

Study of the influence of stereoelectronic interactions on the vibrational frequencies of a series of peroxy fluorocarboxygenated compounds

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ABSTRACT

Stereoelectronic effects were investigated in a series of peroxy fluorocarboxygenated compounds, using experimental infrared data, theoretical calculations and NBO analysis. The influence of inductive, anomeric and mesomeric interactions over the C=O and O–O stretching vibrations were evaluated for all the molecules. The carbonylic stretching mode is mainly affected by the inductive interaction, while the lone pair delocalization $\text{LpO} \rightarrow \sigma_{\text{O}-\text{C}}^*$ shows a stronger influence on the O–O stretching vibrations. The mesomeric interaction is relevant in determining the planar geometry of the XC(O)O group around the Csp² atom.

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1. Introduction

The study of the geometries and conformations adopted by many molecules with general formula X–O–O–X [1–8], has served as a basis to the understanding of the structural behavior of a series of new fluorinated compounds possessing groups with similar characteristics, such as the S–S and S–O moieties. For instance, known molecules with X=CF₃ [1], CH₃ [2], SF₅ [3], Me₃Si and Butyl [4], FC(O) [5,6], CF₃C(O) [7], and CF₃OC(O) [8] were analyzed, and some of them were used as reference for the comparison with disulfides (X–S–S–X) and sulfenic esters (X–S–O–X) compounds. From these, geometrical features such as the dihedral angles around the O–O, S–S or S–O bonds, or the bond lengths themselves, have been inferred [9]. It has been found, for symmetrically substituted compounds possessing a sp³-atom linked directly to the O–O, S–S or S–O entities, that the dihedral angle is higher than 120°. However, when the p-character of the hybrid orbitals changes, i.e. in the case where both linked-atoms have sp² instead of sp³ hybridization, the angle is less than 90°. The relatively smaller number of molecules being asymmetrically substituted – linked-atoms that bear both sp² and sp³ hybridization –, are expected to present dihedral angle values between 90° and 120° (*gauche* conformation).

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¹ This work is to honor Prof. Dr. Heinz Oberhammer with whom we have had a very fruitful and longstanding collaboration, working in the elucidation of the structure of new fluorinated compounds.

These conformational preferences are commonly explained invoking an electronic delocalization arisen from one lone pair orbital located at one of the oxygen or sulfur atoms to a vicinal σ non-bonding orbital of the second O or S atom [10]. Firstly determined in carbohydrates or six-membered heterocycles, this electronic effect was a qualitative measurement of the tendency of the electronegative substituents to assume the axial rather than the equatorial position. It quickly became a general phenomenon for molecules containing R–X–A–Y moieties (where X = lone pair containing atom; A = atom with intermediate electronegativity, and Y = O, N or S) and it was given the name anomeric effect [11]. Recently, the structures of a series of disulfide compounds in which the substituents adopt the *gauche* (*syn*) instead of the *antiperiplanar* (*anti*) position, were understood as favored by the anomeric effect through an electron donation from the sulfur lone pair into the empty σ^* orbitals of the opposite S–S bond [12]. Though other sources about the origin of the anomeric effect have been suggested [13], the electronic delocalization contribution has been demonstrated to be the most suitable alternative when evaluating the magnitude of this effect [14]. The NBO analysis derived and implemented in calculation programs by Weinhold and Brunck [15] allows its quantitative description.

On an absolute basis, other interactions (see Table 1) namely mesomeric and/or inductive (explained below), are considerably higher in energy than the anomeric effect. However, in this study we will show that the anomeric interaction is the most important in determining the dihedral angles, as well as the O–O stretching frequencies, independently of its magnitude *per se*.

Table 1

Experimental and calculated frequencies of O–O and C=O stretching modes; stabilization energies for anomeric, mesomeric and inductive effects.

