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Quantum Chemical Descriptions of FOOF: The Unsolved Problem of Predicting Its Equilibrium Geometry

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Single determinant Møller−Plesset perturbation (MP) theory at second order (MP2), third order (MP3), and fourth order (MP4) with standard basis sets ranging from cc-pVDZ to cc-pVQZ quality predicts the equilibrium geometry of FOOF qualitatively incorrect. Sixth-order MP (MP6), CCSD(T), and DFT lead to a qualitatively correct FOOF equilibrium geometry r_e, provided a sufficiently large basis set is used; however, even these methods do not succeed in reproducing an exact r_e geometry. The latter can be achieved only by artificially increasing anomeric delocalization of electron lone pairs at the O atoms into the $\sigma^*(OF)$ orbitals by selectively adding diffuse basis functions, adjusting exponents of polarization functions, or enforcing an increase of electron pair correlation effects via the choice of a rigid basis set. DFT geometries of FOOF can be improved in a similar way and, then, DFT presents the best cost-efficiency compromise currently available for describing FOOF and related molecules. DFT and CCSD(T) calculations reveal that FOOF can undergo either rotation at the OO bond or dissociation into FOO and F because the corresponding barriers (trans barrier: 19.4 kcal/mol; dissociation barrier 19.5 kcal/mol) are comparable. Previous estimates as to the height of the rotational barriers of FOOF are largely exaggerated. Rotation at the OO bond raises the barrier to dissociation because the anomeric effect is switched off. The molecular dipole moment is found to be a sensitive antenna for probing the quality of the quantum chemical description of FOOF.

1. Introduction

Molecules composed of strongly electronegative atoms such as oxygen and fluorine are known to possess unusual chemical properties.[1−3] A typical example is difluoro peroxide (**1**), which is known to act as a powerful fluorinating agent.[4] This is relevant for nuclear processing because **1** reacts at or below room temperature, much lower temperature than any other molecular fluorinating agent except KrF_2.[5] Molecule **1** is also of considerable interest in structural chemistry because it has an unusual geometry with a very short OO bond length close to 1.22 Å and very long OF bond lengths of 1.58 Å,[6,7] which are more reminiscent of a system composed of O_2 ($r(OO) = 1.21$ Å[8]) with loosely attached F atoms rather than a peroxide (HOOH: r_e (OO) = 1.45 Å[9]). Typical OF bond lengths as found in HOF or FOF are 1.44[10] and 1.41 Å,[11] respectively, so that the geometry of **1** differs considerably from any standard geometric model made up by the covalent radii of singly bonded oxygen and fluorine.

The microwave investigation of **1** carried out by Jackson[6] in 1962, which was the first to establish its unusual geometry, was at the focus of many quantum chemical studies aimed at reproducing the experimental geometry[12−25] and explaining it in terms of common models of chemical bonding.[2,9,13] In the beginning, failures of reproducing the microwave geometry led to doubts as to the accuracy of experimental measurements. However, a careful electron diffraction investigation carried out by Hedberg and co-workers in 1988[7] erased all doubts. The r_g geometry determined by these authors fully confirmed the r_s/r_0 geometry[6] of the microwave study. Also, theoretical work on FO molecules (see, e.g., Lee, Rice, Dateo,[20] and others[22−25]) demonstrated that the range of *normal* FO bond distances is larger than can be expected from molecules such as HOF or FOF.

In the past 20 years, **1** was studied with almost each quantum chemical method available including Hartree−Fock (HF) theory, Møller−Plesset perturbation theory at second order (MP2), third order (MP3), and fourth order (MP4), configuration interaction theory with single (S) and double (D) excitations (CISD), the coupled electron pair approximation (CEPA), quadratic CI with S and D (QCISD), coupled cluster (CC) theory with S and D excitations (CCSD), CCSD with a perturbative inclusion of triple excitations (CCSD(T)), QCISD(T), complete active space SCF theory (CASSCF), and externally contracted CI (CCI).[12−20] With each higher level of theory, a better approximation to the experimental geometry was reported although deviations from the experimental geometry remained relatively large.

From time to time investigations appeared in the literature that showed that by adjusting selectively the set of basis functions used in the ab initio calculation, the geometry of **1** could be reproduced in a reasonable way. For example, Mack and Oberhammer[16] added an extra set of d-type polarization functions at the O atoms to a standard DZ basis and modified the exponents of these additional functions to reproduce the experimental geometry at the MP2 level. Similarly, CCSD(T) theory was used to obtain a partially optimized geometry of **1** with a TZ2P basis with two sets of d-type polarization functions having the same exponents for O and F and being augmented by a set of f-type polarization functions with different exponents for O and F.[19] The CCSD(T)/TZ2Pf investigation led to the best agreement with the experimental geometry ever calculated, even though a deviation of 0.014 Å for the OF bonds remained.[19] In this connection we cite from a publication of Schaefer and co-workers[17] who pointed out that *modification of the one particle basis in an unbalanced fashion (without regard to established procedures) in order to obtain the experimental structure ⋯ is of limited value in the study of similar, but as yet experimentally unknown compounds.*

