Differentiation of Sulfonyl Oxygens in Cyclic Systems by ^{17}O NMR Lanthanide Induced Shifts

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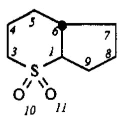
^{17}O NMR spectroscopy has gained much attention as an important method for studying molecular structure and conformational and dynamic properties of organic compounds.[1,2] The NMR characteristics of most oxygen functional groups are now available, including those of the terminal oxygens of four coordinate S^{VI} functional groups.[3]

It was early shown on that discrete ^{17}O NMR resonances may be observed for the diastereotopic oxygens of the sulfonyl functional group, $-SO_2-$, and that the oxygen chemical shifts of this rather "rigid" moiety are very sensitive to interactions with the rest of the molecular skeleton (although less than the more "soft" -SO- moiety).[4-9]

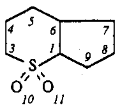
Recently, Evans *et al.*[10,11] have made an interesting observation, namely that the axial and equatorial oxygen atoms of a sulfonyl group belonging to a conformationally rigid or a conformationally restricted six membered ring undergo complexation by $Eu(fod)_3$ at a different rate, with the equatorial oxygen showing a greater aptitude to complexation. The different rate of complexation of the two oxygens leads to different ^{17}O NMR LIS effects from which binding constants for two distinct diastereomeric lanthanide–sulfone complexes can be determined, suggesting that LIS effects could be used as a probe for assessing the steric inhibition to oxygen–metal binding in these systems.

Evans' finding implies that it should be possible to differentiate by LIS effects the axial and the equatorial sulfonyl oxygens of compounds for which a single ^{17}O NMR signal is observed because of rapid conformational equilibrium in the NMR time scale. Of course, this should only be possible in cases where the equilibrating forms are not equienergetic, since in that case the chemical shifts of the axial and the equatorial oxygen would always be strictly the same (*cf. trans*-2,6-diphenyl-4-oxothiane described by Evans[10]). A further and more subtle implication of Evans' finding is that if an optically active shift reagent is added to a rigid molecular framework with an $-SO_2-$ group close to a chiral center, a different rate of formation should, in principle, be measured for each one of the diastereomeric lanthanide–oxygen complexes formed. For example, in the case of a rigid six-membered ring compound *four* different binding constants should be measured because of the formation of *four* distinct lanthanide–oxygen diastereomeric complexes, two for the equatorial and two for the axial oxygen.

We report here an ^{17}O NMR study of the LIS effects on the sulfonyl oxygens of three isomeric bicyclic compounds, *i.e.*, the *trans* and *cis* epimers of 2-thiabicyclo[4.3.0]nonane 2,2-dioxide (**I** and **II**) and *trans*-8-thiabicyclo[4.3.0]nonane 8,8-dioxide (**III**) depicted below:



I



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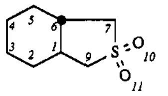

III

The *trans* configuration of **I**, the *cis* configuration of **II**, and the *trans* configuration of **III** are unambiguously defined by the known configuration of the parent sulfides and sulfoxides from which they were obtained (see Experimental Section).[12-15] In **I** and **II** the sulfonyl group belongs to the six-membered ring moiety and in **III** to the five-membered one. While **I** and **II** have no symmetry elements, **III** has a C_2 symmetry axis since the *trans* ring fusion obliges the five-membered ring to assume a half-chair conformation with the sulfur atom on the top (see Figure 1). In all compounds the bridgehead carbons are chiral centers, next to the sulfonyl group in **I** and **II** and two bonds apart in **III**.

Owing to the *trans* ring fusion, **I** is a rigid system and the sulfonyl group is in a geometrical environment similar to that of the *trans*-thiadecalin 1,1-dioxide examined by Evans.[10,11] Therefore, lanthanide binding constants of the same order as those of thiadecalin should be found for the axial and the equatorial oxygens, which, in the absence of shift reagent, are anisochronous and resonate at 123.1 and 147.7 ppm ($W_{1/2}$ = 150 Hz).

