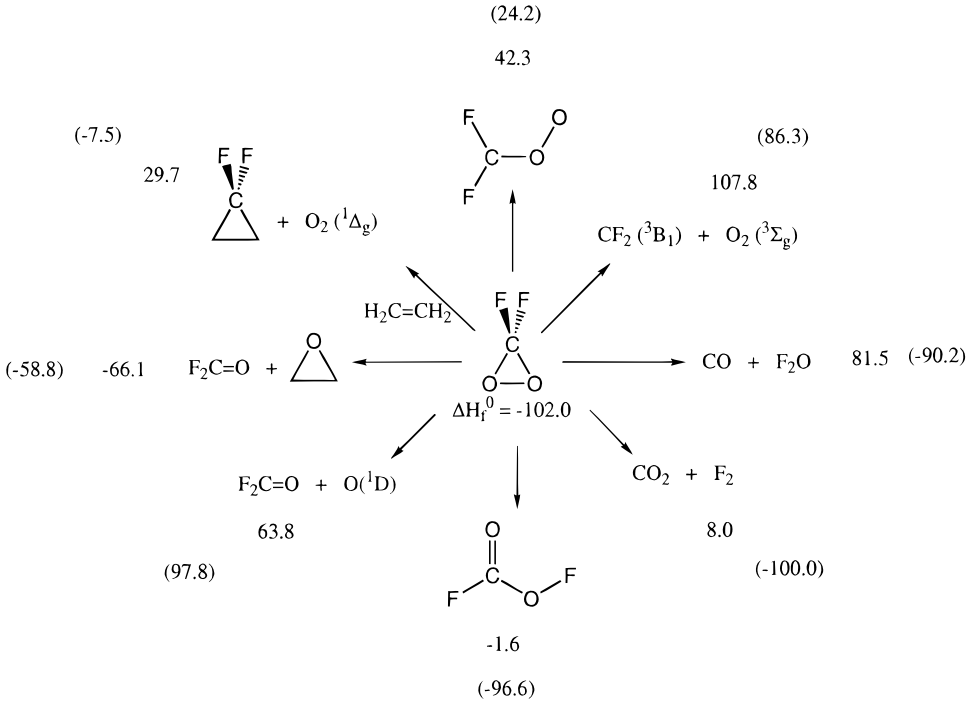



**Figure 3.** Reaction enthalpies $\Delta\Delta H_f°(298)$ (kcal/mol) for various dissociation and rearrangement reactions of difluorodioxirane (**2**) as determined from experimental and calculated $\Delta H_f°(298)$ values. The corresponding values for dioxirane (**1**) [7] are given in parentheses.

epoxidation reaction of ethylene, which is −66 kcal/mol (−59 kcal/mol for **1**[7]).

The calculated reaction enthalpies shown in Figure 3 suggest that **2** is most likely formed in the gas-phase ozonolysis of fluorinated ethylene or 1,1-difluoroalkenes by isomerization of carbonyl oxide **3** (energy barrier: 11 kcal/mol). Therefore, trapping of difluorocarbene in an oxygen-doped matrix, subsequent oxidation to **3**, and isomerization should lead to a controlled generation of **2** as an attractive alternative to the experiments by Russo and DesMarteau.[12] Dioxirane **2** epoxidizes alkenes similarly as dialkyldioxiranes do, however in view of its gaseous form at room temperature it may be a less useful agent for synthesis. Its major decomposition path should be characterized by OO cleavage and a subsequent F shift thus leading to the somewhat more stable isomer **4**. However, this reaction has not been observed experimentally.[12,59]

**Dipole Moment and Charge Distribution.** Compared to the dipole moment of **1** (2.48 Debye[7]) the calculated dipole moment of **2** is rather small. CCSD(T) calculations with the TZ2P+f basis sets suggest a value close to 0.60 D, which is a result of the fact that both F and O are strongly electronegative atoms. The dipole moment vector is directed from the $CF_2$ group (positive end, chemical notation of dipole moment) to the center of the OO bond (negative end).

Calculated Mulliken, natural, and virial charges lead to the same charge distribution: C is strongly positively charged (1.69 e) while F and O are negatively charged (−0.40 and −0.45 e) thus leading to charges of ±0.89 for the $CF_2$ (+) and $O_2$ (−) groups. This charge distribution differs strongly from that of **1**, for which the corresponding charges are 0.19 (C), 0.14 (H), −0.23 (O), and ±0.46 ($CH_2$, +; $O_2$, −). This means that the charge transfer from the $CX_2$ group to the peroxide unit almost doubles when replacing $CH_2$ (**1**) by $CF_2$ (**2**). These data add further support for the enhanced $\pi$-donor capacity of F in **2**. Basically, F is a strong $\sigma$-acceptor; however, part of the accepted charge is back-donated in the form of $\pi$-charge to C and transmitted to the OO unit.