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TABLE 1: Specification of the Basis Set Used

basis set	(primitive basis) [contracted basis]	# basis func.	comment	ref
6-31G(d)	(10s4p1d) [3s2p1d]	60	Cartesian d	53
6-311+G(3df)	(12s6p3d1f) [5s4p3d1f]	156	spherical pol. functions	54
TZ2Pf	(10s6p3d1f) [5s3p2d]	124	α_d (O): 2.8, 0.8, 0.67 α_d (F): 3.57, 1.057, 0.7 α_f (O): 1.4; α_f (F): 1.85	55 56,58 19
TZ2Pf(S)	(10s6p2d1f) [5s3p2d]	124	α_d (O) = α_d (F): 1.5; 0.35 α_f (O): 1.4; α_f (F): 1.85	19, 56,57 19
cc-pVDZ	(9s4p1d) [3s2p1d]	56	spherical pol. functions	40
cc-pVTZ	(10s5p2d1f) [4s3p2d1f]	120		40
cc-pVQZ(-g)	(12s6p3d2f) [5s4p3d2f]	184	g not included	40
cc-pVQZ	(12s6p3d2f1 g) [5s4p3d2f1 g]	220		40
cc-pV5Z	(14s8p4d3f2 g1h) [6s5p4d3f2 g1h]	364		40
aug-cc-pVDZ	(10s5p2d) [4s3p2d]	92	diff. spd functions	41
aug-cc-pVTZ	(11s6p3d2f) [5s4p3d2f]	184	diff. spdf functions	41
aug-cc-pVQZ(X)	(13s7p4d3f) [6s5p4d3f]	216	diff. functions only at X = O or F	41
aug-cc-pVQZ	(13s7p4d3f2 g) [6s5p4d3f2 g]	320	diff. spdfg functions	41
aug-cc-pV5Z	(15s9p5d4f3 g2h) [7s6p5d4f3 g2h]	508	diff spdfgh functions	41

In the mid eighties, first reports appeared[21] revealing that density functional theory (DFT) reproduces the experimental geometry of **1** surprisingly well, although not with that accuracy normally expected from wave function theory.[21−25] Jursic[24] published a comparative study of **1**, FOO, F_2OO, FOOOF, and FOOCl, employing different functionals which showed that DFT in general reproduced the OO bond length reasonably well for most functionals, whereas calculated OF bond lengths scattered relatively strongly bracketing the experimental value.

In this work we will attack the question whether quantum chemical methods based on single-determinant theory can provide a reliable description of the equilibrium geometry of **1**. For this purpose, we will present highly correlated ab initio calculations with large basis sets, which provide a basis from which to estimate the geometry of **1** at the complete basis set (CBS) limit at a given level of theory. We employ MP2 up to sixth-order MP (MP6)[26−30] to understand the importance of electron correlation in the case of **1**. With this knowledge, we will analyze the CBS limit of the geometry of **1** obtained at the CCSD(T) level of theory.[31] Also, we will investigate how DFT performs in relationship to wave function methods in the case of **1**. Our analysis is aimed to get a better understanding of the electron structure of **1**, to describe bonding in the molecule, and to clarify which level of theory is needed to represent other molecular properties of **1** in a satisfactory manner.

2. Computational Methods

Standard MP2, MP3, and MP4 theory[26−29] with unfrozen core and analytical energy gradients[32] was employed throughout this work. In addition, MP6 theory within the M7 approximation[30] and with frozen core was used where the geometry of **1** was calculated numerically with the Davidon−Fletcher−Powell algorithm.[33] While the MP calculations were done either with the quantum chemical program packages COLOGNE99[34] or GAUSSIAN98,[35] all CCSD(T) calculations were carried out with ACES II.[36]

Various extrapolation techniques are documented in the literature to predict molecular properties for infinitely large basis sets.[37−39] Such approaches require that basis sets of systematically increasing size are available so that a given molecular parameter, such as a bond length or a molecular dipole moment, can be extrapolated in a meaningful way. Dunning[40−45] solved this problem by developing the correlation consistent polarized basis sets cc-pVmZ, where m is the cardinal number that determines the size of the basis set ($m = 2$: cc-pVDZ; 3: cc-pVTZ; 4: cc-pVQZ; 5: cc-pV5Z; etc.). By stepwise increasing both the sp basis and the number of polarization functions added to the sp basis, polarized basis sets of monotonically increasing flexibility were obtained (see Table 1). Dunning and co-workers[46] demonstrated that use of the cc-pVmZ basis sets leads to energies and other molecular properties, which converge monotonically toward the CBS limit. He and Cremer[47] recently showed that the three-parameter function of eq 1 suggested by Dunning[37,38,46d] is useful for the calculation of MPn limit geometries:

$$Q(m) = Q(\infty) + Ae^{-m} + Be^{-m^2} \tag{1}$$

where Q represents a geometric parameter calculated at the HF, MPn (n: order of perturbation theory), or CCSD(T) level of theory, $Q(\infty) = Q(\text{CBS})$ denotes the CBS limit of this geometric parameter, and A and B are fitting parameters, which have to be determined in a least-squares minimization procedure. The latter becomes the more accurate the more $Q(m)$ values are calculated. However, simple estimates can also be obtained with just three $Q(m)$ values obtained for example with a cc-pVDZ, a cc-pVTZ, and a cc-pVQZ basis set, provided $Q(m)$ values change smoothly.[47]

Because the cc-pVDZ basis set is too small for the description of higher order correlation effects,[48] results obtained with this basis at an advanced level of theory (MP4, MP6, CCSD(T), etc.) are questionable. We tested the usefulness of cc-pVDZ geometries in these cases by comparing the coefficients A and B of eq 1 for different methods. They reveal that trends in the basis set dependence observed at a lower level of ab initio theory repeat themselves at a higher level of ab initio theory and that the use of cc-pVDZ results in eq 1 does not spoil these trends.[47,49] Similar observations have been made by other authors. For example, the similarities in the basis set dependence of different correlation corrected methods are the basis for the Gp (p = 1, 2, 3) methods of Curtiss, Raghavachari, Pople and co-workers;[50−52] they can also be utilized when estimating the CBS limit of molecular geometries at a given level of theory from just one or two optimized geometries provided the form of eq 1 is known for a closely related method. For example, we used coefficients A and B calculated at the MP2 level to obtain the MP6/CBS geometry.

