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A Theoretical Study of Substituted Dioxiranes: Difluorodioxirane, Fluorofluoroxydioxirane, (Fluoroimino)dioxirane, and Hydrazodioxirane

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Equilibrium geometries and harmonic vibrational frequencies of three substituted dioxiranes, CO_2FOF, CO_2NF, and $CO_2(NH)_2$, which have not been previously investigated, are reported. Results are based on second-order Møller−Plesset (MP2) and quadratic configuration interaction through single and double excitation (QCISD) calculations using 6-31G(d) and 6-311G(d,p) basis sets. Molecular geometric characteristics, vibrational frequencies, dipole moments, as well as local atomic charges, are compared with those of known dioxiranes (CO_2H_2, CO_2F_2, CO_2N_2, CO_4). It is found that bond lengths and angles of the dioxirane ring are sensitive to the electropositivity of the central carbon. Hydrazodioxirane, $CO_2(NH)_2$, is found to be a high-energy density molecule; whereas fluorofluoroxydioxirane (CO_2FOF) may be of further interest as a powerful oxidizer. Equilibrium geometries and vibrational frequencies of the previously uncharacterized energetically low-lying 1^3B_1 and 1^3B_2 triplet states of CO_2F_2 and the ground state of its cation, $CO_2F_2^+(1^2A_2)$, are predicted and analyzed.

Introduction

The chemistry of dioxiranes has received widespread attention following the recent discovery by Murray and Jeyaraman[1] that solutions of dioxiranes can be prepared and used to carry out a variety of synthetically useful reactions, including, and of particular note, regio- and stereoselective epoxidations.[2−4] At the present time, a number of substituted dioxiranes are known and are used as powerful oxidants.[1−9] Dioxiranes have also been investigated as potential high-energy metastable compounds[13] (e.g., CO_4 and CO_2N_2[10−12]). Despite the interest in and importance of such compounds, significant questions remain concerning, first of all, their molecular properties; the relatively low thermal stability of such compounds and their high reactivity make their molecular properties quite difficult to study experimentally. In particular, even preparation and isolation of dioxiranes proves to be a quite difficult problem,[14] and, in most cases, they can only be stored as dilute solutions in ketones.[1]

The parent, or unsubstituted, dioxirane, CO_2H_2, was prepared by the low-temperature gas-phase ozonolysis of ethylene by Lovas and Suenram.[15,16] Subsequent experimental and theoretical investigations have shown, however, that the parent dioxirane is a rather labile structure and can only be stabilized by appropriate substitution (see refs 17 and 18). On the basis of ab initio calculations, Cremer and co-workers predicted that, in contrast to CO_2H_2, difluorodioxirane (CO_2F_2) should possess considerable thermodynamic stability;[19] and recently, this dioxirane has been synthesized by Russo and DesMarteau[20] by the reaction of its isomer FC(═O)OF with ClF, Cl_2, or F_2 in the presence of CsF. Difluorodioxirane is the only known dioxirane that is stable in the gas phase at room temperature; consequently, this unusual molecule continues to attract both experimentalists and theorists to determine its properties. Investigations of the vibrational spectrum of this molecule established that it has C_{2v} symmetry.[20−23] More recent determination of its vibrational frequencies and geometry, based on IR and electron diffraction measurements, were performed by Casper et al.[24] The ab initio investigations of Kraka, Cremer, Schaefer, and co-workers,[25] at the CCSD(T) level, showed that difluorodioxirane is the most stable isomer of this molecule and they predicted its heat of formation ($\Delta H_f°(298) = -102 \pm 1.5$ kcal/mol), reaction enthalpies, dipole moment (0.60 D), and ^{13}C and ^{17}O NMR spectra.

Studies of difluorodioxirane thus far have only focused on its ground electronic state. However, the structurally similar CO_4 molecule was predicted (on the basis of MP2/6-31G(d) calculations[12]) to have low-lying triplet excited states. In analogy, one can expect that the difluorodioxirane molecule also has low-lying excited states in which the molecule retains a dioxirane ring similar to that in the ground state. In the present work, on the basis of ab initio calculations, it is shown that difluorodioxirane does indeed have low-lying excited triplet states. Such information is likely to be important not only for future spectral investigations of CO_2F_2 but also for calculating reliably thermodynamic properties of difluorodioxirane at elevated temperatures. In addition, it will also be shown that there exists at least one local minimum on the potential energy surface (PES) of the 1^2A_2 state of the cation, $CO_2F_2^+$. The predicted equilibrium structures of the excited states of difluorodioxirane and of the cation prove to be quite rigid systems relative to vibrational deformations, and from this point of view, they might be observable.