	$\nu_{C=O}$ (cm ⁻¹) ^a		ν_{O-O} (cm ⁻¹) ^a		Electronic effects (Kcal/mol)			Dihedral angles (°) ^c	
	Exp.	Calc. ^b	Exp.	Calc.	Inductive	Mesomeric	Anomeric	XC1(O3)O1	O1C1(O3)Y
CF ₃ OOCF ₃	–	–	890	862	–	–	2.91	–	–
CF ₃ C(O)OOCF ₃	–	1846	–	879	28.21	37.82	2.97	179.1	–
CF ₃ OC(O)OOCF ₃ ^d	1885	1859	910	875	37.29	35.18	2.70	179.5	–
FC(O)OOCF ₃	1911	1898	884	859	41.73	36.39	2.63	179.5	–
CF ₃ C(O)OOC(O)CF ₃	1869	1857 (sym)	892	884	55.98	80.52	4.90	178.5	178.5
	1843	1825 (asym)							
CF ₃ C(O)OOC(O)OCF ₃	–	1861 (sym)	–	914	64.39	73.68	5.69	178.5	180.0
	–	1831 (asym)							
CF ₃ C(O)OOC(O)F	–	1895 (sym)	–	897	68.86	74.21	5.45	179.1	179.9
	–	1839 (asym)							
CF ₃ OC(O)OOC(O)OCF ₃	1887 ^d	1866 (sym)	903	926	73.17	61.19	5.76	180.0	180.0
	1866 ^d	1839 (asym)							
CF ₃ OC(O)OOC(O)F	–	1896 (sym)	924	914	77.50	71.32	5.54	179.2	180.0
	–	1848 (asym)							
FC(O)OOC(O)F	1934	1907 (sym)	910	906	77.70	71.56	5.32	179.9	179.9
	1907	1877 (asym)							

^a Scaled by the factor 0.9679.^b sym, symmetric; asym, antisymmetric.^c Dihedral angles of peroxides with the general structures defined as XC(O)OOC(O)Y.^d This work.

According to the NBO philosophy, the lone pair orbitals are formally located either at the oxygen or at the sulfur atoms. Delocalizing interactions evaluated by a second-order perturbation approach, reveal that these orbitals (which are pure p-type [Lp_(O,S)] lone pairs) contribute to resonant interactions with the pi antibonding orbital [Lp_(O,S) → π*_{(C=O)] and receive the name of mesomeric effect. This interaction with a carbonyl group, is the most important donor-acceptor electronic property in XC(O)O– and XC(O)S– groups. Compounds such as acetamide, methyl formate, carbonylsulfenylacetate, dimethyl carbonate and their derivatives, have been evaluated in the literature [16–22] and it was concluded that the mesomeric interaction plays an important role in the planar structure around the Csp² atom [16–19,22].}

For compounds possessing either the O–O, S–S or S–O bonds and an adjacent carbonyl, the inductive interaction involves the electron delocalization from one of the lone pair orbitals of the carbonylic oxygen to the same vacant σ*_(C–X) anti-bonding orbital [Lp_(O) → σ*_{(C–X)] (where X represents either an F atom or the C atom of a CF₃ or CF₃O group).}

In this work we attempt to bring new information about the role of the electron delocalization effects on the structure of some fluorocarboxygenated compounds and on the vibrational frequencies of some selected bands, namely those comprising the O–O and C=O stretchings. In pursuing this goal, a series of fluorinated peroxy compounds was analyzed using the NBO program [15a]. The molecules involved in the present study were: CF₃OOCF₃ [1], CF₃C(O)OOCF₃ [23], CF₃OC(O)OOCF₃, FC(O)OOCF₃ [24], CF₃C(O)OOC(O)CF₃ [7], CF₃C(O)OOC(O)OCF₃, CF₃C(O)OOC(O)F, CF₃OC(O)OOC(O)OCF₃ [25], CF₃OC(O)OOC(O)F [26], and FC(O)OOC(O)F [5,6]. CF₃C(O)OOCF₃, CF₃C(O)OOC(O)OCF₃ and CF₃O–C(O)OOC(O)F have not been reported as stable molecules so far, but were included in the calculations in order to complete the series of possible interactions. All the molecules are depicted in Fig. 1, together with the atom number assigned.

2. Computational details

All the calculations reported in this work were performed using the GAUSSIAN 03 program suite [27]. Full geometry optimizations were carried out without any symmetry constraint for the species. The corresponding optimized structures were characterized by frequency calculations as being minima without imaginary vibration

frequencies. The B3LYP/6-311+G* basis set was used, and the restricted open shell formalism at DFT method has been performed. The NBO analysis was carried out using the 3.1 version of the NBO package [15] included in GAUSSIAN 03 program at the same level of theory as all the other calculations. The NOSTAR keyword was used in NBO calculations to determine the energy of the corresponding hypothetical Lewis molecules.