Because of the *cis* ring fusion, **II** is a conformationally mobile system and shows a single signal for the sulfonyl oxygens, at 145.8 ppm. MM2 studies from this laboratory indicate that there is a slight energy difference between conformers **IIa** and **IIb** (see below). This means that the chemical shifts of the sulfonyl oxygens of **II** are different but that the difference is smaller than the line width ($W_{1/2}$ = 250 Hz) and that distinctive responses of the oxygen

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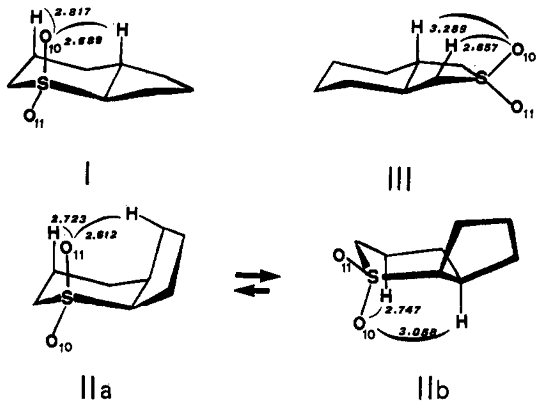

Figure 1. Stereoview and relevant oxygen-hydrogen distances (in angstroms, from MM2 calculations) of compounds **I**, **II**, and **III**.

atoms to shift reagent addition should be observed, leading to progressive separation of the oxygen signals.

In the last rigid system, **III**, the sulfonyl oxygens are magnetically equivalent and resonate at 168.2 ppm ($W_{1/2}$ = 150 Hz). Contrary to the oxygen atoms of **II**, the oxygen atoms of **III** should give rise to a single signal even in the presence of the shift reagent. Compound **III** is also a good model to verify the steric nature of LIS effects on oxygen resonances, as the geometrical environment and the steric compression of the sulfonyl oxygens in this system are of a completely different nature from those of **I** and **II**.

For all compounds the LIS effects have been measured in the presence of Eu(fod)$_3$ and for **I** also in the presence of the optically active tris[3-((heptafluorpropyl)hydroxymethylene)-*d*-camphorato]praseodymium(III).

Results and Discussion

It is known that force field MM2 calculations[18] are a very reliable way to obtain molecular energies and geometries. MM2 calculations on the mobile *cis*-2-thiabicyclo[4.3.0]nonane 2,2-dioxide (**II**) show that only two conformers are populated, namely **IIa** and **IIb**, whose structures are reported in Figure 1. The energies and the relative populations of **IIa** and **IIb** are reported below:

energy (kcal mol^{-1})	rel population (%)
IIa 18.33	65
IIb 18.70	35

Since **IIa** and **IIb** are not equienergetic, LIS effects should, in principle, be able to lead to the differentiation of the resonance of the prevalently axial oxygen from that of the prevalently equatorial one. In that, as recalled above, the behavior of **II** in the presence of the shift reagent should be different from that of **III**, whose oxygen atoms are expected to be magnetically equivalent and isochronous in the absence as well as in the presence of the shift reagent.

The stereoview and the relevant oxygen-hydrogen distances (in angstroms) of compounds **I**, **II**, and **III**, determined from MM2 calculations, are given in Figure 1. The dihedral angles describing the puckering around sulfur in the same compounds are reported in Table I.

Table I. Dihedral Angles (deg) Describing the Puckering around Sulfur of Compounds I, II, and III According to MM2 Force Field Calculations

	1-2-3-4	*3-2-1-6*	*10-2-3-4*	*11-2-3-4*
I	−55	59	61	−170
IIa	−58	51	−173	60
IIb	54	−47	−63	170

	1-9-8-7	*1-9-8-10*	*1-9-8-11*
III	14	−100	130

The data in Table I show that the presence of the sulfonyl group in the six-membered ring moiety of **I** does not significantly alter the ring geometry with respect to that of cyclohexane; the values of the dihedral angles indicate that there is only a slight flattening of the ring in the region around sulfur. From Figure 1 it is seen that the axial oxygen is less accessible to attack by the lanthanide than the equatorial one, owing to the steric interactions with the syn axial H4$_{ax}$ and the bridgehead H6$_{ax}$ hydrogens.