**Vibrational Spectra.** In view of the fact that f-functions are absolutely necessary to determine a reliable geometry of **2**, it is not astonishing that the same is true in the case of vibrational frequencies (Table 4). Without exception, f-functions lead to an increase of the vibrational frequencies of **2**. On the average this increase is 10.1, 15.9, 17.4, 19.2, and 20.6 $cm^{-1}$ in the case of SCF, MP2, MP4, and CCSD calculations with a TZ2P basis set (Table 5). In this way, the calculated frequencies listed in Table 4 provide a striking example for the fact that the importance of f-functions increases with the amount of correlation effects covered by a particular method. In the case of CCSD(T) (f-effect: 20 $cm^{-1}$), no further increase is observed, where one has to consider that the comparison is made once for the TZ2P and once for the cc-VTZ2P basis. There is a higher f-function effect for CISD than for MP4; however, this has to do with the fact that in the former case f-functions are used for both extending the wave function by additional "f-configurations" and improving it variationally. The smallest influence of f-functions (9 $cm^{-1}$) is found in the case of the DFT calculations, which is reasonable in view of the fact that the amount of correlation covered is predominantly determined by the prefixed form of the functional used in the DFT calculations.

While the influence of f-functions on the $\omega$-values of **1** is strongest (ca. 30 $cm^{-1}$) for CO and OO stretching frequencies,[8] f-functions increase all stretching frequencies of **2** by 20−40 $cm^{-1}$ (CO symmetric stretch: 42; CF and CO asymmetric stretch: 30; OO symmetric stretch: 25; CF symmetric stretch: 20 $cm^{-1}$, Tables 4 and 5). This clearly indicates that an accurate description of **2** cannot be done without f-functions and that even g-functions may lead to small changes in $\omega$-values.

Previous CCSD(T) calculations of harmonic vibrational frequencies $\omega$ have shown that one should use scaling factors of 0.96−0.98 depending on the basis set used to reproduce experimental frequencies $\nu$. At CCSD(T)(full)/cc-VTZ2p+f, which is the highest level of theory applied in this work, we find an averaged ratio $\nu/\omega$ of 0.963 for all stretching frequencies of **2** and 0.978 for the remaining frequencies thus leading to an overall ratio of 0.970. Using the latter value as an appropriate scaling factor, vibrational frequencies are obtained, which differ from experimental ones on the average by 7 $cm^{-1}$. When both

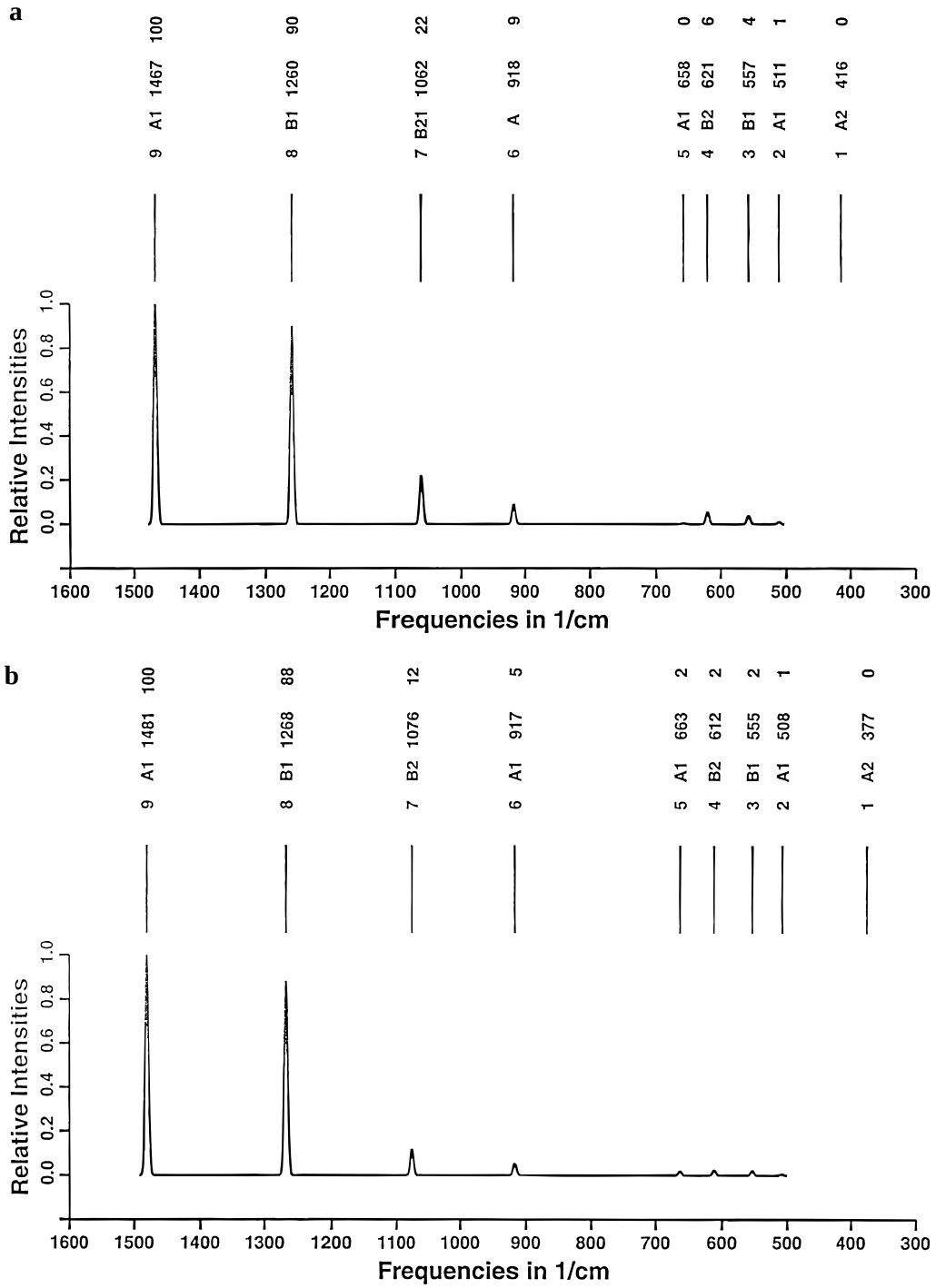



**Figure 4.** Comparison of (a) experimental and (b) CCSD(T)(full)/cc-VTZ2P+f infrared (IR) spectrum of dioxirane **2**. Calculated frequencies have been scaled by 0.970 (see text). Frequencies are given in $cm^{-1}$, intensities relative to the strongest band. For the assignment of IR bands and absolute intensities, see Tables 4 and 6.

scaling factors are used, the values denoted in Table 4 as "best" are obtained that differ from experimental values on the average just by 3 $cm^{-1}$.