2.1. Natural Bond Orbital analysis

NBO (Natural Bond Orbital) analysis [28] is based on a method that transforms wave functions into a one center (lone pair) and two center (bond) representation. This approach has been frequently used on the evaluation of the anomeric effect, as the diagonal elements of the Fock matrix represent the energy of the localized bonds, lone pairs and antibonds; and the off-diagonal elements represent bond/antibond, lone pair/antibond, and antibond/antibond interactions, respectively. Besides, the NBO analysis allows estimating the energy of the molecule with the same geometry but in the absence of any electronic delocalization. The electrostatic and steric interactions are considered through the E_{Lewis} term, corresponding to the hypothetical Lewis molecule in which delocalizations are absent. Thus, this analysis allows the separation of the total molecular energy into the purely bond contribution and delocalization energy [14] (see Table 2).

3. Results and discussion

Since calculations at the B3LYP level are known to provide very good results for molecular geometries, our results were performed using it with the 6-311+G* basis set. In order to allow a straightforward correlation among the species, we collected in Table 3 experimental and calculated geometrical parameters.

According to the table, a broad agreement between both experimental and calculated bond distances can be noted, especially around the O–O bond length. Fig. 2, shows the correlation between the experimental and calculated O–O bond lengths. Despite some slight deviations, an almost linear trend (depicted by the solid line in the figure) indicates a good concordance for the entire set experimentally determined but one. It is evident at a glance the lengthening for the unique compound lacking carbonyl groups

