A comparison of some properties of C=O and C=S bonds

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Dedicated to Prof. William F. Bailey on the occasion of his 65th Birthday

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Abstract
The properties of compounds with carbonyl and thiocarbonyl groups have been examined theoretically, and the results have been compared with the available experimental data. The properties include the bond dissociation energies, the vibrational force constants, the n→π* transitions and the charge distributions. The origin of the differences in properties are discussed

Keywords: Carbonyl group, thiocarbonyl group, bond dissociation energies, n→π* transitions, charge distributions

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Introduction

There are significant and interesting differences between compounds with carbonyl and thiocarbonyl groups. The C=S bond length (~1.6 Å)[1] is considerably longer than C=O (~1.25 Å). As a result, one would expect the bond strengths to differ significantly. The π-bond also might be expected to be strongly affected in view of the orbital size mismatch between first and second row atoms. On the other hand, thioamides are known to have larger rotational barriers than amides, where the barrier arises from the interaction of the amide nitrogen with the adjacent C=O or C=S group.[2]

Another interesting difference is found in the position of the n-π* transition that is shifted into the visible spectrum by the sulfur.[3] As a result the thiocarbonyl derivatives have interesting colors with phenyl thiocarbonyl chloride being red (λ_{max} = 530 nm). The transitions are shifted by about 2eV (~50 kcal/mol) to the red as compared to the corresponding carbonyl compounds.

There are also significant differences in reactivity. Benzoyl chloride has been found to be nine times more reactive toward methanol than thiobenzoyl chloride.[4] The reactions of phenoxycarbonyl chloride and phenoxythiocarbonyl chloride with trifluoromethyl phenyl carbinol in the presence of triethylamine has been examined,[5] and whereas the carbonyl chloride reacts normally with the intermediate acylammonium ion to give the ester, the thiocarbonyl chloride reaction occurs by nucleophilic attack at an ethyl on the N in the thioacylammonium ion, leading to a thioamide as the product. Phenylisocyanate reacts with cyclohexanol with 5 mol% *N*-methylimidazole as the catalyst to give a carbamate within 24 hr, but phenylisothiocyanate gives no product under these conditions.[4] The rate of the uncatalyzed reaction of phenylisocyanate with ethanol proceeds 48,000 times as fast as the corresponding reaction of phenylisothiocyanate.[4]

We have explored some of these differences, both experimentally and computationally, in order to learn more about the origin of the differences. In this report, we will be concerned with the differences in physical properties of compounds with C=O and C=S groups. It should be noted that the σ and π bond strengths of X=Y systems have received considerable study.[6]

Results and Discussion

Bond strengths

One of the most important quantities that characterize a bond is the bond strength. This can be expressed either as the bond dissociation energy or the force constant for stretching the bond. The first refers to complete cleavage, and the latter to the effects of small deviations from the equilibrium geometry.

The bond dissociation energies at 289K (D_{298}) are available for formaldehyde and thioformaldehyde as well as related compounds (Table 1).[7] The C=O bond is almost 50 kcal/mol stronger than the C=S bond. The values correspond to breaking both the σ and π parts of the bond. In some cases, such as ethene, it is possible to derive the π bond strength from the rotational barrier.[8] This is clearly not possible with the present compounds. The strength of a C-O or C-S single bond may be taken as the D_{298} of methanol and methanethiol. As an approximation, the D_{298} of the π part of the double bonds might be taken as the difference between the total D_{298} and the D_{298} of the single bonds. This will give too large a value because it does not take into account that the C-H bonds in ethene are stronger than those in ethane.[7] But, it will give relative π bond strengths.

The experimental values are summarized in Table 1 that also includes ethene for comparison.It is interesting to note that whereas the C=O bond is generally considered to be very strong, presumably because of its dipolar character, it is only slightly stronger than the C=C bond. The C=S dissociation energy is 50 kcal/mol smaller.

The C=C "π bond" energy estimated as described above is as expected ~20 kcal/mol larger than the activation energy for rotation about this bond. The values for the C=O and C=S π bonds are also probably too large, but the difference between them, 35 kcal/mol, is probably significant.

Formaldehyde and thioformaldehyde are not typical carbonyl and thiocarbonyl compounds. Acetone is more stable than formaldehyde; for example it is not significantly hydrated in aqueous solution whereas formaldehyde is. One might expect a similar effect of methyl substitution with the thiocarbonyl compounds.