In Table 5, the performance of the various methods used to calculate the vibrational modes of **2** is analyzed with the aid of mean deviations between calculated $\omega$-values and experimental frequencies $\nu$ or CCSD(T)(full)/cc-VTZ2P+f frequencies as well as the correlation coefficients resulting from linear regressions between calculated and experimental frequencies. Clearly, SCF and CI results are rather poor no matter what criterion is taken for the comparison. The best performance seems to be provided by CCSD(T), MP4, and DFT calculations when mean deviations between $\omega$-values and experimental frequencies are compared. However, in view of the fact that these two sets of frequencies are not directly comparable, it is better to compare how different methods reproduce CCSD(T)(full)/cc-VTZ2P+f frequencies which we consider as the most accurate harmonic frequencies obtained in this work. When this is done, stepwise improvement from DFT to MP2 and MP4 accompanied by an improvement of the basis set leads to the better approximation to CCSD(T)-(full)/cc-VTZ2P+f values.

The situation is somewhat different at the CC levels of theory used in this work. Since calculated bond lengths decrease with increasing basis set, one can expect the reverse trend in calculated frequencies. Indeed, this is found at all levels of theory if TZ2P-type basis sets are used. However, the smaller

**Table 4.** Harmonic Vibrational Frequencies (in $cm^{-1}$) and IR Intensities (in km/mol) for Difluorodioxirane (**2**) at Various Levels of Theory[a]

| method/basis | $\omega_1(a_1)$ CO sym str | $\omega_2(a_1)$ CF sym str | $\omega_3(a_1)$ OCO def | $\omega_4(a_1)$ $CF_2$ scissor | $\omega_5(a_2)$ $CF_2$ twist | $\omega_6(b_1)$ CF asym str | $\omega_7(b_1)$ $CF_2$ rock | $\omega_8(b_2)$ CO asym str | $\omega_9(b_2)$ $CF_2$ wag |
|---|---|---|---|---|---|---|---|---|---|
| Becke3YLP/6-311+g(3d) | 1464(386) | 934(36) | 716(4) | 510(2) | 382 | 1214(350) | 550(7) | 1026(48) | 610(7) |
| Becke3YLP/6-311+g(3df) | 1476(391) | 949(36) | 730(4) | 515(3) | 386 | 1233(352) | 553(7) | 1031(51) | 615(7) |
| HF/DZP | 1743(512) | 1094(31) | 846(2) | 571(5) | 447 | 1468(435) | 610(16) | 1146(59) | 704(16) |
| HF/TZ2P | 1688(451) | 1079(31) | 839(2) | 571(4) | 448 | 1433(387) | 610(12) | 1115(52) | 699(11) |
| HF/TZ2P+f | 1709(460) | 1091(30) | 852(2) | 574(4) | 451 | 1445(391) | 613(13) | 1133(56) | 705(12) |
| MP2(full)/cc-VTZ2P | 1476(390) | 937(27) | 712(6) | 525(2) | 386 | 1268(352) | 564(8) | 1124(84) | 618(9) |
| MP2(full)/cc-VTZ2P+f | 1515(394) | 954(25) | 731(6) | 531(3) | 391 | 1301(348) | 569(8) | 1131(81) | 630(9) |
| MP4(SDTQ,full)/cc-VTZ2P | 1450(381) | 904(21) | 656(8) | 511(1) | 380 | 1248(341) | 558(7) | 1085(50) | 608(9) |
| MP4(SDTQ,full)/cc-VTZ2P+f | 1494(386) | 924(20) | 679(7) | 520(2) | 386 | 1278 | 563 | 1095 | 618 |
| CISD/DZP | 1652(456) | 1033(31) | 790(3) | 545(5) | 415 | 1391(402) | 584(13) | 1140(61) | 663(14) |
| CISD/TZ2P | 1599(414) | 1024(31) | 790(3) | 550(3) | 420 | 1360(365) | 588(10) | 1105(54) | 663(10) |
| CISD/TZ2P+f | 1643(424) | 1048(31) | 814(2) | 556(4) | 427 | 1387(368) | 593(11) | 1134(58) | 674(11) |
| CISD/cc-VTZ2Pf | 1673(431) | 1065(30) | 823(3) | 561(4) | 431 | 1417(371) | 601(12) | 1148(62) | 686(12) |
| CCSD/DZP | 1559(419) | 953(35) | 696(6) | 520(3) | 391 | 1321(377) | 564(11) | 1117(55) | 629(13) |
| CCSD/TZ2P | 1497(381) | 941(25) | 696(6) | 522(2) | 393 | 1281(343) | 565(8) | 1076(48) | 626(9) |
| CCSD/TZ2P+f | 1544(390) | 964(25) | 720(5) | 530(3) | 401 | 1311(346) | 571(9) | 1104(51) | 637(10) |
| CCSD/cc-VTZ2Pf | 1584(396) | 988(24) | 734(5) | 538(3) | 408 | 1350(346) | 583(10) | 1126(54) | 654(11) |
| CCSD(T)/DZP | 1517(415) | 921(22) | 642(9) | 506(2) | 381 | 1293(375) | 558(10) | 1095(48) | 617(12) |
| CCSD(T)/TZ2P | 1441(376) | 902(22) | 638(8) | 503(1) | | 1240(340) | 557(7) | | |
| CCSD(T)(full)/cc-VTZ2P | 1484(381) | 924(21) | 658(8) | 515(2) | 390 | 1277(342) | 566(8) | 1081(46) | 620(9) |
| CCSD(T)/TZP2P+f | 1490(384) | 925(21) | 661(7) | 511(2) | | 1270 | 563 | | |
| CCSD(T)(full)/cc-VTZ2P+f | 1526(387) | 945(20) | 683(7) | 524(2) | 398 | 1307 | 572 | 1109 | 631 |
| scaled (0.970) | 1481 | 917 | 663 | 508 | 386 | 1268 | 555 | 1076 | 612 |
| scaled, best | 1470 | 910 | 658 | 512 | 389 | 1259 | 559 | 1068 | 617 |
| exp | 1467 | 918 | 658 | 511 | 416(?) | 1260 | 557 | 1062 | 621 |