In addition to the studies of difluorordioxirane, we report the results of ab initio studies of three possible new dioxiranes, (fluoroimino)dioxirane (CO_2NF), fluorofluoroxydioxirane (CO_2FOF), and hydrazodioxirane ($CO_2(NH)_2$). These new dioxiranes (together with CO_2F_2, CO_4, and CO_2N_2) are analyzed to elucidate the effect of substitution of the hydrogen atoms in the parent dioxirane by other atoms (or groups) on the CO_2 fragment structure. The 0 K thermodynamic stabilities of the substituted dioxiranes relative to unimolecular dissociation

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products are also analyzed with the intent of identifying potential new metastable compounds for further detailed study. Although the molecules in question are sure to have many different isomers, only structures containing the dioxirane CO_2 ring will be considered in the present work.

The calculations were carried out using the GAUSSIAN94 package of programs (B-2 and E-2 versions)[26] running on UNIX DEC Alphas. The geometries were optimized and energies were calculated using the Hartree−Fock method (HF), second-order Møller−Plesset perturbation theory (MP2) with frozen core,[27−28] and quadratic configuration interaction method through single and double excitations (QCISD)[29] with the 6-31G(d) and 6-311G(d,p) basis sets.[30] The harmonic vibrational frequencies were calculated by the MP2/6-311G(d,p) method at the geometries optimized at the same level of theory. Additional geometry optimizations were performed on CO_2N_2 at the MP4(SDQ)/6-311G(d,p), MP4(SDTQ)/6-311G(d,p) and MP4(SDQ)/cc-pVTZ levels to elucidate the effects of triple excitations and higher polarization functions.

Results and Discussion

Geometries and Charge Distributions. The geometrical parameters R_{CO}, R_{OO}, and ∠OCO of the CO_2 fragment in the dioxiranes under consideration, optimized at various levels of theory and the 6-311G(d,p) basis set, are listed in Table 1. Kraka et al.[25] have previously pointed out that though difluorodioxirane represents a rather difficult correlation problem, structural parameters prove to be predicted quite accurately at the MP2 level of theory with a polarized triple split valence basis, perhaps due to a cancelation of basis set and correlation errors. Calculated structural parameters from Figure 1 may be compared with experimental data for CO_2H_2[15,16] (R_{CO} = 1.388(4) Å, ∠OCO = 66.2(2)°, R_{CH} = 1.090(2) Å, ∠HCH = 117.3(2)°) and for CO_2F_2[24] (R_{CO} = 1.348(8) Å, ∠OCO = 71.7(5)°, R_{CF} = 1.317(6) Å, ∠FCF = 108.8(7)°). This comparison shows the close agreement between the MP2/6-311G(d,p) results and the experimental values. Furthermore, agreement for both the unsubstituted and fluorine-substituted dioxirane suggests that MP2/6-311G(d,p) should allow one to describe quite reliably the effects of substitution on the geometrical parameters of the CO_2 fragment. Moreover, the calculated MP2/6-311G(d,p) dipole moments of the parent dioxirane (2.56 D) and difluorodioxirane (0.62 D) are, perhaps surprisingly, close to the experimental value of 2.48 ± 0.07 D for CO_2H_2 (2.51 D at the CCSD(T) level[18]) and to the value of 0.60 D recently predicted for CO_2F_2 by Kraka et al. at the CCSD(T) level with a cc-VTZP+f basis set. To further address the adequacy of the MP2/6-311G(d,p) level of theory for describing the various substituted dioxiranes, we performed additional calculations on CO_2N_2, which has a quite different charge distribution than does CO_2F_2. Table 2 shows that the inclusion of triple excitations (i.e., MP4(SDTQ)/6-311G(d,p) vs MP4(SDQ)/6-311G(d,p)) increases the predicted bond lengths, i.e., 0.010 Å for R_{CO} and 0.005 Å for R_{OO}, and the bond angle of the dioxirane ring. On the other hand, inclusion of higher polarization functions (i.e, MP4(SDQ)/cc-pVTZ vs MP4(SDQ)/6-311G(d,p)) slightly decreases the bond lengths, i.e., 0.002 Å for both R_{CO} and R_{OO}, and decreases the bond angle. Parenthetically, we note that 6-31G(d) overestimates bond lengths and, generally, the OCO bond angle, at all levels of theory, relative to 6-311G(d) for CO_2N_2; similar deviations are found for the other substituted dioxiranes and the unsubstituted dioxirane (N.B. 6-31G(d) results may be obtained directly from the authors). Taking these results into

TABLE 1: Geometrical Parameters R_{CO} and R_{OO} (Å) and ∠OCO (deg) of Dioxiranes at Various Levels of Theory