In Table 1, the basis sets used in this work are listed. Preliminary calculations were carried out with Pople's 6-31G-

(d)[53] and 6-311+G (3df) basis sets.[54] In some cases the cc-pVmZ basis sets of Dunning were slightly changed either by augmenting them with a set of diffuse functions at both O and F or one of these atoms (indicated by (X) where X = O or F, see Table 1). Also in some cases, g-type polarization functions contained in Dunning's cc-pVQZ basis set had to be excluded from the basis set (indicated by cc-pVQZ(-g), Table 1) because of computational limitations. Finally, a TZ2Pf basis composed of a (10s6p) primitive basis of Huzinaga,[55] contracted by Dunning to [5s3p][56] and augmented by 2d and 1f sets of polarization functions was used to reproduce CCSD(T) results of Scuseria.[19] This author used α_d (O) = α_d(F) according to Duijneveldt.[57] Different exponents were applied for the f-type polarization functions (composition denoted by (S) in Table 1 and throughout this text), while for the normal TZ2Pf basis Dunning exponents[58] are chosen, as listed in Table 1.

The density functionals were selected in the way to have one typical representative for the local density approximation (LDA), the generalized gradient approximation (GGA), the hybrid functional, and the modified one-parameter hybrid functional description of **1**. For this purpose, we used the SVWN functional (LDA representative: Slater exchange[59] plus Vosko−Wilk−Nusair (VWN) correlation functional[60]), the BLYP functional (GGA representative: Becke exchange[61] plus Lee−Yang−Parr correlation functional[62]), the B3LYP functional (hybrid functional: Becke's three parameter functionals[63]), and the mPW1PW91 functional (the one parameter functional of Barone and Adamo[64] based on the modified Perdew−Wang 91 exchange functional mPW91 and the Perdew−Wang 91 correlation functional[65]).

In all cases considered, restricted DFT (RDFT) calculations were carried out; however, a stability test[66] was used to determine potential external instabilities of the RDFT description, which led to an unrestricted DFT (UDFT) description of lower energy. Because an R/U instability indicates the importance of nondynamic electron correlation, the lowest eigenvalue λ of the stability matrix was used to asses the degree of multireference character of **1**.

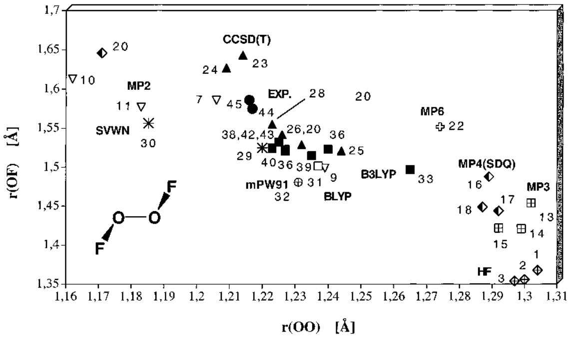

Figure 1. Calculated OO and OF bond lengths of FOOF. Numbers identify the entries in Table 2.

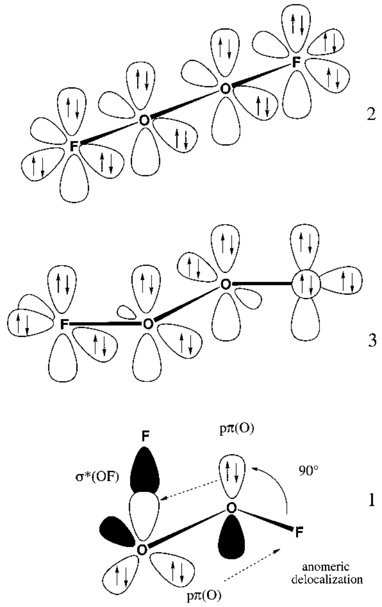

Figure 2. Schematic description of electron pair distributions in **1**, **2**, and **3**. Anomeric delocalization of the π-electron lone pairs at O into the neighboring σ*(OF) orbital is indicated for **1**.

3. Results and Discussion

In Table 2, all equilibrium geometries of **1** calculated in this work are listed together with the corresponding energies and dipole moments. Table 3 gives a summary of CBS limit geometries determined with eq 1, whereas Table 4 provides information on the rotational potential of **1** as calculated at the B3LYP/cc-pVTZ level of theory.

Calculations performed in this work confirm results of previous investigations.[12−25] At all levels of theory, **1** is described to possess a gauche conformation with a dihedral angle τ (FOOF) and an angle α (FOO) close to the experimental values of 88.1° and 109.5°, respectively[7] (Table 2). However, most methods applied in this work fail seriously to correctly describe the OO and OF bond lengths of **1**. Figure 1 reveals that there is an almost linear relationship between the calculated OO length and the corresponding OF length in the way that if the former is predicted too long (short) the latter will be predicted too short (long). Of all results, only MP2, CCSD(T), and DFT with a relatively small basis set predict experimental values with reasonable accuracy. The MP2 results of Tables 2 and 3 (Figure 1) indicate that there is a chance of finding a truncated basis set that closely reproduces the experimental geometry of **1** because of a fortuitous cancellation of basis set and correlation errors. Mack and Oberhammer[16] were the first to take advantage of this fact and adjusted a VDZ basis set in such a way that a surprisingly accurate geometry of **1** was obtained at the MP2 level. Clearly, such a procedure does not solve the FOOF problem as was noted by Schaefer and coworkers.[17]

To get a better understanding of calculated results and the electronic effects covered or not covered by a given method, we will first discuss the electron structure of **1** in general terms. Molecules composed of just electronegative atoms such as O and F are characterized by (a) regions of strong electron clustering (contraction of the valence spheres because of a relatively large positive nuclear charge) and (b) regions with strong electron (lone pair−lone pair) repulsion. Depending on the geometry of the compound in question, effects (a) and (b) can lead to strong destabilization of the molecule as can be shown for a hypothetical linear FOOF molecule (**2**, Figure 2).