[a] Intensities are given in parentheses. Values in italics have been obtained by adding f-function increments to the corresponding TZ2P values (see text). Scaled values have been obtained from CCSD(T)(full)/cc-VTZ2P+f frequencies by multiplying with 0.970, "best" scaled values by multiplying stretching frequencies by 0.963, and all other frequencies by 0.978.

**Table 5.** Mean Deviations, Correlation Coefficients, and f-Function Effects of Calculated Harmonic Vibrational Frequencies of Difluorodioxirane (**2**) at Various Levels of Theory[a]

| | mean deviations | | | f-function effect | |
|---|---|---|---|---|---|
| method/basis | exp | CCSD(T) | $R^2$ exp | av | OO str |
| Becke3YLP/6-311+g(3d) | 20.6 | 39.4 | 0.994 | | |
| Becke3YLP/6-311+g(3df) | 20.8 | 34.3 | 0.993 | 9.1 | 14 |
| HF/DZP | 131.8 | 103.8 | 0.988 | | |
| HF/TZ2P | 115.4 | 87.4 | 0.987 | | |
| HF/TZ2P+f | 125.6 | 97.6 | 0.986 | 10.1 | 13 |
| MP2(full)/cc-VTZ2P | 19.2 | 19.4 | 0.996 | | |
| MP2(full)/cc-VTZ2P+f | 34.4 | 12.7 | 0.997 | 15.9 | 19 |
| MP4(SDTQ,full)/cc-VTZ2P | 10.1 | 32.8 | 0.999 | | |
| MP4(SDTQ,full)/cc-VTZ2P+f | 14.0 | 15.3 | 0.999 | 17.4 | 23 |
| CISD/DZP | 85.6 | 57.6 | 0.994 | | |
| CISD/TZ2P | 72.9 | 45.8 | 0.993 | | |
| CISD/TZ2P+f | 92.6 | 64.6 | 0.992 | 19.7 | 24 |
| CISD/cc-VTZ2P+f | 106.9 | 78.9 | 0.992 | | |
| CCSD/DZP | 34.1 | 10.8 | 1.000 | | |
| CCSD/TZ2P | 17.1 | 13.8 | 0.999 | | |
| CCSD/TZ2P+f | 37.7 | 11.0 | 0.999 | 20.6 | 24 |
| CCSD/cc-VTZ2P+f | 58.0 | 30.0 | 0.999 | | |
| CCSD(T)/DZP | 17.0 | 18.3 | 0.999 | | |
| CCSD(T)/TZ2P | 15.0 | 46.0 | 1.000 | | |
| CCSD(T)(full)/cc-VTZ2P | 8.2 | 20.0 | 1.000 | | |
| CCSD(T)(full)/cc-VTZ2P+f | 28.0 | 0 | 1.000 | 20.0 | 25 |

[a] Mean deviations are given with regard to experimental frequencies (exp) and CCSD(T)(full)/cc-VTZ2P+f values. Correlation coefficients $R^2$ have been calculated from linear correlations between calculated and experimental frequencies. Changes in frequencies due to the addition of f-functions (f-function effect, in $cm^{-1}$) are given as averaged values for all frequencies and for the OO stretching frequency.

DZP basis set leads to larger frequencies although bond lengths are on the average longer than those calculated at the same level of theory with the TZ2P basis set. On the average calculated frequencies do increase again upon further enlargement of the basis. This leads in the case of CCSD and CCSD(T) to an accidental reproduction of experimental frequencies for the TZ2P basis and stronger deviations for TZ2P+f values. Clearly, it is not appropriate to compare harmonic frequencies directly with experimental frequencies when the former are based on high accuracy calculations.

Correlation coefficients $R^2$ reflect how a given method reproduces trends in experimental frequencies that should also be present in harmonic frequencies. Clearly, CCSD(T) performs in this respect best ($R^2 = 1.000$, Table 5) while reasonable results are also obtained at the MP4 and CCSD levels of theory. The performance of MP2 and DFT is also acceptable even though they lack the accuracy of methods that contain connected T or at least disconnected T effects as pointed out above.