Table 1. Bond dissociation energies (D_{298}), kcal/mol

Compound	Observed[7]	Calculated		
		CCSD	CBS-QB3	CBS-APNO
$H_2C{=}O$	179.0±0.4	175 .2	181.4	179.7
$H_2C{=}S$	132±2	127.3	133.8	(b)
$H_2C{=}CH_2$	174.1±0.3	172.1	176.1	175.3
$H_3C\text{-}OH$	92.1±0.1	91.6	93.2[c]	92.4
$H_3C\text{-}SH$	74.7±0.2	74. 6	75.4[c]	(b)
$H_3C\text{-}CH_3$	90.1±0.1	90.0	90.7[c]	90.7
π C=O	(87)			
π C=S	(52)			
π C=C	(84)[a]			
$Me_2C{=}O$			187.9	186.8
$Me_2C{=}S$			136.7	(b)

[a] The value derived from the rotational barrier is 65 kcal/mol.[8]

[b] The APNO basis set for sulfur has not been defined.

[c] The energies of the radicals were calculated using ROCBS.[9]

Experimental data are not available for acetone and thioacetone. In order to see what theoretical level would be needed in order to estimate their BDE's, we have calculated D_{298} for formaldehyde and thioformaldehyde. In one set of calculations, geometry optimizations were carried out at the CCSD/aug-cc-pVTZ level and the energies were calculated at the CCSD(T,full)/aug-cc-pVTZ level. The vibrational frequencies needed for the zero-point energy corrections and correction to 298K were calculated at the B3LYP/6-311+G* level. In other calculations, the CBS-QB3 and CBS-APNO model procedures were used and include the zero-point and thermal corrections.[9] The D_{298} values were obtained from the equations

$$H_2C{=}O \rightarrow {}^3H_2C + {}^3O$$
$$H_2C{=}S \rightarrow {}^3H_2C + {}^3S$$

The CBS-APNO calculations reproduced the observed dissociation energies very well. CBS-QB3 uses somewhat smaller basis sets for the individual step and as expected gives slightly less satisfactory results. The CCSD calculations also are fairly satisfactory.

The energies of acetone, thioacetone and triplet dimethylcarbene were calculated in the corresponding fashion and this allowed the calculation of the D_{298} values. The dissociation energies are about 5 kcal/mol greater than for formaldehyde and thioformaldehyde.

Force constants

Vibrational force constants are usually obtained via a normal coordinate analysis or a calculation of the vibrational frequencies. This presents problems because there is always coupling between the C=O (or C=S) vibration with other vibrational modes. In order to obtain force constants for local mode stretching of the C=O or C=S bonds, a series of B3LYP/6-311+G* calculations were carried out in which the energies were obtained for structures where the equilibrium double bond lengths were increased and decreased by 0.01 and 0.02 A, without altering the remaining structure. Fitting the data to a third order polynominal gave the force constant and also the cubic term. The harmonic terms along with the corresponding bond lengths are given Table 2.

The force constants are larger than commonly associated with these groups, but this is a result of using local modes. Coupling with other modes would reduce the force constants. The chlorides give the largest force constants whereas the amides give the smallest values. This is approximately correlated with the C=O/S bond length, especially with the carbonyl compounds as shown in Figure 1.

Table 2. Force constants (mdyne/Å) for carbonyl and thiocarbonyl compounds

Compound	k_2	r C=O,S (Å)
acetyl chloride	26.03	1.181
acetone	23.14	1.212
methyl acetate	23.48	1.207
dimethylacetamide	20.88	1.224
benzoyl chloride	24.99	1.187
acetophenone	22.01	1.217
methyl benzoate	22.67	1.210
benzamide	21.67	1.220
thioacetyl chloride	11.65	1.613
thioacetone	10.90	1.636
methyl thioacetate	9.53	1.645
dimethyl thioacetamide	9.29	1.674
thiobenzoyl chloride	11.01	1.626
thioacetophenone	10.23	1.649
methyl thiobenzoate	9.84	1.654
thiobenzamide	9.61	1.665