In **2**, there are 8 π-type and 2 σ-type electron lone pairs, which generate a cylindric electron density distribution with strong electron repulsion causing an increase of the energies of the frontier orbitals. Both bonding and antibonding orbitals are occupied, which explains the unrealistically long OO (1.921 Å, Table 4), but relatively short OF bonds (1.353 Å) predicted by constrained B3LYP geometry optimization of **2**.

Because the RB3LYP description of **2** is externally unstable (λ < 0, Table 4), a UB3LYP geometry optimization was performed, which leads to considerable lowering of the energy of **2** relative to that of **1** (from 85.5 to 41.9 kcal/mol, Table 4)

TABLE 2: Calculculated Equilibrium Geometries of FOOF as Obtained with Various Methods and Basis Sets[a]

method	#	basis set	energy	r(OO)	r(OF)	α(FOF)	τ(FOOF)	μ
			A Wave Function Method					
HF	1	cc-pVDZ	−348.24358	1.304	1.368	106.0	84.4	0.57
	2	aug-cc-pVDZ	−348.27787	1.299	1.362	105.9	85.4	0.56
	3	cc-pVTZ	−348.36616	1.300	1.356	106.3	84.9	0.54
	4	aug-cc-pVTZ	−348.37259	1.300	1.356	106.4	85.3	0.54
	5	cc-pVQZ	−348.39482	1.297	1.354	106.4	85.2	0.53
	6	aug-cc-pVQZ	−348.39681	1.297	1.354	106.4	85.2	0.53
MP2	7	cc-pVDZ	−349.02428	1.206	1.586	109.4	87.4	1.30
	8	aug-cc-pVDZ	−349.12376	1.140	1.752	112.2	89.9	2.43
	9	cc-pVTZ	−349.41115	1.239	1.499	108.2	86.8	0.98
	10	aug-cc-pVTZ	−349.45133	1.162	1.613	110.4	88.7	1.80
	11a	cc-pVQZ(-g)	−349.56700	1.183	1.577	109.8	88.0	1.50
	11b	cc-pVQZ	−349.59519	1.200	1.542	109.2	87.6	1.30
	12	aug-cc-pVQZ	−349.61122	1.156	1.631	110.0	87.6	
MP3	13	cc-pVDZ	−349.01677	1.302	1.454	106.3	85.8	0.62
	14	cc-pVTZ	−349.39778	1.299	1.421	106.3	85.8	0.58
	15	cc-pVQZ(-g)	−349.55146	1.292	1.422	106.5	86.0	0.60
MP4(SDQ)	16	cc-pVDZ	−349.03432	1.289	1.488	106.9	86.5	0.79
	17	cc-pVTZ	−349.41341	1.292	1.444	106.8	86.2	0.70
	18	cc-pVQZ(-g)	−349.56645	1.287	1.449	106.9	86.5	0.74
MP4(SDTQ)	19	cc-pVDZ	dissociation					
	20	cc-pVTZ	−349.46566	1.171	1.646	110.6	88.7	1.83
	21	cc-pVQZ(-g)	dissociation					
MP6(M7)	22	6-31G(d,p)	−348.99212	1.274	1.552	107.9	87.0	
CCSD(T)	23	cc-pVDZ	−349.06597	1.214	1.643	109.6	88.3	1.34
	24	aug-cc-pVDZ	−349.16532	1.209	1.627	109.2	88.7	1.62
	25	cc-pVTZ	−349.45649	1.244	1.521	108.2	87.2	1.06
	26	aug-cc-pVTZ	−349.49881	1.226	1.542	108.5	87.7	1.06
	27	cc-pVQZ	−349.64156	1.232	1.529	108.4	87.5	1.16
	28	aug-cc-pVQZ	−349.65714	1.223	1.545	108.6	87.8	
			(B) DFT Method					
SVWN	29	6-31G(d)	−348.20201	1.220	1.525	109.8	87.1	1.10
	30	aug-cc-pVQZ(-g)	−348.40050	1.185	1.557	110.5	88.3	1.65
BLYP	31	aug-cc-pVQZ(-g)	−349.89698	1.237	1.502	108.8	87.9	1.22
mPW1PW91	32	aug-cc-pVQZ(-g)	−349.89124	1.231	1.481	108.8	87.8	1.14
B3LYP	33	6-31G(d)	−349.80381	1.265	1.497	108.3	86.7	0.86
	34	cc-pVDZ	−349.83318	1.240	1.523	109.0	87.3	1.14
	35	aug-cc-pVDZ	−349.87539	1.225	1.532	109.2	88.2	1.38
	36	cc-pVTZ	−349.95523	1.235	1.515	109.1	87.6	1.23
	37	aug-cc-pVTZ	−349.96542	1.227	1.523	109.3	88.1	1.33
	38	6-311+G(3df)	−349.95031	1.223	1.522	109.2	88.1	1.33
	39	cc-pVQZ	−349.98775	1.227	1.521	109.2	87.9	1.29
	40	aug-cc-pVQZ(-g)	−349.98999	1.223	1.525	109.3	88.2	1.37
	41	aug-cc-pVQZ	−349.99131	1.223	1.524	109.3	88.2	1.34
	42	cc-pV5Z	−349.98999	1.223	1.525	109.3	88.2	1.34
	43	aug-cc-pV5Z	−349.99901	1.223	1.524	109.3	88.0	1.34
exp.	44	r_s/r_0	ref 6	1.217(3)	1.575(3)	109.5(5)	87.0(5)	1.44(4)
	45	r_g	ref 7	1.216(2)	1.586(2)	109.2(2)	88.1(4)	
	46	r_e, est.	ref 16	1.214(3)	1.571(3)			