In Figure 3, the calculated IR spectrum based on scaled frequencies is compared with an "experimental" spectrum that has been derived from the experimental data of Christen and co-workers[19] and the measurements of Bürger and co-workers.[17] Both calculated frequencies and intensities convincingly agree with experimental values. The accuracy of our results leads us to question the reported Raman frequency of 416 $cm^{-1}$ for the $CF_2$ twisting motion $\omega_5$ of **2**, which was measured for a $CF_3Cl$ solution of **2**.[12] Our best estimate of $\omega_5$ (398 $cm^{-1}$, Table 4) is smaller than the experimental value. Considering anharmonic corrections, a value of 389 $cm^{-1}$ for $\omega_5$ is likely, which would imply a solvent effect of 27 $cm^{-1}$.

Isotopic shifts have been measured for $^{18}O$ and $^{13}C$ substitution of **2** by Christen and co-workers.[19] They are listed in Table 6 together with calculated isotopic shifts determined in this work. Both DFT and CCSD(T) isotopic shifts reproduce trends in measured shifts where the agreement between theory and experiment is clearly better at the CCSD(T) level of theory. Despite the fact that just three out of nine vibrational modes involve the O atoms of **2** according to the assignments given in Table 4, significant isotopic shifts are calculated for six vibrational modes upon single $^{18}O$ substitution ($\Delta\omega > 5$ $cm^{-1}$)

**Table 6.** Comparison of Becke3YLP, CCSD(T), and measured $^{13}C$ and $^{18}O$ isotopic shifts of the vibrational frequencies of difluorodioxirane (**2**)[a]

| | Becke3YLP method 6-311+G(3df) basis | | | CCSD(T) method cc-VTZ2P/cc-VTZ2P+f basis | | | experiment | |
|---|---|---|---|---|---|---|---|---|
| mode | $^{16}O^{18}O$ | $^{18}O^{18}O$ | $^{13}C$ | $^{16}O^{18}O$ | $^{18}O^{18}O$ | $^{13}C$ | $^{16}O^{18}O$ | $^{13}C$ |
| $\omega_1$ | 9.8 | 19.8 | 40.8 | 8.4 | 17.0 | 42.6 | 8.8 | 45.4 |
| | | | | *8.8* | *17.3* | *43.9* | | |
| $\omega_2$ | 14.2 | 26.8 | 2.2 | 11.3 | 22.0 | 0.8 | 11.1 | |
| | | | | 11.5 | 23.1 | 0.8 | | |
| $\omega_3$ | 12.3 | 25.3 | 2.0 | 11.2 | 22.6 | 2.4 | 11.2 | |
| | | | | *12.2* | *24.7* | *2.4* | | |
| $\omega_4$ | 4.6 | 8.7 | 0.5 | 6.1 | 12.0 | 0.2 | 6.2 | |
| | | | | *5.3* | *11.0* | *0.3* | | |
| $\omega_5$ | 7.8 | 15.3 | 0 | 7.8 | 15.2 | 0 | | |
| $\omega_6$ | 0.1 | 0.3 | 36.0 | 0.1 | 0.2 | 37.3 | 0.5 | 39.1 |
| $\omega_7$ | 4.2 | 8.8 | 2.4 | 4.4 | 9.1 | 2.5 | 4.2 | |
| $\omega_8$ | 7.3 | 16.1 | 27.8 | 8.1 | 16.9 | 29.3 | 8.0 | 29.4 |
| $\omega_9$ | 11.7 | 24.0 | 4.1 | 11.8 | 23.9 | 4.1 | 11.7 | |

[a] Isotopic shifts in $cm^{-1}$. The second entry in the CCSD(T) columns (in italic) has been calculated with the cc-VTZ2P+f basis. Experimental values from ref 19.

**Table 7.** Adiabatic Mode Analysis[a]

| | | | | adiabatic frequencies | | | |
|---|---|---|---|---|---|---|---|
| | | mode analysis | | symmetry coord | | internal coord | |
| mode | sym | difluorodioxirane (**2**) | dioxirane (**1**) | **2** | **1** | **2** | **1** |
| 1 | $a_1$ | 62.6% CO sym str (29.3% CF sym str; 5.5% $CF_2$ scissor) | 89.4% CO sym str (9.5% OO str) | 1349 | 1290 | 1189, CO | 1121, CO |
| 2 | $a_1$ | 60.3% CF sym str (27.2% OO str; 12.5% CO sym str) | 99.5% CH sym str | 1149 | 3127 | 1200, CF | 3180, CH |
| 3 | $a_1$ | 84% OO str (8.9% CF sym str; 7% CO sym str) | 93.4% OO str (6.1% CO sym str) | 800 | 844 | 800, OO | 844, OO |
| 4 | $a_1$ | 88% $CF_2$ scissor 5.6% CO sym str | 93.8% $CH_2$ scissor | 636 | 1568 | 688, FCO | 1267, HCO |
| 5 | $a_2$ | 100% $CF_2$ twist | 100% $CH_2$ twist | 386 | 1047 | 688, FCO | 1267, HCO |
| 6 | $b_1$ | 78.2% CF asym str (21.8% $CF_2$ rock) | 99.9% CH asym str | 1238 | 3231 | 1200, CF | 3180, CH |
| 7 | $b_1$ | 92.5% $CF_2$ rock (7.5% CF asym str) | 99.9% $CH_2$ rock | 811 | 1216 | 688, FCO | 1267, HCO |
| 8 | $b_2$ | 66.7% CO asym str (33.3% $CF_2$ wag) | 99.6% CO asym str | 1033 | 950 | 1189, CO | 1121, CO |
| 9 | $b_2$ | 73.2% $CF_2$ wag (26.8% CO asym str) | 96.1% $CH_2$ wag | 851 | 1301 | 688, FCO | 1267, HCO |