	CO_2H_2			$CO_2F_2(1\ ^1A_1)$			CO_4			CO_2FOF			CO_2NF			$CO_2N_2H_2$(cis)			$CO_2N_2H_2$(trans)		
method/basis set	R_{CO}	∠OCO	R_{OO}	R_{CO}	∠OCO	R_{OO}	R_{CO}	∠OCO	R_{OO}	R_{CO}	∠OCO	R_{OO}	R_{CO}	∠OCO	R_{OO}	R_{CO}	∠OCO	R_{OO}	R_{CO}	∠OCO	R_{OO}
HF/6-311G(d,p)	1.355	63.8	1.432	1.313	68.1	1.470	1.304	69.1	1.480	1.313	68.0	1.469	1.290	70.4	1.487	1.321/1.327	67.1	1.464	1.324	67.1	1.464
MP2/6-311G(d,p)	1.388	66.1	1.514	1.345	71.5	1.571	1.341	72.6	1.588	1.345	71.5	1.572	1.324	75.2	1.615	1.353/1.362	70.4	1.565	1.357	70.5	1.566
QCISD/6-311G(d,p)	1.384	65.7	1.502	1.340	71.1	1.558	1.335	72.3	1.576	1.340	71.2	1.559	1.320	74.2	1.593	1.349/1.355	70.0	1.551	1.351	70.0	1.550

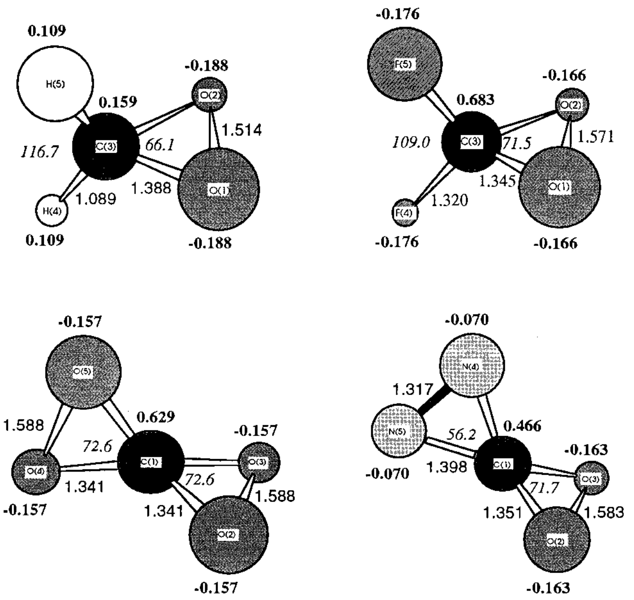


Figure 1. Optimized MP2/6-311G(d,p) structures and Mulliken charges of CO_2H_2, CO_2F_2, CO_4, and CO_2N_2.

TABLE 2: Geometrical Parameters R_{CO} and R_{OO} (Å) and ∠OCO (deg) and Reaction Energy of Azodioxirane at Various Levels of Theory

method/basis set	geometry R_{CO}	geometry ∠OCO	geometry R_{OO}	reaction energy $CO_2 + N_2 \rightarrow CO_2N_2$
HF/6-31G(d)	1.327	68.3	1.489	211.1
HF/6-311G(d,p)	1.320	67.8	1.472	218.3
MP2/6-31G(d,p)	1.363	71.7	1.597	193.8
MP2/6-311G(d,p)	1.351	71.7	1.583	201.4
QCISD/6-31G(d)	1.358	71.4	1.584	189.8
QCISD/6-311G(d,p)	1.346	71.0	1.564	198.4
MP4(SDQ)/6-311G(d,p)	1.346	71.2	1.567	198.3
MP4(SDTQ)/6-311G(d,p)	1.356	73.0	1.613	197.6
MP4(SDQ)/cc-pVTZ	1.344	70.7	1.555	193.5

account, one may expect the accuracy of the MP2/6-311G(d,p) method used in this study to be sufficient to describe quite reliably the structures and the electronic properties of the substituted dioxiranes in question.

All but one of the dioxiranes in Table 1 and Figures 1 and 2 may be seen to contain a C_{2v} symmetry CO_2 fragment. The only exception is the cis-isomer of $CO_2(NH)_2$, in which CO bond lengths (1.353 and 1.362 Å) are different by 0.01 Å. In the case of CO_2NF, which has a planar C_s structure, the position of the fluorine atom is asymmetric relative to the dioxirane ring. Nevertheless, C−O bond lengths in the CO_2 fragment of CO_2NF are nearly equal, perhaps due to the relatively large O−F distances; although, charges on the oxygen atoms are slightly different (−0.11 and −0.12 e). The length of the C−O bonds (1.324 Å) and OCO angle (75.2°) in this molecule prove to be the shortest and largest, respectively, among all species considered in the present work. These structural parameters of the CO_2 fragment in CO_2NF are close to the analogous parameters of the dioxirane ring in CO_3 (R_{C-O} = 1.334 Å and ∠OCO = 73.4° at the CCD/6-31G* level[31]). This similarity is not surprising, however, since carbon atoms in CO_3 and CO_2NF form double bonds (C═O and C═N, respectively).