[a] All energies are given in Hartree, bond lengthes in Å, angles in degree, and dipole moments in Debye. For the notation of basis sets, see Table 1.

while the OO distance increases to 3.2 Å. This means that linear FOOF is not stable and dissociates into two OF fragments, suggesting a dissociation energy > 42 kcal/mol relative to **1**. This is in line with results of Kieninger and co-workers[67] who determined the dissociation energy D_0 of **1** to be 44.2 kcal/mol (exp. value: 46.1 kcal/mol[1]).

Clearly, **2** is a typical multireference system with high lying occupied, low-lying unoccupied orbitals and very small HOMO−LUMO, sub-HOMO−LUMO, etc. gaps. Also, high order correlation effects are necessary for a reasonable description of electron correlation both in the valence shells of the atoms and in the bonding region. Destabilization caused by lone pair−lone pair repulsion can be partially reduced by bending **2** in a trans (**3**) or a cis geometry (**4**), which converts two π-type lone pairs into σ-type lone pairs with some FOO bonding character (Figure 2). Perpendicular to the plane of **3** and **4** there are now 4 π-type lone pairs, which still lead to considerable lone pair−lone pair repulsion, high-lying occupied MOs, small HOMO−LUMO gaps, and by this to systems, which are difficult to describe quantum chemically.

Forms **3** and **4** are transition states of rotation at the OO bond as indicated by imaginary frequencies of 162i (trans) and 326i cm^{-1} (cis) (Table 4). The relative energies of **3** and **4** are 22 and 26 kcal/mol, respectively, at B3LYP; CCSD(T) calculations lead to 20 and 24 kcal/mol (Table 4). Hence, rotation at the OO bond in **1** is very slow, and the molecule can be considered as being configurationally stable occupying either the minimum at $\tau = 87°$ (or 273°). Experimental estimates of the barriers (30 kcal/mol[6,68]) are in qualitative agreement only because the barriers could be estimated only in a crude fashion from the measured torsional frequency.[6]

A second possibility of reducing lone pair−lone pair repulsion is given when FOOF adopts a dihedral angle close to 90°. In this case, the π-type lone pair at O can delocalize in a low-lying σ*(OF) orbital (anomeric effect,[69] Figure 2). The resulting stabilization increases with the square of the overlap between

TABLE 3: Estimated CBS Limit Geometries of FOOF[a]

method	*r*(OO)	*r*(OF)	α(FOF)	τ(FOOF)	comment
HF	1.296	1.353	106.4	85.3	normal basis sets
aug	1.295	1.353	106.4	85.3	adding effects of diffuse functions
MP2	1.150	1.624	110.8	88.7	cc-pVQZ(-g) basis used
g-functions	1.177	1.568	109.7	88.1	cc-pVQZ basis used
aug	1.149	1.639	111.3	87.6	adding effects of diffuse functions
MP3	1.288	1.423	106.6	86.1	cc-pVQZ(-g) basis used
MP4(SDQ)	1.284	1.451	107.0	86.6	cc-pVQZ(-g) basis used
MP4					dissociation into F + OO +F
MP6	1.217	1.588	109.2	88.4	A, B from MP2
CCSD(T)	1.225	1.534	108.5	87.8	cc-pVQZ basis used
aug	1.221	1.547	108.8	88.0	adding effects of diffuse functions
B3LYP	1.221	1.526	109.3	88.3	cc-pVQZ basis used
aug	1.221	1.524	109.4	88.2	adding effects of diffuse functions
exp., r_g	1.216	1.586	109.2	88.1	

[a] Calculated with eq 1. Bond lengths in Å, angles in degree. Experimental values from ref 7. The abbreviation aug indicates that the CBS limit was calculated using the basis sets aug-cc-pVmZ for $m = 2, 3, 4$.

TABLE 4: Different Forms of FOOF Calculated at the B3LYP/cc-pVTZ Level of Theory[a]

form	sym.	*E*, Δ*E*	*r*(OO)	*r*(OF)	α (FOF)	τ (FOOF)	μ	ZPE	ω_{low}	λ
gauche (**1**)	C_2	−349.95523 (−349.41860)	1.235	1.515	109.1	87.6	1.23	5.5	226	0.072
cis (**4**)	C_{2v}	26.0 (23.8)	1.514	1.388	108.2	0.	0.22	5.3	326i	0.060
trans (**3**)	C_{2h}	22.4 (19.6)	1.480	1.398	99.6	180.	0	5.3	162i	0.074
linear (**2**)	$D_{\infty h}$	85.5 (54.9)	1.921	1.353	0	0	0	4.4	223i, 201i	−0.125, −0.065
	[b]	41.9	3.208	1.350	0	0	0	3.5	71i, 40i	

[a] Absolute energies *E* are given in Hartree, relative energies Δ*E* and zero point eneregies (ZPE) in kcal/mol, bond lengths in Å, angles in degree, and dipole moments μ in Debye. CCSD(T)/cc-pVTZ energies calculated at B3LYP/cc-pVTZ geometries are given in parentheses. [b] UB3LYP/cc-pVTZ results.

the corresponding orbitals and with decreasing energy difference of the orbitals involved, where in particular the second factor plays an important role. The anomeric effect and the fact that the π-type lone pairs at the O atoms are orthogonal to each other is responsible for the shortening of the OO bond (by adding two partial π-type bonds the OO bond decrease from 1.48 to 1.21 Å), the weakening of the OF bonds (occupation of a σ* orbital and increase from 1.40 to 1.58 Å), and the overall stabilization of the molecule by about 20 kcal/mol.