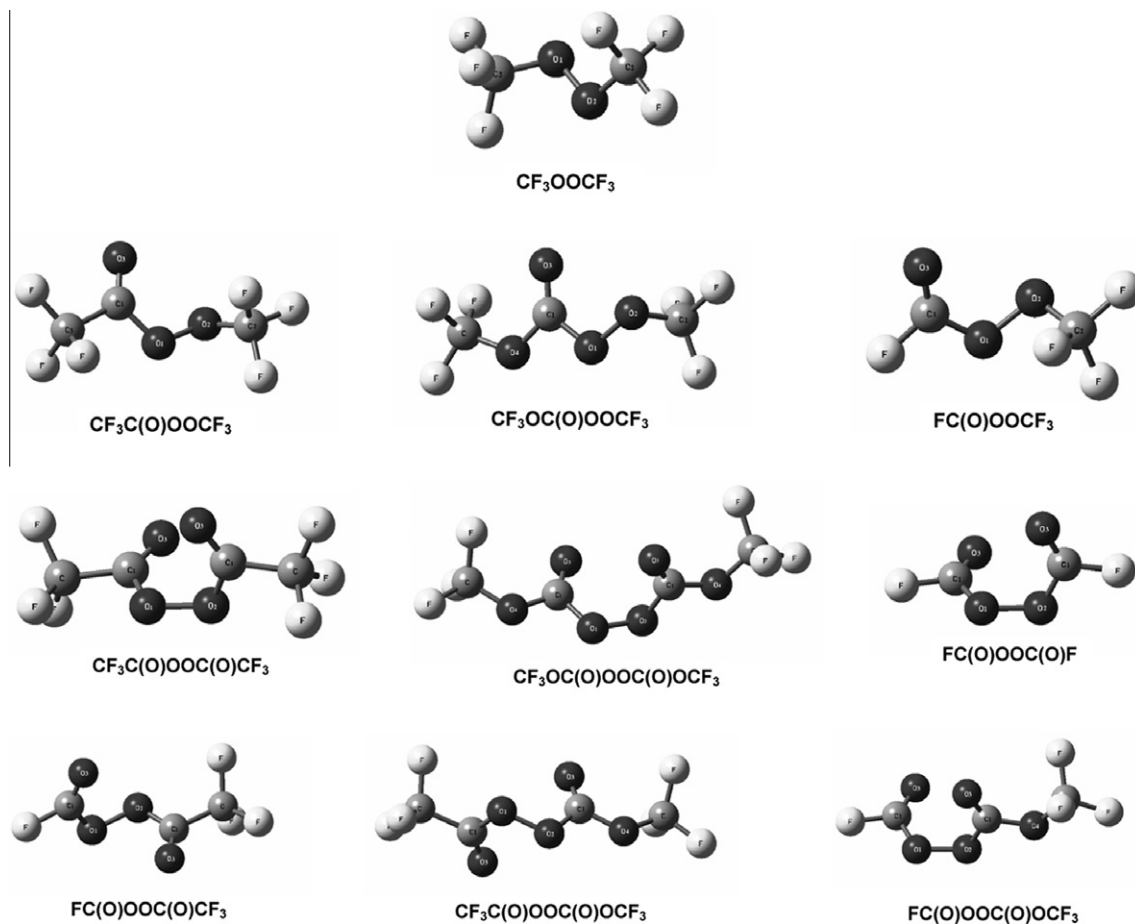


Fig. 1. Atom numbering for all the peroxy compounds.

Table 2

Total energy (a.u.), Lewis energy (E_{Lewis}) and electronic delocalization contributions ($\Delta E_{\text{(total-Lewis)}}$) to the electronic effects (in a.u.).

	Total energy	E_{Lewis}	Delocalization energies, $\Delta E_{\text{(total-Lewis)}}$
CF_3OOCF_3	-824.615267	-824.550712	-0.064
$\text{CF}_3\text{C}(\text{O})\text{OOCF}_3$	-939.242696	-938.075349	-1.167
$\text{FC}(\text{O})\text{OOCF}_3$	-701.384637	-700.446780	-0.938
$\text{CF}_3\text{C}(\text{O})\text{OOC}(\text{O})\text{CF}_3$	-1052.259491	-1050.797347	-1.462
$\text{FC}(\text{O})\text{OOC}(\text{O})\text{F}$	-576.885236	-575.955958	-0.929
$\text{CF}_3\text{OC}(\text{O})\text{OOC}(\text{O})\text{F}$	-888.718397	-888.271401	-0.447
$\text{CF}_3\text{OC}(\text{O})\text{OOC}(\text{O})\text{OCF}_3$	-1202.738681	-1200.796671	-1.942
$\text{CF}_3\text{OC}(\text{O})\text{OOCF}_3$	-1014.175920	-1012.675666	-1.500

(CF_3OOCF_3). This behavior would be anticipated since molecules possessing C=O groups experience electronic interactions other than the anomeric effect as has been pointed before.

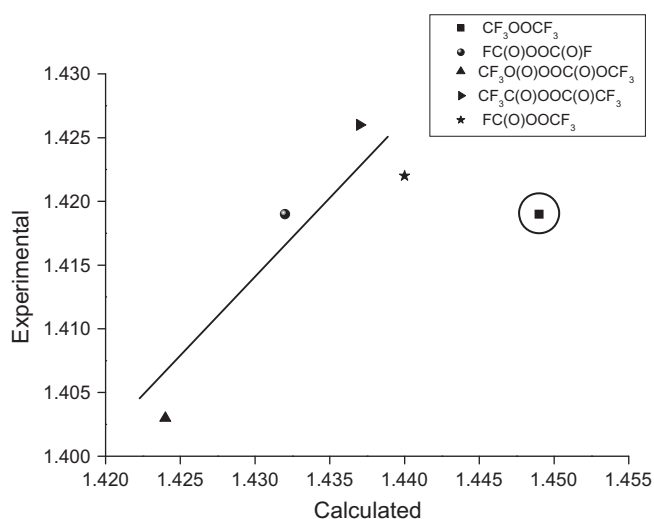
However, it is not straightforward to find a simple correlation between either O—O bond distances or frequencies of the O—O stretching vibration and stereoelectronic effects. Erben et al. [9d] have interpreted their results on S—S bond lengths in disulfide compounds resorting solely to the anomeric effect. On the same line of thought, it would seem reasonable to expect similar behavior in peroxy compounds. In Fig. 3 we present the frequency of the stretching vibration vs. the calculated O—O bond lengths, where a good correlation is observed. Only molecules containing two C=O groups were included in the figure, leaving the molecules containing only one carbonyl group ($\text{CF}_3\text{C}(\text{O})\text{OOCF}_3$, $\text{CF}_3\text{OC}(\text{O})\text{OOCF}_3$ and $\text{FC}(\text{O})\text{OOCF}_3$) for a separate analysis. A linear relationship between