Substitution of the hydrogen atoms in the parent dioxirane by other atoms or groups may be seen from Table 1 to lead to decreasing substantially the length of the C−O bonds (by 0.031−0.047 Å) and to increasing the OCO angle (by 4.3−6.5°) within the CO_2 fragment. To some degree, the changes may be explained by the fact that substitution is accompanied by essentially increasing the positive charge on the carbon atom (by 0.31−0.55 e) (see Figures 1 and 2), while the negative charges on the oxygen atoms of the CO_2 fragment decrease (i.e., absolute values) only a little (by 0.005−0.031 e). It may also be noted that, and as should be expected on the basis of the high electronegativity of the OF group, the structural parameters for the CO_2 fragments in the molecules CO_2F_2 and CO_2FOF are almost the same. Table 2 reports the symmetry and calculated dipole moments of the equilibrium structures of the dioxiranes considered in the present work. As may be seen from this table, redistribution of electron densities as a result of substitution of hydrogen atoms in the parent dioxirane leads to significant changes in the dipole moments. The largest dipole moment (about 3.1 D) is predicted for the cis-isomer of $CO_2(NH)_2$.

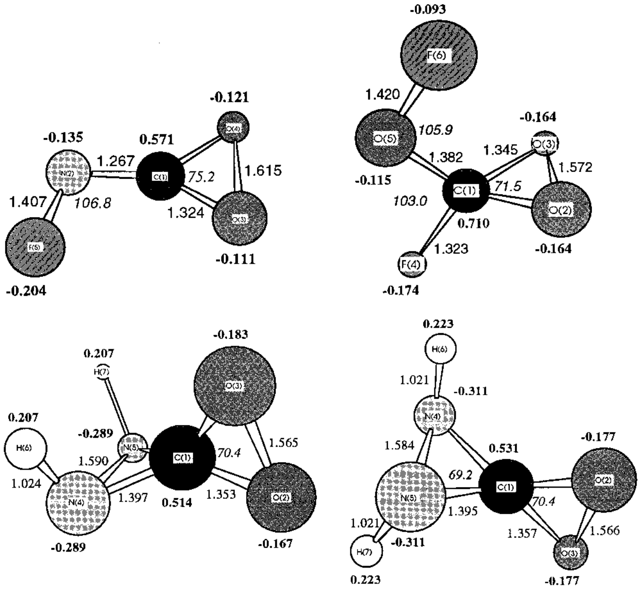


Figure 2. Optimized MP2/6-311G(d,p) structures and Mulliken charges of new dioxiranes: CO_2NF, CO_2FOF, $CO_2N_2H_2$(cis), and $CO_2N_2H_2$(trans).

TABLE 3: Molecular Symmetry of Equilibrium Structures and Calculated Dipole Moments of Dioxiranes

molecule	molecular symmetry	dipole moment (D)
CO_2H_2	C_{2v}	2.56
CO_2F_2	C_{2v}	0.62
CO_4	D_{2d}	0.00
CO_2N_2	C_{2v}	0.46
CO_2NF	C_s	1.24
CO_2FOF	C_s	0.54
$CO_2N_2H_2$(cis)	C_s	3.17
$CO_2N_2H_2$(trans)	C_s	1.44

Vibrational Frequencies and Energetic Stability. Harmonic vibrational frequencies and IR intensities for the dioxiranes under consideration, calculated at the MP2/6-311G(d,p) level, are listed in Tables 3 and 4. Table 3 also includes the results of recent state-of-the-art calculations[18] for CO_2H_2 and experimental measurements[24] for CO_2F_2. The comparison shows that the MP2/6-311G(d,p) method is able to predict vibrational frequencies and IR intensities of dioxiranes reliably (N.B. mean deviation for CO_2F_2 is 3.7%).

From these tables, it is seen that substitution of hydrogen atoms in CO_2H_2 leads to increasing the frequency and IR intensity of symmetric C−O stretching within the dioxirane ring. This result is in complete agreement with the aforementioned observation of shorter C−O bonds in substituted dioxiranes.