The relative stabilities of **1**, **2**, and **3** lead to some interesting conclusions as to the topology of the potential energy surface in the vicinity of the minimum occupied by **1**. Dissociation of **1** into FOO and F requires just 19.5 kcal/mol,[1,67] which is comparable to the trans barrier (ZPE corrected CCSD(T) value: 19.4 kcal/mol). Hence, the molecule can undergo with the same probability rotation or dissociation contrary to previous claims that the latter process should exclude the former.[21] It is also not possible that the molecule once at the top of the trans (or cis) barrier dissociates spontaneously. In the planar forms, the anomeric weakening of the OF bond is suppressed, and hence the OF bonds are considerably strengthened confirmed by calculated bond lengths of 1.39 to 1.40 Å (Table 4).

HF and MPn Geometries. The HF/ and MP2/CBS limit geometries (Table 3) clearly indicate that these levels are insufficient to provide a qualitatively correct description of **1** because in the first case anomeric delocalization is underestimated while it is exaggerated in the second case. MP3 and MP4(SDQ), which both introduce coupling between pair correlation effects, revert bond lengths in the direction of the HF values indicating that pair correlation is not sufficient to describe the electron distribution in **1** correctly (Figures 1 and 3). The inclusion of three-electron correlation effects, which provide the simplest mechanism of correlating electrons in a multiple bond or in the valence sphere of an electronegative atom, also leads to an exaggeration of anomeric delocalization. At MP4/cc-pVTZ (Table 2), the OO bond (OF) is even shorter (longer) than the value(s) obtained at the MP2 level with the same basis. For the cc-pVDZ and the cc-pVQZ(-g) basis set, **1** dissociates into F + OO + F.

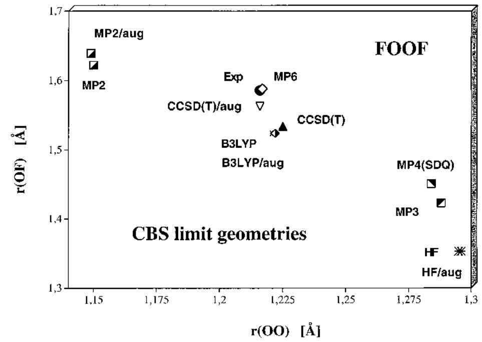

Figure 3. CBS limit bond lengths of FOOF. Method/aug denotes limit values obtained with aug-cc-pVmZ basis sets.

The MP6/CBS geometry of **1**, which is based on the assumption that changes in the geometry caused by an extension of the cc-pVDZ basis to the CBS limit are parallel at the MP2 and the MP6 level of theory, reproduces the r_g-geometry of Hedberg and co-workers rather accurately (see Figure 3).[7] This indicates that coupling between three-electron correlation effects (described by the TT terms at MP5 and higher MPn levels) and four-electron correlation effects (connected Q excitations first introduced at MP6) seem to play an important role for a balanced description of anomeric delocalization and lone pair−lone pair repulsion in **1**.

TABLE 5: Equilibrium Geometry of FOOF with Valence Triple Basis Sets[a]

method	basis set	energy	r(OO)	r(OF)	α(FOF)	τ(FOOF)	μ	ref
BLYP	TZ2Pfg(S)	−349.99674	1.205	1.639	111.3	89.2	1.79	this work
BL3YP	TZ2Pfg(S)	−349.97278	1.225	1.527	108.9[b]	87.8[b]	1.06	this work
CCSD(T)	cc-pVTZ	−349.45649	1.224	1.521	108.2	87.2	1.06	this work
CCSD(T)	TZ2Pf(S)	−349.45483	1.226	1.562	108.9[b]	87.8[b]	1.27	this work
CCSD(T)	TZ2Pf	−349.49281	1.236	1.538	108.9[b]	87.8[b]	1.21	this work
CCSD(T)	TZ2Pf(S)		1.218	1.589	108.9[b]	87.8[b]		19

[a] Energies are given in Hartree, bond lengths in Å, angles in degree, and dipole moments μ in Debye. For the description of basis sets, see Table 1. [b] Angles are not optimized, values taken from ref 19.

CCSD(T) Geometries. Calculations with the cc-pVDZ basis lead again to a surprisingly good reproduction of the OO bond (1.214 Å, Table 2) while the OF bonds (1.643 Å) are calculated 0.07 Å too long. Although CCSD(T) calculations with the cc-pVTZ or the cc-pVQZ basis set lead to a better overall agreement with experiment, deviations (cc-pVQZ: 0.015 and 0.046 Å, Table 2) are still relatively large, which is disappointing in view of the fact that Scuseria[19] could reproduce the experimental r_o-geometry within 0.03 and 0.014 Å (only 0.002 Å deviation with regard to the r_g bond lengths, Table 5). Therefore, we repeated the CCSD(T) calculations of Scuseria according to the basis set and geometry specifications (freezing angles α (OOF) and τ (FOOF)) described in ref 19 (see Table 5). Various attempts to reproduce the CCSD(T)/TZ2Pf(S) geometry of **1** failed, although similar bond lengths were obtained (see Table 5). It turned out that the bond lengths depend critically on the choice of the exponents of the d-type polarization functions: If the exponents suggested by Dunning for use with the TZ2P basis set[58] were employed (see Table 1) poor agreement with experiment was obtained, whereas for the choice α_d (O) = α_d (F) (Table 1) improved bond lengths resulted (Table 5).