the magnitude of the anomeric effect and the stretching frequencies is also observed in Fig. 4. In fact, for compounds containing two C=O groups, the higher the stabilization energy arisen from the anomeric effect, the higher the wavenumber of the O—O stretching vibration (see Table 1 and Fig. 4). In order to reflect as clearly as possible the influence of the anomeric delocalization on the dihedral angle C—O—O—C, in Fig. 5 we present the relative energy of the anomeric interaction calculated for the $\text{FC}(\text{O})\text{OO-C}(\text{O})\text{F}$ molecule when the dihedral angle (C—O—O—C) is changed in 10° steps, together with the total electronic energy obtained for each step. Interestingly, for the 90° angle, the relative energy value is a maximum according to the $\text{LpO} \rightarrow \sigma_{\text{C-O}}^*$ delocalizations, and the relative electronic energy is a minimum, denoting that the molecular conformation preference adopted (angle 91.9°) depends mainly on the anomeric delocalization magnitude.

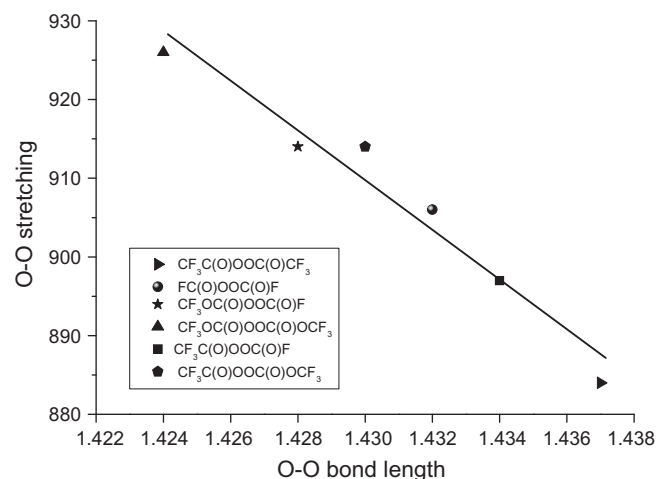
Table 3

Experimental and calculated geometrical parameters at B3LYP/6-311+G* level or theory.

Molecules ^a	Bond length (Å)				Angle X–C1–O1 (°)		Dihedral angle (°)		
	O1–O2		O2–C2		O1–C1/O2–C1		C–O–O–C		
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	
CF ₃ OOCF ₃ ^b	1.419	1.449	1.399	1.392	–	–	123.3	120.8	
CF ₃ C(O)OOCF ₃	–	1.443	–	1.391	–	1.368	106.6	121.6	
CF ₃ OC(O)OOCF ₃	–	1.436	–	1.391	–	1.376	102.5	–118.5	
FC(O)OOCF ₃ ^c	1.422	1.440	1.393	1.392	1.376(11)	1.366	103.6	119.1	
CF ₃ C(O)OOC(O)CF ₃	1.426	1.441	–	–	1.361(12)	1.366	–	86.5	86.3
CF ₃ C(O)OOC(O)OCF ₃	–	1.430	–	–	–	1.369/1.377	–	–	90.4
CF ₃ C(O)OOC(O)F ^d	–	1.434	–	–	–	1.367	–	–	91.2
CF ₃ OC(O)OOC(O)OCF ₃ ^f	1.403	1.424	–	–	1.372(5)	1.376	–	87.1	90.6
CF ₃ OC(O)OOC(O)F ^e	–	1.428	–	–	–	1.367/1.377	–	–	91.7
FC(O)OOC(O)F ^g	1.419	1.432	–	–	1.355(4)	1.369	–	83.5	91.9

^a For the atoms numbering see Fig. 1.^b Ref. [1].^c Ref. [24].^d Ref. [7].^e Ref. [5,6].^f Ref. [25].^g Ref. [26].**Fig. 2.** Graphic correlation between experimental and calculated (Å) bond lengths for the series of peroxy compounds. In O is enclosed the value correspond to the CF₃OOCF₃ molecule.