[a] Decomposition of normal modes in %. Second and third contributions are given in parentheses to facilitate reading. Adiabatic frequencies in $cm^{-1}$ according to MP2(full)/cc-VTZ2P calculations are given with regard to symmetry coordinates and internal coordinates specified after each frequency as CO for CO stretching frequency, FCO as FCO bending frequency, etc.

or double $^{18}O$ substitution ($\Delta\omega > 10$ $cm^{-1}$). This is in line with the fact that vibrational modes in a three-membered ring strongly couple, in particular when their masses are all similar. There are just three modes which are sensitive to replacement of $^{12}C$ by $^{13}C$. These are the CO stretching modes ($\omega_1$ and $\omega_9$) and the asymmetric CF stretching mode ($\omega_6$). CCSD(T) leads to shifts of 43, 37, and 29 $cm^{-1}$ in close agreement with experiment (45, 39, 29, Table 6) and also provides all shifts $<5$ $cm^{-1}$, which are difficult to measure.

Since all vibrational modes of **2** are coupled, it is interesting to determine and analyze the frequencies of the pure internal vibrational modes with the aid of the adiabatic mode analysis of Konkoli and Cremer.[43] They are shown in Table 7 together with the results of an adiabatic mode analysis of the calculated normal modes of **2**. Mode 1 is dominated by symmetric CO stretching (63%); however, it possesses also a strong admixture of symmetric CF stretching (30%) and 5% of $CF_2$ scissoring. Mode 2 is made up of 60% symmetric CF stretching, 27% OO stretching, and 13% symmetric CO stretching. Modes 3 (84% OO stretching), 4 (88% $CF_2$ scissoring), 5 (100% $CF_2$ twisting), and 7 (92% $CF_2$ rocking) are less coupled with the remaining contributions being <10%. Again, strong coupling is found in modes 6 (78% asymmetric CF stretching, 22% $CF_2$ rocking), 8 (67% asymmetric CO stretching, 33% $CF_2$ wagging), and 9 (73% $CF_2$ wagging, 27% asymmetric CO stretching). Comparison with the mode analysis of 1 also shown in Table 7 reveals that for the parent dioxirane just two of the nine normal modes, namely the two symmetrical ring stretching modes, modestly couple with each other (admixtures <10%) while all other modes are almost uncoupled. This strikingly shows the influence of mass in mode coupling.

The calculated adiabatic frequencies reveal that the CO stretching modes increase by 70 $cm^{-1}$ upon geminal F-substitution while the uncoupled OO stretching mode frequency decreases by just 44 $cm^{-1}$. Compared to oxirane (adiabatic CO stretching $\omega = 1130$ $cm^{-1}$ [43]), the adiabatic CO stretching frequency of **1** (1121 $cm^{-1}$, Table 7) is normal while it is considerably increased for **2** (1189 $cm^{-1}$). This confirms results of the stability analysis in so far as the decrease of the CO bond lengths is energetically more important than the increase in the OO bond length.

**NMR Chemical Shifts.** In recent work, Kraka and coworkers[62] have shown that reliable $^{13}C$ and $^{17}O$ chemical shifts can be obtained for dioxiranes and carbonyl oxides using SOS-

(62) Kraka, E.; Sosa, C.; Cremer, D. *Chem. Phys. Lett.* Submitted for publication.

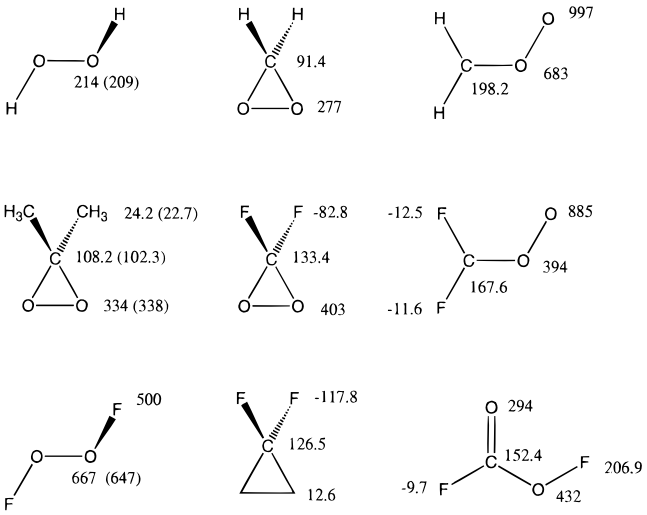



**Figure 5.** SOS-DFPT/VQZ2P NMR chemical shifts of **1**, **2**, and relevant reference compounds. Numbers in parentheses are experimental values. $^{13}C$ shifts are given relative to TMS, $^{17}O$ shifts relative to gaseous $H_2O$, and $^{19}F$ shifts relative to $CFCl_3$.