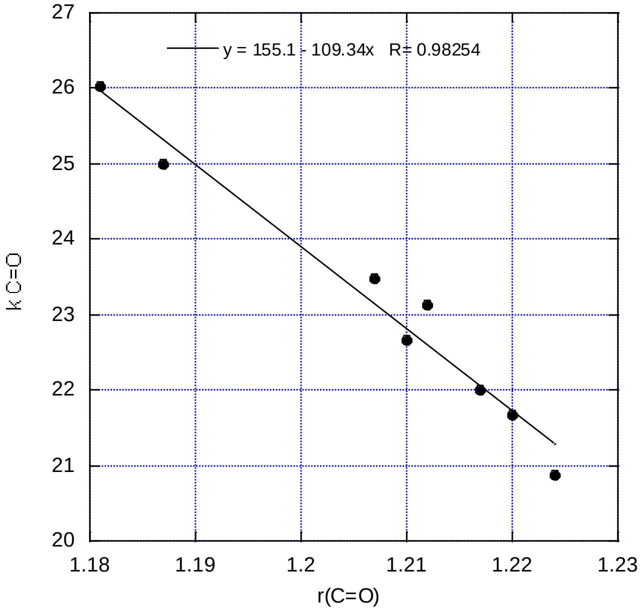

Figure 1. Relationship between the carbonyl force constant and the C=O bond length.

The C=O force constants are about twice as large as those for C=S, in agreement with the bond dissociation energies. The phenyl derivatives have slightly smaller force constant and slightly longer bond lengths than the corresponding methyl derivatives. But, the effect is small and indicates only a small interaction between the phenyl groups and the substituents.

Charge distributions

There is a considerable difference in electronegativity between oxygen and sulfur,[10] and therefore the charge distribution should be different between carbonyl and thiocarbonyl compounds. The definition of atomic charges in molecules presents difficulties.We prefer methods that directly involve the charge distribution.[11] We have previously given the charges for some of these compounds[2] using Bader's AIM theory,[12] but this is not ideal for direct comparisons between compounds since the volume associated with an atom is related to its electronegativity. The Hirshfeld definition[13] in which the electron density is allocated to the atoms by comparison with the electron density derived from a set of spherically symmetrical proatoms at the nuclear positions of the molecule in question appears to be the more satisfactory for comparing related compounds. The charges are obtained by adding the nuclear charges to the integrated difference densities. The charges thus calculated are given in Table 3

Table 3. B3LYP/6-311+G* Hirshfeld charges for XYC=O and XYC=S

X	Y	group	C=O	C=S	C=O rot	C=S rot
Me	Cl	Me	0.108	0.093		
		C	0.228	0.095		
		O/S	-0.206	-0.126		
		Cl	-0.134	-0.061		
Me	Me	Me[a]	0.046	0.064		
		C	0.172	0.062		
		O/S	-0.265	-0.190		
Me	OMe	Me	0.065	0.071		
		C	0.220	0.118		
		=O/S	-0.284	-0.243		
		-O-	-0.136	-0.100		
		Me	0.135	0.154		
Me	NMe_2	Me	0.037	0.052	0.051	0.059
		C	0.170	0.074	0.211	0.101
		O/S	-0.320	-0.322	-0.255	-0.186
		NMe_2	0.113	0.197	-0.007	0.026
Ph	Cl	Ph	0.115	0.109		
		C	0.212	0.085		
		O/S	-0.207	-0.141		
		Cl	-0.120	-0.053		
Ph	Me	Ph	0.049	0.077		
		C	0.163	0.058		
		O/S	-0.258	-0.188		
		Me	0.046	0.053		
Ph	OMe	Ph	0.050	0.061		
		C	0.212	0.154		
		O/S	-0.277	-0.236		
		-O-	-0.123	0.090		
		Me	0.139	0.111		
Ph	NH_2	Ph	0.047	0.062	0.040	0.069
		C	0.231	0.078	0.193	0.086
		O/S	-0.367	-0.299	-0.245	-0.210
		NH_2	0.089	0.158	0.012	0.055

[a] Each methyl group.

There are interesting changes in charge that result from the substituents and on going from C=O to C=S. It might first be noted that the charge on the thiocarbonyl carbon is considerably smaller than that at the carbonyl carbon in accord with the difference in electronegativity between O and S. Thus the thiocarbonyl carbon should have reduced electrophilicity. This contributes to the reduced reactivity toward nucleophiles.