TABLE 4: Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of CO_2H_2, CO_2F_2, CO_4, and CO_2N_2[a]

		CO_2H_2		CO_2F_2			
	mode	present work	Schaefer et al.[18]	present work	exp[24]	CO_4	CO_2N_2
$\nu_1(a_1)$	CO sym str	1316 (35)	1311 (38)	1523 (420)	1467	1684 (446)	1727 (264)
$\nu_2(a_1)$	CX sym str	3128 (31)	3187 (28)	936 (7)	918	999 (9)	1255 (4)
$\nu_3(a_1)$	OCO def	772 (1)	759 (1)	697 (8)	658	709 (19)	610 (8)
$\nu_4(a_1)$	CX_2 scissor	1582 (3)	1578 (3)	525 (3)	511	593 (0)	482 (12)
$\nu_5(a_2)$	CX_2 twist	1047 (0)	1050 (0)	391 (0)	416	338 (0)	421 (0)
$\nu_6(b_1)$	CX asym str	3232 (35)	3109 (34)	1286 (384)	1260	1111 (89)	1121 (68)
$\nu_7(b_1)$	CX_2 rock	1208 (11)	1200 (8)	570 (10)	557	549 (14)	474 (16)
$\nu_8(b_2)$	CO asym str	958 (27)	931 (19)	1145 (91)	1062	1111 (89)	1091 (24)
$\nu_9(b_2)$	CX_2 wag	1297 (0)	1292 (3)	627 (11)	621	549 (14)	867 (0)

[a] Intensities are given in parentheses.

TABLE 5: Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of CO_2NF, Co_2FOF, $CO_2N_2H_2$(cis), and $CO_2N_2H_2$(trans)[a]

	CO_2NF	CO_2FOF	$CO_2N_2H_2$(cis)	$CO_2N_2H_2$(trans)
ν_1	218 (7)	164 (0)	354 (15)	360 (3)
ν_2	293 (1)	281 (2)	439 (37)[d]	437 (6)
ν_3	546 (13)	393 (0)	440 (37)[e]	437 (6)
ν_4	564 (5)[a]	481 (1)	518 (7)	527 (6)
ν_5	669 (9)	481 (1)	709 (6)	712 (6)
ν_6	933 (32)	605 (11)	951 (86)	946 (26)
ν_7	1095 (34)	639 (12)	951 (86)[b]	976 (0)
ν_8	1249 (65)[b]	681 (10)[a]	975 (5)	987 (183)
ν_9	1926 (242)[c]	912 (14)	1065 (21)	1086 (143)
ν_{10}		1001 (7)	1070 (52)	1138 (7)
ν_{11}		1120 (87)[b]	1284 (80)	1279 (7)
ν_{12}		1528 (340)[c]	1308 (3)	1292 (19)
ν_{13}			1658 (298)[c]	1664 (304)
ν_{14}			3473 (5)	3519 (7)
ν_{15}			3495 (10)	3523 (28)

[a] Vibrational modes: [a]OCO scissors. [b] CO asymmetric stretch. [c] CO symmetric stretch. [d] OCO deformation. [e] CO_2 rocking.

From this point of view, it is not surprising that the largest symmetric C−O stretching frequency is observed in the case of CO_2NF where the C−O bond is the strongest. In addition, as should be expected on the basis of the similarity of the structural data of CO_2FOF and CO_2F_2 (vida supra), these molecules have almost the same characteristic vibrational frequencies for the dioxirane ring.

The absence of imaginary frequencies in Tables 3 and 4 confirms that the structures of the new dioxiranes (CO_2NF, CO_2FOF, cis- and trans-isomers of $CO_2(NH)_2$), shown in Figure 2, correspond to (local) minima on their PESs. The structures of both isomers of $CO_2(NH)_2$ prove to be quite rigid relative to vibrational distortions (N.B. their lowest frequencies are about 350 cm^{-1}), and from this point of view, such structures might be observable. CO_2NF and CO_2FOF are essentially less rigid. The normal mode corresponding to the lowest frequency in CO_2NF (218 cm^{-1}) is dominated by the valence angle bend of the fluorine atom across the C═N bond, conserving the planar structure of the molecule. This valence angle bend connects two equivalent local minima on the PES of CO_2NF, corresponding to two equivalent positions (i.e., right or left) of F relative to the C═N bond (see Figure 2). In the case of CO_2FOF, the lowest vibrational frequency (164 cm^{-1}) corresponds to a displacement of the fluorine atom of the OF fragment out of the molecule's symmetry plane.

The relative energies of the dioxiranes with respect to their lowest dissociation limits, containing the molecules H_2, N_2, O_2, F_2, F_2O, NF, and linear CO_2 in their ground electronic states, are given in Table 5. The values in Table 5 are corrected for zero-point vibrational energy. It should also be noted that, in general, an adiabatic curve will not necessarily connect the dioxiranes in question to the particular dissociation limits. In the case of CO_2F_2, the calculated energy (−10.4 kcal/mol) of the reaction $CO_2 + F_2 \rightarrow CO_2F_2$ is relatively close to the most accurate theoretical value (−8.0 kcal/mol) obtained at the CCSD(T)/VTZP+f level by Kraka et al.[25] However, in the case of CO_2H_2 the 0 K reaction energies of $CO_2 + H_2 \rightarrow CO_2H_2$ calculated in the present work (108.2 kcal/mol) and by Cremer et al.[17] at the CCSD(T)/TZ+2P level of theory (101.9 kcal/mol) are different by 6.3 kcal/mol. From Table 2, the MP2/6-311G(d,p) reaction energy of CO_2N_2 (201.4 kcal/mol) is seen to be over 11 kcal/mol larger than the results from more accurate calculations.[10,11] We note that MP4(SDQ) reduces the predicted reaction energy to 198.3 kcal/mol; inclusion of triples provides a further reduction of 0.7 kcal/mol; use of the cc-pVTZ basis instead of 6-311G(d,p) at the MP4(SDQ) level causes a reduction of 4.8 kcal/mol. Hence, although it is clear that quantitative reaction energies for these molecules require triple excitations and higher polarization functions, MP2/6-311G(d,p) results are sufficiently accurate to be useful in assessing relative stabilities of the substituted dioxiranes.