From the dihedral angles reported in Table I, it is also seen that the energetically more stable conformer **IIb** is more flattened around the sulfur region than **IIa**. This leads to an increase of the distance between O$_{ax}$ and H6$_{ax}$ and to a consequent decrease of the syn axial steric interactions, *cf.* again the hydrogen-oxygen bond distances given in Figure 1. Figure 1 also shows that in the less stable conformer **IIa** the axial oxygen is sterically more hindered than that in **IIb** or in **I**, owing to the interaction with the H7-*endo* hydrogen.

In **III**, the five-membered ring is rigidly held in the half-chair conformation and the oxygen atoms occupy the bisectional position. The five-membered ring is much less puckered than the six-membered one (Table I) and the sulfur region in **III** is much more flattened than that in **I** and **II**. Thus, in **III**, the long-range interactions of the oxygen atoms with the bridgehead axial protons are much smaller, as shown by the oxygen-hydrogen distances reported in Figure 1.

The axial or equatorial arrangement of the oxygen atoms in **I** is easily identified on the basis of their chemical shifts. By analogy with the *trans*-thiadecalin 1,1-dioxide, the axial arrangement can be safely attributed to the oxygen resonating at lower frequency, owing to the shielding γ effect exerted by the syn axial hydrogens.[5] The oxygen atoms of **III** are deshielded by more than 20 ppm compared to those in **I**, in agreement with what has been observed for several substituted thiolane *S,S*-dioxides.[16] In **II**, both $\delta(O_{10})$ and $\delta(O_{11})$ (see Figure 1) are the result of an average between the axial and the equatorial orientations in conformers **IIa** and **IIb**, *i.e.*, $\langle\delta(O_{10})\rangle = 0.35\delta_{eq}(\mathbf{IIa}) + 0.65\delta_{ax}(\mathbf{IIb})$ and $\langle\delta(O_{11})\rangle = 0.35\delta_{ax}(\mathbf{IIa}) + 0.65\delta_{eq}(\mathbf{IIb})$. As recalled above, a single signal is observed for the oxygen atoms at δ = 145.8 ppm and the chemical shift difference between O$_{10}$ (having a greater axial character) and O$_{11}$ (having a greater equatorial character) is smaller than the line width.

The theoretical aspects of lanthanide-sulfone complexation equilibria have been analyzed by Evans, who has demonstrated that the ratio of experimental LISs for the two nonequivalent oxygens of a rigid six-membered ring is equal to the ratio of the two lanthanide binding constants.[10] According to Evans, for low lanthanide-substrate molar ratios only one-to-one complexes are formed between one of the sulfonyl oxygens and the shift reagent and there is no experimental evidence that the

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Table II. ^{17}O **Chemical Shifts**[a] **of Compounds I, II, and III in the Presence of Varying Amounts of Eu(fod)$_3$**

I			II			III	
[Eu(fod)$_3$]/[substrate]	$\delta(O_{eq})$	$\delta(O_{ax})$	[Eu(fod)$_3$]/[substrate]	$\delta(O_{eq})$	$\delta(O_{ax})$	[Eu(fod)$_3$]/[substrate]	$\delta(O)$
0	147.7	123.0	0	145.8	145.8	0	168.2
0.01	141.0	118.5	0.02	140.2	143.8	0.1	136.1
0.02	137.8	117.5	0.045	135.2	140.8	0.2	118.6
0.03	132.4	114.8	0.06	127.2	137.0	0.3	90.4
0.04	128.5	112.7	0.085	123.4	134.0	0.35	75.6
0.05	125.0	111.0	0.13	104.5	124.0		
0.06	121.8	110.0					
0.07	118.0	108.0					

[a] In ppm, with respect to deionized water.