The charges at the corresponding O or S are of more interest. The oxygen generally has a larger negative charge than sulfur, but the difference decreases as the substituent becomes more electron donating and with NR_2 the charges become equal. In order to further explore this difference, the structures of the amide rotational transition states were obtained and the charges were calculated. They are included in Table 3. Now, the positive charge at carbon increases, the positive charge at NMe_2 decreases and the negative charges at O and S decrease, but the effect at sulfur (42%) is much larger than at oxygen (20%). This clearly shows that charge transfer from the N lone pair to the thiocarbonyl S is larger than that to the carbon O in accord with our model for the higher rotational barrier for thioamides.[2]

The charges at methyl and phenyl are about equal for all of the compounds indicating no special interaction across the C=O and C=S bonds. They are largest with X=Cl in accord with the electronegativity of Cl. The charges at all of the atoms of the Me and Ph carbonyl and thiocarbonyl derivatives are linearly related as shown in Figures 2 and 3.

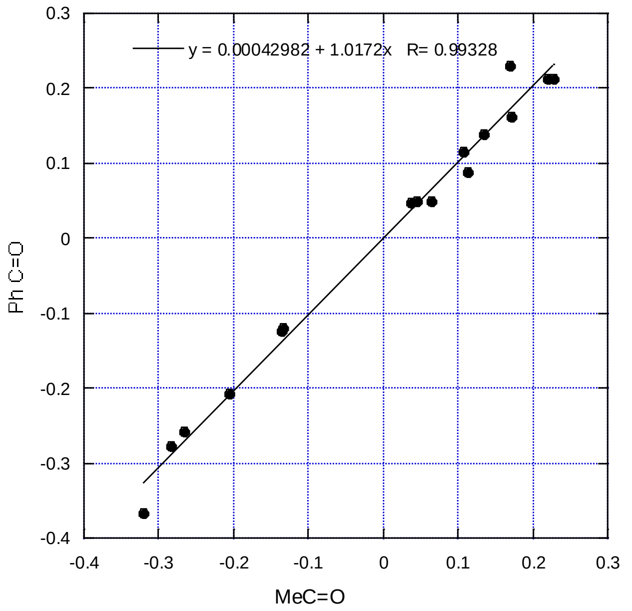

Figure 2. Relationship between the Ph and Me charges in PhYC=O and PhYC=S respectively.

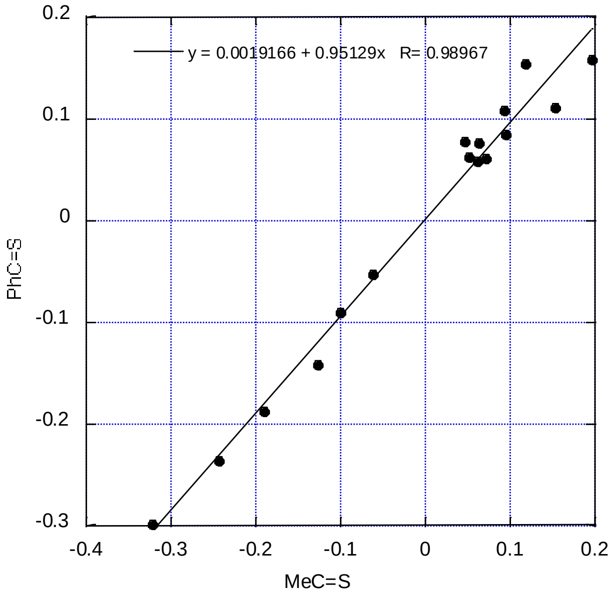

Figure 3. Relationship between the Ph and Me charges in PhYC=S and MeYC=S respectively.

n→π* Transitions

Compounds with C=O or C=S bonds typically have a low energy n→π* transition that is followed by a series of transitions from the n orbital to one of the higher virtual orbitals, leading to Rydberg character.[14] The n→π* transitions for many thiocarbonyl compounds have been located in cyclohexane solution.[15] They are easily observed because they are well separated from other transitions. The corresponding carbonyl n→π* transitions are more difficult to locate because they give broad bands that are near other transitions. Some of the available data are given in Table 4. It can be seen that the sulfur shifts the transitions about 2 eV (~50 kcal/mol) to the red as compared to the carbonyl compounds. It would be desirable to calculate all of the transition energies at the EOM-CCSD/6-311++G** level, but it is not practical for phenyl derivatives. Therefore, we have also made use of TDDFT calculations at the B3P86/6-311++G** level, using B3LYP/6-311+G* geometries. It is known that this level of theory often is satisfactory for the lower transitions of carbonyl compounds.[16] The results are included in Table 4. The agreement between the two levels of theory and with the experimental values is fairly good.