DFPT in the form suggested by Olsson and Cremer.[40] This is also reflected by the data summarized in Figure 5. For example, for dimethyldioxirane $^{13}C$ shifts of 102 and 23 ppm and the $^{17}O$ chemical shift of 338 ppm (relative to gaseous $H_2O$) have been measured by Curci and co-workers[63] while the corresponding SOS-DFPT values (see Figure 5) are 108, 24, and 334 ppm, respectively. $^{17}O$ NMR chemical shifts of peroxides are in general well reproduced (HOOH in Figure 5[40]) while multireference systems such as carbonyl oxides require empirical corrections with regard to $^{17}O$ chemical shifts, but not with regard to $^{13}C$ chemical shifts.[62]

For **2**, SOS-DFPT/VQZ2P values of $^{13}C$ and $^{17}O$ NMR chemical shifts are 133 and 403 ppm. For comparison, the $^{13}C$ shift of $CF_4$ is 131 ppm[64] while those of $CF_3$ or $CF_2$ groups are typically 118 or 109 ppm.[65] Thus, the $^{13}C$ shift of **2** is among the most downfield chemical shifts observed for the $CF_2$ group. This suggests strong diamagnetic deshielding of the C nucleus which is in line with its unusually large positive charge of 1.69 e.

$^{17}O$ NMR chemical shifts of acyclic peroxides are typically in the region of 250−300 ppm[66] which covers also the $^{17}O$ shift of 277 ppm calculated for **1**. For dioxetane, a value of 275 ppm has been measured where, of course, it has to be considered that solvent effects may lead to a difference up to 30 ppm between measured and calculated $^{17}O$ shifts that correspond to the gas phase.[40] Apart from this, the $^{17}O$ shift of **1** is not unusual for a cyclic or even an acyclic peroxide.[67] Replacing the $CH_2$ by the $CF_2$ group leads to a downfield shift of 126 ppm and a shift value (403 ppm, Figure 5) that so far has only been observed for transition metal peroxides, not for organic peroxides.[66] The value is reminiscent of the 647 ppm measured for FOOF[66] and confirmed by the SOS-DFPT/VQZ2P calculations of this work (667 ppm, Figure 5).

$^{17}O$ NMR chemical shifts are often dominated by paramagnetic rather than diamagnetic shielding contributions.[66] If low-lying excited states exist, which can be detected by analyzing HOMO-LUMO energy differences, paramagnetic contributions will be particularly large. In **2**, both the HOMO is raised in energy due to interactions between the $a_2$ orbitals of the $CF_2$ and $CO_2$ units and the lowest unoccupied orbitals are lowered in energy relative to those of **1**. Hence, the $^{17}O$ chemical shift of 403 ppm is mainly due to strong paramagnetic shielding contributions caused by the $CF_2$ group. We note that both $^{13}C$ and $^{17}O$ NMR chemical shifts of **2** are so unusual that they can easily be used for the identification of the molecule by NMR spectroscopy.

The calculated $\delta^{19}F$ value of −83 ppm differs by −50 ppm from the experimental value of Russo and DesMarteau ($\delta^{19}F$ = −29.9 ppm).[12] Errors in calculated $\delta^{19}F$ values up to 30 ppm and more are possible; however, these are always positive because of the basic deficiency of DFT based methods to underestimate screening of the nuclei by negative charge thus leading to an overestimation of paramagnetic and an underestimation of diamagnetic effects.[40] Hence, a computational error of −50 ppm can be excluded and, accordingly, the calculated $\delta^{19}F$ value of −83 ppm suggests an error in the experiment. We note in this connection that the measured $\delta^{19}F$ value of $F_2C$-(OCl)(OF), which is closely related to **2**, is −79.9 ppm[59] and, by this, differs just 3 ppm from our calculated $\delta^{19}F$ value for **2**. On the other hand, the calculated $\delta^{19}F$ value of **4** is −9.7 ppm and that of $F_2C{=}O$ is 4.9 ppm, suggesting experimental values in the range −20 to −30 ppm. We conclude that in the experiment most likely $F_2C{=}O$ rather than **4** was measured.

## Conclusions

Dioxirane **2** is an unusual molecule with regard to all its properties.

(1) Its geometry is characterized by a rather long OO bond of 1.578 Å, which is the longest OO bond ever calculated or measured. With FOOF on the one side[20] and **2** on the other side, the range of known OO single bond distances stretches now from 1.22 to 1.58 Å, which is similar or larger than the corresponding range of CC single bonds (depending on what one considers the longest CC bond ever measured).

(2) Despite the unusual OO bond length, the most revealing geometrical parameter as to the electronic nature of **2** is the FCF bond angle (108.8°), which is 8° smaller than the HCH angle in **1** and indicates strong CF,CF bond interactions that significantly influence the electronic structure of **2**.

(3) Stabilizing bond−bond interactions increase the stability of **2** relative to that of **1** by 32 kcal/mol. Part of this increase in stability is due to a decrease in ring strain from 32.8 to 20.5 by 12 kcal/mol (due to C−F,C−O bond interactions) while another part (30 kcal/mol) results from C−F,C−F interactions. The unusually high thermodynamic stability of **2** is reflected by its $\Delta H_f°$ value of −102 kcal/mol.

(4) The change in ring strain can be split into a CO bond strengthening (17 kcal/mol) and an OO bond weakening part (4.6 kcal/mol), which both result from transfer of negative charge from the F atoms to the antisymmetric Walsh MO. Noteworthy is that the lengthening of the OO bond does not indicate the conversion of the ring to an open bisoxymethylene biradical, which would be destabilized by geminal F substituents.