Irrespective of the fact that we were not able to reproduce the CCSD(T)/TZ2Pf(S) geometry given in ref 19, inspection of the literature reveals that the TZ2P basis always leads to too much longer OF bonds for both CC and DFT methods.[20,22] This is reflected by CCSD(T) calculations of Lee and co-workers[20] as well as DFT calculations of Amos and co-workers.[22] A comparative study of the composition and the exponents of the TZ2P and the cc-pVTZ basis sets reveals that the former is constructed to describe a somewhat more contracted (larger exponents) electron density distribution, whereas the latter should make it possible that electron density expands into space. Dunning's correlation consistent basis sets are optimized at the CI level of theory, which means that the basis functions adjust to the more expanded character that the orbitals adopt under the impact of electron correlation added to a HF description. Basis set optimization at the CI level also implies that the ratio of the exponents of basis functions at O and at F increases, indicating reduced charge transfer from O to the more electronegative F atom. It is typical of HF calculations that the polarity of polar bonds, the partial charges at the corresponding atoms, and, by this, molecular dipole moments are exaggerated, which is corrected by correlation methods. The correlation effects are needed to correct for the exaggeration of ionic terms at the HF level.

The TZ2P basis was optimized at the HF level[55,56] and, therefore, accommodates increased charge transfer, high bond polarity, and large dipole moments. If one combines the use of an electron correlation method with an HF-optimized basis set, the polarity of the OF bond will be artificially increased, reflected by a larger dipole moment μ as confirmed by the data of Table 5 (μ(TZ2Pf(S)) = 1.27; μ(cc-pVTZ) = 1.06 D). Hence, the TZ2Pf basis increases the effective electronegativity of the F atom relative to that of the O atom, which leads to a lowering of the energy of the σ*(OF) orbital and a subsequent increase of the anomeric effect, thus lengthening the OF bond. Of course, such a choice of the basis is problematic because it is not based on a systematic description of molecules with correlation corrected methods and, accordingly, has little predictive power, as was emphasized by Schaefer and co-workers.[17]

For a correct description of lone pair electrons, diffuse functions are generally considered to be important. Therefore, HF, MP2, CCSD(T), and B3LYP calculations were carried out with the aug-cc-pVmZ basis set (m = 2, 3, 4; maximally 320 basis functions) to assess the changes in geometry caused by a set of diffuse spd, spdf, or spdfg functions on all atoms (Table 2). CBS limit geometries based on the aug-cc-pVmZ basis sets were also calculated to test the reliability of the CBS/cc-pVmZ geometries. As can be seen from Tables 2 and 3, diffuse functions do hardly change CBS geometries calculated for HF and B3LYP, which simply reflects the fact that for a reliable extrapolation procedure (calculations with large enough m) the cc-pVmZ and aug-cc-pVmZ series should converge to the same limit. For correlation corrected wave function methods, the basis set truncation error for a given m becomes larger, i.e., a larger cardinal number m has to be used for the basis set to guarantee that the cc-pVmZ and aug-cc-pVmZ series converge to the same limit. The data in Table 3 reveal that there is significant influence of the diffuse functions on the calculated CBS geometries both at the MP2 and CCSD(T) level of theory where the former case is not interesting because MP2 leads to a qualitatively incorrect geometry of **1**. However, in the case of CCSD(T), the diffuse functions improve the calculated geometry both for m = 3, m = 4 and in the CBS limit (Tables 2 and 3). Hence, the best CCSD(T) geometry is obtained for CBS/aug-cc-pVmZ (R(OO): 1.221; R(OF): 1.547 Å, Table 3) where for the critical OF bond length the deviation is still 0.039 Å. We conclude that CCSD(T), contrary to previous claims, is not able to describe the OF bond in **1** correctly. Considering the high amount of electron clustering at the O and the F atom, it is likely that connected four-electron correlation effects cannot be neglected in this case, as was recently shown for other molecules with electron clustering.[70]

DFT Geometries. Various authors showed that the LDA approach leads to reasonable descriptions of the geometry of **1**.[21−25] This was attributed to the fact that LDA will perform satisfactorily if there is a fairly high electron density and the latter does not exhibit steep gradients where both requirements are largely fulfilled in the case of **1**.[21] The use of cc-pVmZ basis sets, however, deteriorates the performance of DFT irrespective of the functional used so that the LDA results of Table 2 cannot compete with results of previous investigations based on HF-optimized basis sets (Table 5).[21,22]

Similarly as for the MP2 and CCSD(T) description of **1**, we find that for certain compositions of the basis set a fortuitously accurate geometry of **1** is obtained; however, if standard correlation consistent basis sets are stepwise increased to reach the CBS limit at DFT, the resulting geometry will be less accurate than the CCSD(T)/CBS limit geometry obtained with the aug-cc-pVmZ basis sets. This holds for all functionals applied in this work where the B3LYP functional performs better than both the BLYP and mPW1PW91 functionals. The experimental value of the dipole moment (1.44 D[6]) is best approximated by the B3LYP calculations using either an augmented cc-pVQZ basis (1.37 D, Table 2) or one of the cc-pV5Z basis sets (1.34 D).

DFT represents an economic method to obtain a reasonable description of the properties of FOOF, however it seems to be incapable of predicting the geometry of **1** with high accuracy, and by this it performs poorer than CCSD(T) or MP6.