As may be seen from Table 5, the energetic stability of dioxiranes in which the hydrogen atoms have been substituted by strongly electronegative atoms (such as O and F) is much greater than that of compounds substituted by N. Difluorodioxirane is the only energetically stable molecule among all the species considered in the present work. Other molecules are energetically metastable relative to their lowest adiabatic dissociation limits, with CO_2N_2 being the most energetic (201.4 kcal/mol). The bicyclic CO_4 structure is more stable than CO_2N_2 presumably due to the higher stability of the CO_2 ring in comparison with the cyclic CN_2 fragment. Table 5 shows also that the previously unknown dioxiranes, CO_2NF, CO_2FOF, *cis*-$CO_2N_2H_2$, and *trans*-$CO_2N_2H_2$, are metastable, with the cis- and trans-forms of $CO_2N_2H_2$ being the most energetic among them. The adiabatic decay of these two species to CO_2, N_2, and H_2 will be accompanied by the release of large quantities of heat (about 180 kcal/mol); and their energetic efficiency, thus, is comparable to that of CO_2N_2. On the basis of the data in Table 5 and the excitation energy of $NF(a^1\Delta)$,[32] we may expect that the adiabatic decay of CO_2NF to $CO_2(X) + NF(a)$ will be accompanied by the release of about 48 kcal/mol of energy. Thus, in contrast to the isomers of $CO_2N_2H_2$, neither CO_2NF nor CO_2FOF may be considered to be high-energy metastable compounds. However, since CO_2FOF has a low decomposition reaction energy (26.8 kcal/mol), and structural and spectroscopic characteristics similar to CO_2F_2, this compound could be a powerful oxidizer.

Low-Lying Excited States of Difluorodioxirane and Its Cation. As mentioned in the Introduction, experimental and theoretical studies of difluorodioxirane have thus far only considered the ground electronic state. However, the recent

TABLE 6: MP2/6-311(d,p) Reaction Energies (kcal/mol) of Dioxiranes

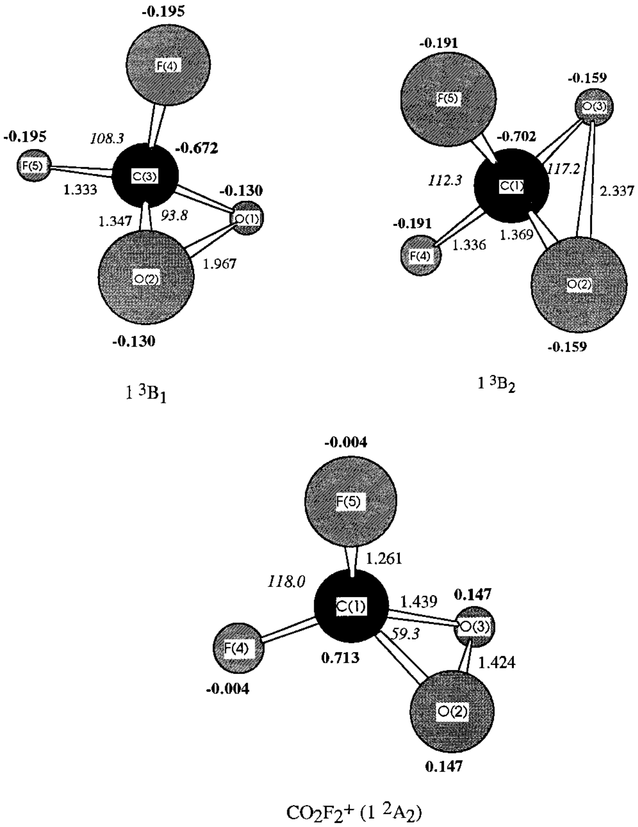
compound	reaction energy	reaction
CO_4	93.2	$CO_2 + O_2 \rightarrow CO_4$
CO_2H_2	108.2	$CO_2 + H_2 \rightarrow CO_2H_2$
CO_2F_2	−10.4	$CO_2 + F_2 \rightarrow CO_2F_2$
CO_2NF	81.4	$CO_2 + NF \rightarrow CO_2NF$
$CO_2N_2H_2$(cis)	181.1	$CO_2 + N_2 + H_2 \rightarrow CO_2N_2H_2$
$CO_2N_2H_2$(trans)	178.6	$CO_2 + N_2 + H_2 \rightarrow CO_2N_2H_2$
CO_2FOF	26.8	$CO_2 + F_2O \rightarrow CO_2FOF$