Table 4. Calculated n→π* transitions, 6-311++G**

			C=O			
X	Y	EOM		TDDFT		obs
		eV	nm	eV	nm	nm
Me	Me	4.54	272.8	4.46	278.9	276.8[a]
Me	Cl	5.28	234.0	5.23	237.0	236[b]
Me	OMe	6.04	205.2	5.89	210.6	~220[c]
Me	NMe_2	5.84	212.2	5.68	218.3	
Ph	Me			3.73	332.6	~350[d]
Ph	Cl			4.47	277.6	
Ph	OMe			4.91	252.6	
Ph	NH_2			4.5	274.4	
			C=S			
X	Y	EOM		TDDFT		Obs[e]
		eV	nm	eV	nm	nm
Me	Me	2.62	472.4	2.57	482.0	499
Me	Cl	2.79	443.8	2.73	447.0	n.a.
Me	OMe	3.55	351.2	3.41	361.4	377
Me	NMe_2	3.62	342.7	3.48	356.7	356
Ph	Me			2.13	583.5	573
Ph	Cl			2.37	522.5	530
Ph	OMe			2.93	423.1	418
Ph	NH_2			2.87	432.0	418

[a] Pappalado, R.R.; Reguero, M.; Robb, M. A.; Frisch, M. *Chem Phys Lett*. **1993**, *212*, 12.

[b] Deshmukh, S.; Hess, W. P. *J. Chem. Phys*. **1994**, *100*, 6429.

[c] Barnes, E. E.; Simpson, W. T. *J. Chem. Phys*. **1961**, *39*, 670.

[d] Shimada, R.; Goodman, L. *J. Chem. Phys*, **1965**, *43*, 2027.

[e] Ref. 15.

In order to provide some additional information concerning these transition, the energies of the n and π orbitals calculated at the B3P86/6-311++G** level are given in Table 5. These values are given in Hartrees, and the differences were converted to eV using 27.21 eV/Hartree. The calculated transition energies were obtained using TDDFT to be consisted with the n and π energy calculations. The Y substituents are given in order of reduced electron attraction, and the n energies are in accord with this order. The π* energies are more variable, as might be expected.

Table 5. Calculated energies (au) of n and π* orbitals

X	Y	n	π*	Δev	calc	difference
	a. carbonyl compounds					
Me	Cl	-0.3527	-0.0735	7.60	5.23	2.32
Me	OMe	-0.3068	-0.0218	7.75	5.89	1.71
Me	Me	-0.2788	-0.0472	6.30	4.46	1.76
Me	NMe_2	-0.2755[a]	-0.0214	6.91	5.68	1.23
Ph	Cl	-0.3260[a]	-0.1118	5.83	4.47	1.36
Ph	OMe	-0.3098[a]	-0.0807	6.23	4.91	1.32
Ph	Me	-0.2823	-0.0915	5.19	3.73	1.46
Ph	NH_2	-0.2849	-0.0746	5.72	4.56	1.16
	b. thiocarbonyl compounds					
Me	Cl	-0.2732	-0.1199	4.17	2.73	1.38
Me	OMe	-0.2539	-0.0765	4.83	3.41	1.28
Me	Me	-0.2450	-0.0995	3.96	2.57	1.34
Me	NMe_2	-0.2324	-0.0542	4.85	3.48	1.23
Ph	Cl	-0.2686	-0.1365	3.60	2.37	1.23
Ph	OMe	-0.2560	-0.1050	4.11	2.93	1.18
Ph	Me	-0.2456	-0.1217	3.37	2.13	1.24
Ph	NH_2	-0.2396	-0.0935	3.98	2.87	1.11

[a] The oxygen n orbital is lower in energy than the HOMO in these cases.

The difference in energy between the n and π* orbitals is larger than the calculated transition energies as should be the case, and with the phenyl substituted carbonyl and all the thiocarbonyl compounds the difference between these values and the calculated transition energies is approximately constant. One difference between the carbonyl and the thiocarbonyl compounds is found in the n orbital energies that are larger by about 0.05 H (32 kcal/mol) for the latter. In addition, the π* energies are smaller (more negative) by a similar amount. So, the sulfur has an effect on both types of orbitals leading to the large red shift.