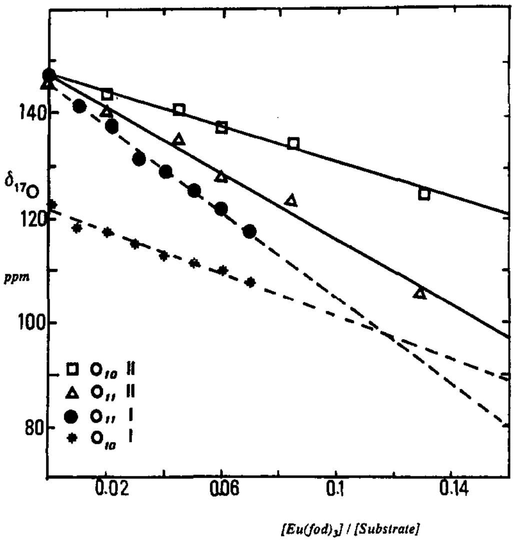

Figure 2. Plot of oxygen chemical shifts of compounds **I** and **II** as a function of the [Eu(fod)$_3$]/[substrate] molar ratio.

sulfonyl group acts as a bidentate ligand, *i.e.*, that Eu(fod)$_3$ forms a complex with both the sulfonyl oxygens of a molecule.[10] In the present work, the maximum addition of lanthanide to **I** and **II** was such that the ratio [Eu(fod)$_3$/[substrate] did not exceed a value of 0.13 and no breaks of the linear plot $\delta(^{17}O)$ *vs* x = [Eu(fod)$_3$/[substrate] were observed, indicating that, in fact, there is no formation of 1:2 complexes in the concentration range used. For **III**, a break of the linear plot $\delta(^{17}O)$ *vs* x = [Eu(fod)$_3$/[substrate] was observed only for values of x higher than 0.4.

Table II gives the ^{17}O chemical shifts of **I**, **II**, and **III** in the presence of varying amounts of Eu(fod)$_3$, while Figure 2 gives the plots of $\delta(^{17}O)$ *vs* x = [Eu(fod)$_3$/[substrate] for **I** and **II**.

Figure 2 shows that addition of increasing amounts of Eu(fod)$_3$ to **I** results in a progressive displacement of the resonance of both the equatorial (O_{11}) and the axial (O_{10}) oxygen toward lower frequencies. As already observed in the case of *trans*-thiadecalin 1,1-dioxide,[10,11] the less hindered equatorial oxygen is more sensitive than the axial one to lanthanide addition. In consequence, the two resonances become progressively closer, than coincident, and then separated again (see Figure 2).[10,11] The regression line of the chemical shift of the axial oxygen *vs* x = [Eu(fod)$_3$]/[substrate] is $\delta(O_{10}) = 121.5 - 201.3x$ ($r = 0.985$), while that of the equatorial oxygen is $\delta(O_{11}) = 145.9 - 412.1x$ ($r = 0.995$). The ratio between the lanthanide–oxygen binding constants for the axial and the equatorial oxygen in **I** is $K_{dias} = K_{O_{eq}}/K_{O_{ax}} = 2.05$, slightly larger than that found for thiadecalin *S,S*-dioxide.[4b]

As in compound **I**, also in compound **II** addition of increasing amounts of Eu(fod)$_3$ results in a progressive displacement of the oxygen resonances toward lower frequencies. More importantly, the different binding rate of O_{10} and O_{11} leads to a progressive increase in their chemical shift difference and two distinct plots of $\delta(O_{10})$ and $\delta(O_{11})$ *vs* x = [Eu(fod)$_3$]/[substrate] may be recognized in Figure 2, *i.e.*, $\delta(O_{10}) = 147.1 - 168.2x$ ($r = 0.990$) and $\delta(O_{11}) = 147.1 - 312.1x$ ($r = 0.991$). The slopes of the regression lines of $\delta(O_{10})$ and $\delta(O_{11})$ *vs* x are remarkably close to the corresponding slopes for the axial O_{11} and the equatorial O_{10} of the rigid compound **I** and $K_{dias} = 1.86$ is of the same order as that of **I**.

In the case of **III** the data reported in Table III show that there is again a progressive displacement of the oxygen resonance upon addition of Eu(fod)$_3$. However, contrary to **II**, a single oxygen resonance is always observed, which varies with x according to the relationship $\delta(O_{10},O_{11}) = 166.4 - 255.8x$ ($r = 0.996$).