calculations on the bicyclic form of CO_4 at the MP2/6-31G(d) level[12] indicate the existence of low-lying $^3B_1$ and $^3B_2$ triplet states generated by excitations localized mainly within the dioxirane ring(s). In analogy with CO_4, one could expect that difluorodioxirane may also have low-lying excited states in which the molecule will have a dioxirane ring.

The calculations performed in the present work, using the unrestricted Hartree−Fock (UHF), MP2 and QCISD methods with 6-31G(d) and 6-311G(d,p) basis sets, show that, at all levels of theory, the lowest $^3B_1$ and $^3B_2$ states of CO_2F_2 turn out to be at least locally bound. The equilibrium structures of the molecule in these states have C_{2v} symmetry and do indeed include a CO_2 fragment. Irreducible representations are derived from a molecular orientation in which the y-axis is parallel to the O−O bond. At the QCISD/6-311G(d,p) level, the excitation energies of the 1^3B_1 and 1^3B_2 states are equal to 1.10 and 1.62 eV, respectively. Their dipole moments, however, are quite different: 0.80 and 0.01 D, respectively. Table 6, which gives the geometrical parameters R_{CO}, R_{OO}, and ∠OCO of the CO_2 fragment in the states in question, shows that the UHF values of R_{CO} are too short and that the structural parameters at the MP2/6-311G(d,p) and QCISD/6-311G(d,p) levels are quite close. The optimized MP2/6-311G(d,p) structures of CO_2F_2 in the 1^3B_1 and 1^3B_2 states are shown in Figure 3. Analysis of the molecular orbitals showed that, as in the case of CO_4, the 1^3B_1 state of CO_2F_2 is related to the ground singlet state by a one-electron excitation $a_2(\pi_{gx}(O_2)) \Rightarrow b_2(\sigma_u(O_2))$ localized mainly on the O_2 moiety. Such an excitation must mainly lead to increasing the O−O bond length (and to increasing the OCO angle) without any significant change to the C−O bond length. Indeed, as seen from Figures 1 and 3, the structural characteristics of CO_2F_2 in its ground and excited 1^3B_1 states are very similar and differ, in fact, only by an increase of the OCO angle and O−O bond length in the triplet state. It may also be inferred from these figures that the excitation connecting the ground and 1^3B_2 states is mainly localized on the CO_2 fragment. However, the nature of the corresponding electronic excitation seems to be essentially more complex than could be expected on the basis of the qualitative model suggested in ref 12. In fact, one observes that this excitation leads not only to a longer O−O bond length but also to an increased C−O bond length.

Comparison of Table 7 with Table 3 shows that vibrational frequencies of the triplet states are in general similar to the vibrational frequencies of the ground state. Large deviations (ν_8 for 1^3B_1 and ν_1 for 1^3B_2) are connected with modes dominated by displacements in the CO_2 moiety.

Taking into account the very simple nature of the excitation generating the 1^3B_1 state, one could expect that removing one electron from the highest occupied orbital $a_2(\pi_{gx}(O_2))$ of the ground state will lead mainly to a decrease of the O−O bond length. In other words, the cation, $CO_2F_2^+(1^2A_2)$, could be expected to have C_{2v} symmetry and also contain a dioxirane ring, perhaps with shorter O−O bond length than the ground state of the neutral, CO_2F_2. The optimized MP2/6-311G(d,p) structure of the cation, $CO_2F_2^+(1^2A_2)$, shown in Figure 3, is in qualitative agreement with this expectation. At this level of theory, the adiabatic ionization potential is equal to 11.45 eV. As seen from Figures 1 and 3, the ionization process is accompanied by a drastic redistribution of charges on the atoms, which leads to not only decreasing the O−O bond length but also to decreasing R_{CF} and to increasing R_{CO} in comparison to the parent molecule CO_2F_2. The orbitals' relaxation effects seem to be quite important for describing this ionization process.



1 $^3B_1$

1 $^3B_2$

$CO_2F_2^+$ (1 $^2A_2$)

Figure 3. Optimized MP2/6-311G(d,p) structures and Mulliken charges of the lowest $^3B_1$ and $^3B_2$ excited states of CO_2F_2 and of the cation $CO_2F_2^+(1^2A_2)$.