Nevertheless, for a more complete analysis on the O–O stretching frequencies, it is necessary not only the consideration of the anomeric contribution, but also the mesomeric one. A general overview of Table 1 shows that, on an absolute basis, the mesomeric interaction appears as one of the dominant effects. The higher energy value (80.52 Kcal/mol) is directly associated to the lower calculated vibrational frequency (892 cm⁻¹) as would be expected since the mesomeric delocalization decreases the electronic density over the O–O bond. This trend can be observed for all the other dicarbonylic peroxides, but one. It is interesting to note the results obtained for CF₃OC(O)OOC(O)OCF₃, which has the lowest mesomeric delocalization energy of the group, and this should lead to the highest stretching wavenumber (also demonstrated by the calculations). However, a significant difference is noticeable between experimental and calculated frequency values, which can be understood with the following arguments. In Table 2 we present the contribution to the delocalization energy as the result of subtracting to the total

**Fig. 3.** Graphic correlation between the calculated O–O bond lengths (Å) and their corresponding stretching frequencies (cm⁻¹).

energy, the purely Lewis contribution. As it can be seen, the highest delocalization (well separated from the other values), is found precisely for CF₃OC(O)OOC(O)OCF₃ and we believe that the unavailability of localized electrons could play a significant role on the experimental stretching frequency that is not directly reflected by the geometrical parameters of Table 3.

For the set of molecules containing only one carbonyl group, CF₃C(O)OOCF₃, CF₃OC(O)OOCF₃ and FC(O)OOCF₃, the occurrence of the LpO → σ_{O–C}⁺ interaction acts reinforcing the O–O bond; thus, the stretching vibrations appear at higher wavenumbers. Fig. 6 shows both the O–O stretching wavenumbers and the stabilization energies arisen solely from the anomeric effect vs. the O–O bond lengths. A good correspondence for both quantities can be seen, thought there is no a clear correlation for each of them. We could also consider, since it could be affecting the length of the peroxy bond, the influence of the steric effects. Apparently, a strong steric repulsion between the CF₃ and O–O groups override the anomeric effect and leads to a lengthened O–O bond distance. This steric

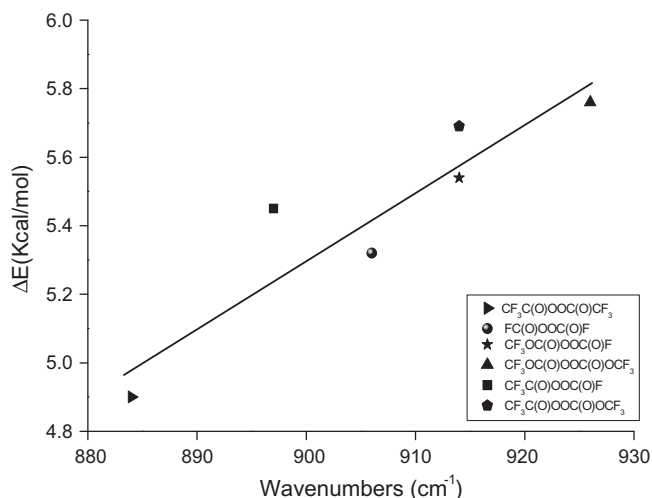


Fig. 4. Graphic correlation between anomeric effect (Kcal/mol) and O—O stretching vibrations (cm^{-1}).

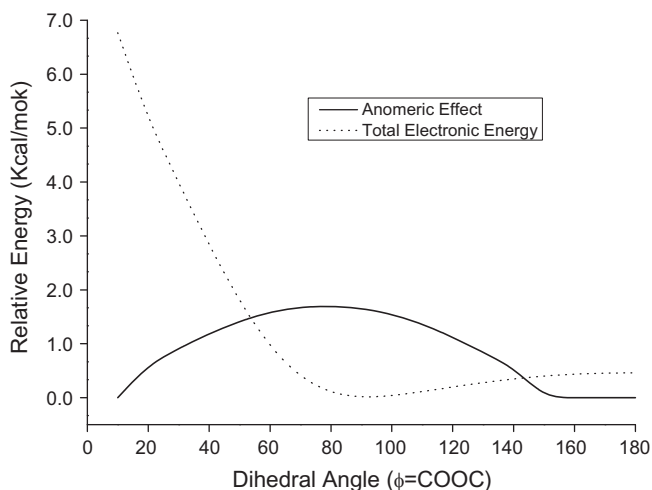


Fig. 5. The relative energy of the anomeric effect and the relative electronic energy for the scan performed around the O—O bond, in 10° steps.