4. Can the FOOF Problem be Solved?

This work has shown that the equilibrium geometry of **1** cannot be obtained accurately with single determinant methods using a finite correlation consistent basis sets. The only accurate geometry obtained in this work is the MP6/CBS geometry (Table 3), which clearly indicates the necessity of higher order electron correlation effects, but does not offer a practical solution based on a finite basis set. Previous calculations as well as those presented in this work provide some guidance as to how standard basis sets would have to be manipulated to obtain a better geometry.

Most important is to increase anomeric delocalization, thus lengthening the OF and strengthening the OO bond. Because anomeric delocalization occurs twice in the molecule, its effect is felt by the OO bond twice but by each OF bond only once. Any method, which provides some reasonable account of the anomeric effects in **1**, will give a better estimate for the exact OO than for the exact OF bonds. As the dissociation energy for the OF bond indicates (19.5 kcal/mol[1,67]), the dissociation potential is rather flat, which implies that already small changes in the composition of the basis set or with regard to the inclusion of higher order electron correlation effects can lead to relatively large changes in the OF bond length.

Using an HF-optimized basis set increases the effective electronegativity of F relative to that of O, which in turn lowers the energy of the σ^*(OF) orbital, thus enhancing anomeric delocalization. The addition of diffuse functions can act in several ways, namely, e.g., expanding the electron density thus reducing electron−electron repulsion. This will lead to a shorter OO bond, indicative of an increased anomeric effect and longer OF bonds. If the exponents of the polarization functions at O and F are forced to be identical, then the overlap between the oxygen lone pair orbitals and the σ^*(OF) orbitals will be improved, again increasing anomeric delocalization and weakening the OF bonds, which become much longer.

It remains to clarify the effects of using a VDZ basis set at a correlated level. In parallel work we showed that use of such a basis at MP2 artificially increases pair correlation effects in systems with strong clustering of electrons.[49] This is equivalent to exaggerating anomeric delocalization, and by this, the lengthening of the OF bonds (see MP2/cc-pVDZ results in Table 2). For methods that cover higher order correlation effects, the use of basis sets saturated in the sp-space and augmented by several sets of polarization functions is absolutely necessary to provide a sufficiently large space for three- and higher-electron correlations. If, however, the basis set is compressed to a VDZ level (equivalent to a reduction of the space for electron correlation), pair correlation effects are artificially exaggerated. Again, the OF bond is lengthened as in the case of the MP3/, MP4/, MP6/, and CCSD(T)/cc-pVDZ calculations performed in this work (Table 2).

Higher order correlation effects introduced with an appropriate method and a sufficiently flexible basis set improve the distribution of electrons, in particular at the F atom, which is similar to an increase of the effective electronegativity at F, a larger charge transfer from O to F, a lowering of the energy of the σ^*(OF) orbital, and an increase of anomeric delocalization. If standard basis sets are used, CCSD(T) seems to be not sufficient to solve the FOOF problem and therefore, CCSDT or, more likely, methods including connected four-electron correlation effects have to be used to get a reliable geometry of **1**.

In conclusion, there are three different ways to solve the FOOF problem. First, there is the possibility of establishing nonstandard basis sets to be used in the case of compounds composed of electronegative atoms such as FOOF, FOF, FOOO, FOOOF, FONO, F_2 NNF_2, etc. Second, there is the possibility of using CCSDTQ[71] or equivalent methods.[70] Finally, the FOOF problem could be solved with standard basis sets applying MR−CI or MR−CC techniques. Results of Rohlfing and Hay[15] seem to confirm the latter possibility, although the basis sets used in their work (6-31G(d) and 6-31G(d) +diff) were too small (see discussion above) to draw definite conclusions.

5. Conclusions

A number of conclusions can be drawn from the present investigation.

(1) Using standard basis sets, the FOOF problem (accurate prediction of its equilibrium geometry) cannot be solved with single determinant methods and standard correlation consistent basis sets. The best geometry obtained in this work (CCSD(T)/aug-cc-pVmZ, Table 2) still deviates by 0.01 to 0.04 Å from the r_o/r_s geometry of Jackson[6] or the r_g geometry of Hedberg and co-workers.[7] This is also true for the CCSD(T)/CBS geometry based on aug-cc-pVmZ basis sets (deviation for the OF bond length: 0.04 Å, Table 3).

(2) At the MP6/CBS level, an accurate FOOF geometry is obtained.

(3) The FOOF problem can be solved by artificially increasing anomeric delocalization. It is possible to add diffuse basis functions at the O atom to a large basis set, equalize the exponents of polarization functions at O and F, or alternatively exaggerate the pair correlation by the use of a VDZ basis set. These recipes, although never described as such, were used in previous investigations claiming a solution of the FOOF problem.

(4) DFT with the B3LYP functional provides a qualitatively correct description of FOOF, although it also fails as all other functionals used in this work to accurately described the equilibrium geometry of **1**.

(5) It is easier to describe the OO bond length than the OF bond lengths, which has to do with the fact that the dissociation potential of the former bond is much steeper (strengthening of the bond by two anomeric delocalization effects) than that of the latter bonds, as reflected by dissociation energies D_0 of 46.1 and 19.5 kcal/mol.[1,67]

(6) Rotation of FOOF at the OO bond is equally as likely as dissociation into FOO and F because the corresponding barriers (cis barrier: 19.6 kcal/mol; dissociation barrier 19.5 kcal/mol) are comparable. Previous estimates as to the height of the rotational barriers of FOOF are largely exaggerated. Rotation at the OO bond raises the barrier to dissociation because the anomeric effect is switched off.

(7) The molecular dipole moment is a sensitive antenna for probing the quality of the quantum chemical description of FOOF.

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