(5) Among the three $CF_2O_2$ isomers, **2** is more stable than difluorocarbonyl oxide **3** by 42.3 kcal/mol while FC(=O)OF (**4**) is slightly more stable than **2** (−1.6 kcal/mol, Figure 3). Rearrangement to **4** is the most likely reaction of **2** although it has not been observed experimentally.

(6) The relatively high thermodynamic stability of **2** also influences its kinetic stability which is reflected by the fact that

(63) Cassidei, L.; Fiorentino, M.; Mello, R.; Sciacovelli, O.; Curci, R. *J. Org. Chem.* **1987**, *52*, 699.
(64) Jameson, A. K.; Jameson, C. J. *Chem. Phys. Lett.* **1987**, *134*, 461.
(65) Kalinowski, H.-O.; Berger, S.; Braun, S. *$^{13}$C-NMR-Spektroskopie*; Thieme Verlag: Stuttgart, 1984.
(66) *$^{17}$O NMR Spectroscopy in Organic Chemistry;* Boykin, D. W., Ed.; CRC Press: Boca Raton, FL, 1991.
(67) (a) Cremer, D.; Schindler, M. *Chem. Phys. Lett.* **1987**, *133*, 293. (b) Adam, W.; Chan, Y.-Y.; Cremer, D.; Gauss, J.; Scheutzow, D.; Schindler, M. *J. Org. Chem.* **1987**, *52*, 2800.

all its decomposition reactions are endothermic (Figure 3). Its most likely reaction is rearrangement to **4** via a bisoxydifluoromethylene biradical and a subsequent F-shift. In the presence of alkenes, **2** will lead to epoxides in a strongly exothermic reaction.

(7) In view of a calculated barrier of just 11 kcal/mol for the isomerization of difluorocarbonyl oxide **3** to yield **2**, one can predict that **2** might be formed in the gas-phase (or solution-phase) ozonolysis of perfluoroethylene or 1,1-difluoroalkenes. A controlled generation of **2** by $O_2$ oxidation of carbene $CF_2$ in the matrix should offer an alternative to the FC(═O)OF/CsF reaction first used by Russo and DesMarteau to generate **2**.[12]

(8) The IR spectrum of **2** is characterized by two strong bands at 1467 and 1260 $cm^{-1}$ corresponding to the symmetric CO stretching mode and the asymmetric CF stretching mode and six other bands of weak intensity. We confirm a OO stretching frequency at 658 $cm^{-1}$. The $CF_2$ twisting mode should be placed at 389 $cm^{-1}$ contrary to a previous solution-phase measurement of this band at 416 $cm^{-1}$.[12]

(9) Calculated isotopic shifts agree within 2−3 $cm^{-1}$ with available experimental values. They suggest strong coupling between the normal modes of **2**.

(10) The degree of mode coupling has been quantified by an adiabatic mode analysis, which shows that 8 out of 9 modes of **2** are coupled. This is a consequence of the similarity of the masses of **2** and does not occur in the case of **1**. According to calculated adiabatic frequencies of **2**, the change in the CO stretching frequencies due to F substitution is significantly larger than that in the OO frequency thus confirming results of the energy analysis.

(11) $^{13}C$ and $^{17}O$ NMR chemical shifts of **2** (133 and 403 ppm) are significantly upfield shifted relative to those of **1** (91 and 277 ppm) or any other organic peroxide. The shift values suggest strong deshielding of the C nucleus and a substantial charge transfer from the F to the O atoms, which is confirmed by calculated charge distributions and the relatively small value of the dipole moment (0.60 D). In view of a calculated $\delta^{19}F$ of −83 ppm, the measured $\delta^{19}F$ value of **2** (−29.9 ppm[12]) is probably due to one of the decomposition products of **2** as for example $F_2C$═O rather than **2** itself.

(12) In conclusion, the unusual electronic structure of **2** is caused by CF,CF bond interactions leading to a relatively small FCF angle and enhanced $\pi$-donation from the F atoms to the antisymmetric Walsh MO.

The inclusion of three-electron correlation effects in connection with the use of TZ2P basis sets augmented by f-functions is essential for a correct description of **2** at the ab initio level. We note that the present work represents the most elaborate ab initio study at correlation corrected levels ever carried out for a five-heavy atom system. Although DFT cannot reach the accuracy of CCSD(T) calculations in the case of **2**, results obtained with the B3LYP functional are rather useful especially if one considers that they can be obtained at relatively modest cost. Apart from this, it has to be stressed that the determination of the energetics of **2** is an extremely difficult calculational problem that requires extensive comparative calculations since the direct calculation of energy differences is flawed even at the CCSD(T)/VTZ2P+f,d level of theory.

**Acknowledgment.** E.K. and D.C. acknowledge useful discussions with Professor Michael L. McKee, Auburn, Alabama, on the stability of difluorodioxirane as well as his work on fluoroformyl hypofluorite prior to publication. At the University of Göteborg support was provided by the Swedish Natural Science Research Council (NFR) and the Nationellt Superdatorcentrum (NSC), Linköping, Sweden. At the University of Georgia, research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Scienes, Fundamental Interactions Branch, Grant No. DE-FG05-94ER14428.

**Supporting Information Available:** Calculated energies, zero point energies, entropies, and heat of formations of 1−33 (1 page). See any current masthead page for ordering information and Internet access instructions.

JA961983W