TABLE 7: Geometrical Parameters R_{CO} and R_{OO} (Å) and ∠OCO (deg) of the Dioxirane Ring of Difluorodioxirane in Its Excited 1^3B_1 and 1^3B_2 States at Various Levels of Theory

	$CO_2F_2(1^3B_1)$			$CO_2F_2(1^3B_2)$		
method/basis set	R_{CO}	∠OCO	R_{OO}	R_{CO}	∠OCO	R_{OO}
HF/6-311G(d,p)	1.312	89.9	1.854	1.357	115.9	2.300
MP2/6-311G(d,p)	1.347	93.8	1.967	1.369	117.2	2.351
QCISD/6-311G(d,p)	1.341	93.6	1.956	1.369	117.3	2.338

TABLE 8: MP2/6-311G(d,p) Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of CO_2F_2 in Its Excited 1^3B_1 and 1^3B_2 States and of the Cation $CO_2F_2^+(1^2A_2)$

	mode	$CO_2F_2(1^3B_1)$	$CO_2F_2(1^3B_2)$	$CO_2F_2^+(1^2A_2)$
$\nu_1(a_1)$	CO sym str	1389 (374)	1231 (223)	1428 (446)
$\nu_2(a_1)$	CF sym str	928 (18)	900 (3)	960 (6)
$\nu_3(a_1)$	OCO def	620 (8)	613 (7)	790 (12)
$\nu_4(a_1)$	CF_2 scissor	443 (0)	396 (0)	525 (6)
$\nu_5(a_2)$	CF_2 twist	415 (0)	580 (0)	393 (0)
$\nu_6(b_1)$	CF asym str	1247 (387)	1210 (332)	1553 (402)
$\nu_7(b_1)$	CF_2 rock	579 (11)	355 (9)	515 (12)
$\nu_8(b_2)$	CO asym str	1892 (4263)	1320 (311)	1964 (3895)
$\nu_9(b_2)$	CF_2 wag	613 (18)	623 (11)	597 (5)

Conclusions

On the basis of results of ab initio calculations of the unsubstituted dioxirane (CO_2H_2) and a number of its derivatives (CO_2F_2, CO_4, CO_2N_2, CO_2NF, and $CO_2(NH)_2$) by the MP2 and QCISD methods using 6-31G(d) and 6-311G(d,p) basis sets, the effect of substitution of the hydrogen atoms by other atoms and groups on the CO_2 fragment structure has been analyzed. It was found that the substitution leads to decreasing substantially the length of the C−O bonds (by 0.031−0.047 Å) and increasing the angle OCO (by 4.3−6.5°) within the fragment and is accompanied by essentially increasing the positive charge on the carbon atom (by 0.31−0.55 e). It was also shown that the energetic stability of dioxiranes in which the hydrogen atoms have been substituted by strongly electronegative atoms (such as O and F) is much greater than that of N-substituted compounds or the unsubstituted dioxirane.

Equilibrium geometries, harmonic vibrational frequencies, reaction energies, and dipole moments of the previously unknown dioxiranes, CO_2NF, CO_2FOF, and $CO_2(NH)_2$, have been predicted. All of these species prove to be metastable relative to their adiabatic decomposition. Fluorofluoroxydioxirane, CO_2FOF, has been predicted to be the most stable of them and to have a low decomposition reaction energy (26.8 kcal/mol). Structural and spectroscopic characteristics of CO_2FOF are expected to be similar to those of CO_2F_2; such a compound might be of interest as a powerful oxidizer. It was also shown that both cis- and trans-isomers of hydrazodioxirane, $CO_2(NH)_2$, belong to the class of high-energy metastable compounds. Their adiabatic decompositions to CO_2, N_2, and H_2 are accompanied by the release of about 180 kcal/mol of heat; and their energy efficiency, thus, is comparable to that of the bicyclic form of CO_2N_2, predicted earlier in refs 10 and 11.

One of the most potentially important results of the present work is the prediction of low-lying excited 1^3B_1 and 1^3B_2 triplet states of difluorodioxirane. It was shown that the excitations connecting the ground state of the molecule with the aforementioned excited states are mainly localized on the CO_2 fragment; the equilibrium structures of the molecule in these states have C_{2v} symmetry and retain a dioxirane ring similar to that in the ground state. The excitation energies of the 1^3B_1 and 1^3B_2 states of difluorodioxirane are predicted to be 1.10 and 1.60 eV, respectively. Their dipole moments, however, are expected to be quite different and to equal 0.80 and 0.01 D, respectively. It was further shown that the molecular cation $CO_2F_2^+(1^2A_2)$ also has a structure containing the dioxirane CO_2 fragment. The corresponding adiabatic ionization potential has been predicted to equal 11.45 eV. The authors hope that these results will be useful for future spectral and mass spectrometric investigations of difluorodioxirane.

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