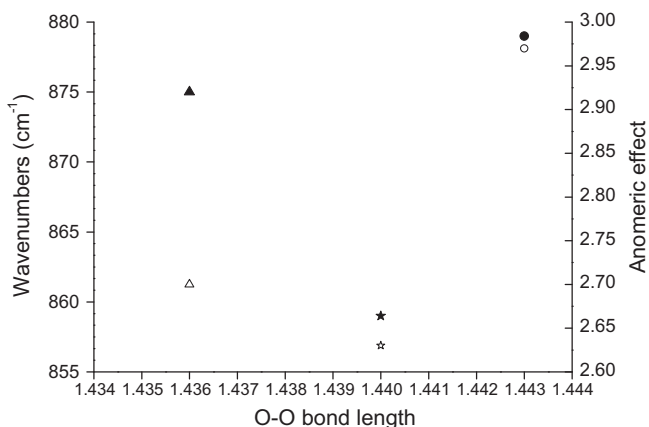


Fig. 6. Relationship between wavenumbers of O—O stretching vibrations (cm^{-1} , filled symbols) and anomeric effect (Kcal/mol, empty symbols), vs. O—O bond lengths (Å). Triangles ($\text{CF}_3\text{OC}(\text{O})\text{OOCF}_3$); stars ($\text{CF}_3\text{C}(\text{O})\text{OOCF}_3$) and circles ($\text{FC}(\text{O})\text{OOCF}_3$).

repulsion is evident from the calculated X—C1—O1 angles (Table 3 with X=O, F or C atoms), which increase from 102.5° ($\text{CF}_3\text{O}-\text{C}(\text{O})\text{OOCF}_3$), to 103.6° ($\text{FC}(\text{O})\text{OOCF}_3$) and to 106.6° ($\text{CF}_3\text{C}(\text{O})\text{OOCF}_3$). These results are in close agreement with the distances calculated. For this group, there is a straightforward correspondence between the anomeric interaction and the O—O stretching vibration – the higher the anomeric delocalization energy, the higher the stretching wavenumber –, despite that there is no correlation regarding the O—O bond distance.

The analysis of the C=O groups in turn, could be approached taking into account two attributes, namely the atoms arrangement themselves and their vibrational frequencies.

On the one hand, the mesomeric interaction, affects the arrangement around the Csp^2 atom, as is shown in the last column of the Table 1, which shows that the dihedral angles impose a planar structure. This fact was also observed in systems possessing amide groups, and it has been understood as the most appropriate spatial arrangement of a p-type lone pair, in order to interact with the electron-deficient carbon atom [18,19]. The dihedral angles support this assessment, since all the calculated values are around 180° ; either for molecules possessing one or two carbonylic groups in the molecule. Moreover, there is not a clear dependence on the dihedral value with the absolute magnitude of this effect, since it reaches its maximum value for each molecule.

On the other hand, the C=O stretching vibration could be rationalized taking into account the influence of the substituents on the C=O moiety. With this purpose, a simpler group of molecules were used as representative of the entire pool (listed in the upper rows of Table 4). $\text{CF}_3\text{C}(\text{O})\text{OOCF}_3$, $\text{CF}_3\text{OC}(\text{O})\text{OOCF}_3$ and $\text{FC}(\text{O})\text{OOCF}_3$, have as substituent on the unique carbonylic C atom a CF_3 , a CF_3O group and an F atom, respectively. The last column summarizes the values of the inductive stabilization energies and shows the order $\text{F} > \text{CF}_3\text{O} > \text{CF}_3$. This is independently confirmed by the calculated infrared frequencies assigned to the carbonyl groups (see Table 1). Only $\text{FC}(\text{O})\text{OOCF}_3$ and $\text{CF}_3\text{OC}(\text{O})\text{OOCF}_3$ have been fully characterized and the experimental vibrational frequencies show the same trend. The generalization of the above assertion to the peroxides containing more than one carbonyl group (lower rows of Table 4), shows that the contribution of the inductive effect perfectly parallels the *a priori* expectations, both for the symmetric and anti-symmetric stretchings, thus supporting the statement “the higher the electron-withdrawing capacity of the atoms bonded to the C=O moiety, the higher the stabilization energy ($\Delta E^{(2)}$)”. The stabilization energy is the result of the contribution of the two lone pairs located on the carbonylic O atom. This situation is fully reported in Table 4 where it can be seen that the larger contribution comes always from the “p” shaped orbitals. The table also depicts the stabilization energies arisen from each electron delocalization ($\text{LpO} \rightarrow \sigma_{\text{C-X}}^*$, with X=F, C or O), the occupancy of the acceptor orbital as a consequence of these interactions and the sum of the stabilization energy of all molecules. The relatively high anti-bonding orbital occupancy with respect to the σ anti-bonding orbitals not involved in the delocalization (results not shown) is about one order of magnitude higher.