Conclusions

Relatively high level computational methods are able to satisfactorily reproduce the available experimental data for carbonyl and thiocarbonyl derivatives. They also allow the estimation of data that are currently not available. Other quantities such as the charge distribution may also be derived from the results of these calculations and are useful in explaining the differences between these compounds.

Calculations

The *ab initio* results and the Hirshfeld charges were obtained using Gaussian-09.[17]

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References

1. Rindorf, G.; Carlsen, L. *Acta Cryst*. **1979**, *B35*, 1179.
2. Wiberg, K. B.; Rablen, P. R. *J. Am. Chem. Soc*. **1995**, *117*, 2201. Hadad, C. M.; Rablen, P. R.; Wiberg, K. B. *J. Org. Chem*. **1998**, *63*, 8668.
3. Fabian, J.; Viola, H.; Mayer, R. *Tetrahedron* **1967**, *23*, 4323.
4. Wiberg, K. B.; Wang, Y-g.; Miller, S. J.; Puchlopek, A. L. A.; Bailey, W. F.; Fair, J. D. *J. Org. Chem***. 2009**, *74*, 3659.
5. Hsu, F.-L; Zhang, X.; Hong, S.-S; Berg, F. J.; Miller, D. D. *Heterocycles*, **1994**, *39*, 801.
6. Schmidt, M. W.; Truong, P. N.; Gordon, M. S. *J. Am. Chem. Soc* **1987**, *109*, 5217. Sun, N.; Hrovat, D.A.; Bordon, W. T. *J. Am. Chem. Soc*. **1987**, *109*, 5275. Nicolaides, A.; Bordon, W. T. *J. Am. Chem. Soc*,. **1991**, *113*, 6750. Kutzelnigg, W. *Angew. Chem. Int. Ed. Engl*. **1984**, *23*, 272. Schleyer, P. v. R; Kost, D. J. J,. *Am. Chem. Soc.* **1988**, *110*, 2105. Wiberg, K. B.; Nakaji, D. *J. Am. Chem. Soc 1993*, **115**, 10658.
7. Blanksby, S. J.; Ellison, G. B *Acc. Chem. Res*. **2003**, *36*, 255. Ruscic, B.; Boggs, J. E.; Burcat, A.; Csaszar, A. G.; Westmoreland, P. R.; Zabel, F.; Berces, T. *J. Phys. Chem. Ref. Data* **2005**, *34*, 573.
8. Douglas, J. E.; Rabinovitch, B . S.; Looney, F. S. *J. Chem. Phys* **1955**, *23*, 315.
9. Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A. Jr, *J. Chem. Phys*. **1996**, *103*, 2598. Montgomery, J. A., Jr; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys*. **2000**, *112*, 6532.
10. Allred, A. L.; Rochow, E. G. J. *Inorg. Nucl. Chem*. **1958**, *5*, 264.
11. See Wiberg, K. B.; Rablen, P. R *J. Comp. Chem*. **1993**, *14*, 1504 for a comparison of charges calculated via different methods.
12. Bader, R. F. W. *Atoms in Molecules*, Oxford Scientific Publ.: Oxford, 1990.
13. Hirshfeld, F. L. *Theor. Chim. Acta*. **1977**, *44*, 129. cf. Ritchie, J. P. *J. Am. Chem.. Soc* **1985**, *107*, 1829. Ritchie, J. P.; Bachrach, S. M. *J. Comp. Chem*. **1987**, *8*, 499. Nalewajski, R. F.; Parr, R. G. *J. Phys. Chem. A*, **2001**, *105*, 7391.

14. Robin, M. S. "*Higher Excited States of Polyatomic Molecules*," Academic Press, N. Y. 1975, Vol 2, pg 121 ff
15. Fabian, J.; Viola, H.; Mayer, R. *Tetrahedron* **1967**, *23*, 4323.
16. Wiberg, K. B.; Stratmann, R. E.; Frisch, M. J. *Chem. Phys. Lett*. **1998,** *297*, 60.
17. Gaussian 09, Rev. A1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchain, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasagawa, J.; Ishida, M.; Nakijima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.,Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomassi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Ausin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc. Wallingford, CT 2009.