4. Conclusions

The anomeric delocalization, acts shortening the O—O bond distance and shifting the O—O stretching vibrations. The stronger the effect, the shorter the distances and the higher the frequencies.

For the C=O stretching vibration, in turn, the inductive effect has more relevance in determining its frequency. The electron-withdrawing capacity of the substituents linked to the carbonyl group ($\text{F} > \text{CF}_3\text{O} > \text{CF}_3$) follows in importance.

Table 4Orbital delocalizations, occupancy of the acceptor orbitals, stabilization energies ($E^{(2)}$, Kcal/mol) and the inductive effect ($\Delta(E^{(2)})$, Kcal/mol).

Molecules ^a	Lone pair orbitals (Lp) ^b		Occupancy	($E^{(2)}$)	Inductive effect	
CF ₃ C(O)OOCF ₃	(s) O ₃	→	σ_{C1-C3}^*	0.127	1.54	28.21
	(p) O ₃				26.67	
CF ₃ OC(O)OOCF ₃	(sp ^{0.67}) O ₃	→	σ_{C1-O1}^*	0.114	2.44	37.29
	(p) O ₃				34.85	
FC(O)OOCF ₃	(s) O ₃	→	σ_{C1-F}^*	0.130	2.63	41.73
	(sp ^{0.64}) O ₃				39.10	
CF ₃ C(O)OOC(O)CF ₃	(sp ^{0.69}) O ₃	→	σ_{C1-C}^*	0.128	1.76	55.98
	(p) O ₃				26.23	
CF ₃ C(O)OOC(O)OCF ₃	(sp ^{0.69}) O ₃	→	σ_{C1-C}^*	0.128	1.76	64.39
	(p) O ₃				26.23	
CF ₃ C(O)OOC(O)OCF ₃	(sp ^{0.67}) O ₃	→	σ_{C1-O4}^*	0.111	2.47	64.39
	(p) O ₃				33.99	
CF ₃ C(O)OOC(O)F	(sp ^{0.70}) O ₃	→	σ_{C1-C}^*	0.127	1.53	68.86
	(p) O ₃				26.40	
CF ₃ C(O)OOC(O)F	(sp ^{0.64}) O ₃	→	σ_{C1-C}^*	0.126	1.53	68.86
	(p) O ₃				26.33	
CF ₃ OC(O)OOC(O)OCF ₃	(sp ^{0.69}) O ₃	→	σ_{C1-F}^*	0.127	2.66	73.17
	(p) O ₃				38.34	
CF ₃ OC(O)OOC(O)OCF ₃	(sp ^{0.69}) O ₃	→	σ_{C1-O4}^*	0.111	2.46	73.17
	(p) O ₃				34.12	
CF ₃ OC(O)OOC(O)OCF ₃	(sp ^{0.69}) O ₃	→	σ_{C1-O4}^*	0.127	2.46	73.17
	(p) O ₃				2.46	
CF ₃ OC(O)OOC(O)F	(sp ^{0.67}) O ₃	→	σ_{C1-O4}^*	0.111	2.47	77.50
	(p) O ₃				33.99	
CF ₃ OC(O)OOC(O)F	(sp ^{0.64}) O ₃	→	σ_{C1-F}^*	0.127	2.65	77.50
	(p) O ₃				38.39	
F(O)OOC(O)F	(sp ^{0.64}) O ₃	→	σ_{C1-F}^*	0.126	2.67	77.70
	(p) O ₃				38.29	
F(O)OOC(O)F	(sp ^{0.64}) O ₃	→	σ_{C1-F}^*	0.126	2.67	77.70
	(p) O ₃				38.29	

^a For atoms numbering see Fig. 1.^b Between parenthesis, the symmetry orbital.

Evaluating the mesomeric delocalization on the peroxides studied here, we conclude that the planarity of the XC(O)O entities is markedly determined by, but nearly independent of the magnitude of this effect.

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