The optically active shift reagent tris[3-((heptafluorpropyl)hydroxymethylene)-*d*-camphorato]praseodymium(III) was added to the rigid substrate **I**, in which the sulfonyl group is next to the chiral bridgehead carbons. For the same lanthanide–substrate molar ratios we observed LIS effects of the same magnitude as those observed for addition of Eu(fod)$_3$. Unfortunately, the line broadening consequent to lanthanide addition prevented the possibility of measuring distinct LIS effects for all the species present in solution. In fact, the chemical shift differences between the couple of axial diastereoisomers which should have been formed, on one side, and the couple of equatorial diastereomers on the other became rapidly smaller than the line broadening. However, with careful addition of small amounts of lanthanide we were able to observe *three* (instead of *four*) partially overlapping signals at 117, 111, and 106 ppm for $x = 0.10$. For larger molar ratios, only a single line for the equatorial oxygen and one for the axial oxygen were observed. Although somewhat deceptive, nevertheless this experiment indicates that differentiation of enantiomeric oxygen sites through addition of optically active shift reagents should be possible.

More definite conclusions may be reached on the basis of the LIS effects relative to compounds **II** and **III**.

The $\delta(^{17}O)$ values observed for conformers **IIa,b** are determined by the relative populations of each oxygen atom in the complexed and the free state. The fact that the rates measured for lanthanide complexation of O_{10} and O_{11} of **II** are *smaller* than those for **I** but of the same order, *i.e.*, there is one regression line corresponding to a quasi-equatorial oxygen and one regression line corresponding to a quasi-axial one, indicates that even in the presence of the shift reagent the conformational equilib-

Table III. MNDO and 3-21G* Calculated Atomic Charges[a] of the Oxygen Atoms of I, II, and III

	MNDO		3-21G*	
	SO_{eq}	SO_{ax}	SO_{eq}	SO_{ax}
I	−726	−724	−614	−611
IIa	−728	−727	−621	−611
IIb	−727	−727	−617	−619
III	−726	−726	−611	−611

[a] In millielectrons.

rium remains displaced toward one of the conformers. It is likely that the position of the conformational equilibrium of the complexed forms of **II** is close to that of the uncomplexed forms. However, this point is irrelevant to our purpose, since the only requirement needed for increasing differentiation of oxygen chemical shifts is that the different forms present in solution remain energetically different. What is important from our point of view is the fact that the LIS data for **II** indicate that $Eu(fod)_3$ complexation may function as an *amplifier* of the chemical shift difference, $\Delta\delta$, between sulfonyl oxygens and may even allow fine tuning of such a $\Delta\delta$ value.

The rate of variation of $\delta(O_{10},O_{11})$ with x in **III** is closer to that of the axial oxygen than to that of the equatorial oxygen of **I**. If LIS effects are entirely steric in origin, this is indicative of nonnegligible steric hindrance to complexation. However, it cannot be excluded *a priori* that the electronic features of the sulfonyl group in **III** (in particular, the negative charge on the oxygen atoms) are somewhat different from those in **I** and **II**, since in **III** the sulfonyl group belongs to the five-membered moiety while in **I** and **II** it belongs to the less strained six-membered moiety. To have an indication of the possible changes of the negative charge on oxygen on going from **I** to **III**, we have performed semiempirical MNDO and ab initio 3-21G* single point calculations on the optimized MM2 geometries of **I**, **II**, and **III**. Table III gives the atomic charges of the sulfonyl oxygens calculated at the different levels. The different levels of calculations, one of which includes the d orbitals on sulfur, give different absolute values for the total charge of the oxygen atoms but the trend of variation with the structure is the same. In fact, for both kinds of calculations the atomic charges of the sulfonyl oxygens are always the same, independent of the axial or equatorial orientation or of the geometrical characteristics of the system being examined. Thus, the fact that the rate of variation of $\delta(O_{10},O_{11})$ with x in **III** is closer to that of the axial rather than to that of the equatorial oxygen of **I** can safely be related to steric factors. In **III**, the major source of steric hindrance to lanthanide–oxygen complexation is not the 1,3 interactions with the bridgehead hydrogens (*cf.* the hydrogen–oxygen distances reported in Figure 1) but rather the 1,2 interactions with the vicinal hydrogens. In this system, in fact, each oxygen atom is nearly eclipsed by a syn vicinal hydrogen, which, according to MM2 calculations, forms with it a dihedral angle of only 15°.

In conclusion, our data are good supporting evidence for the nonequivalent of the oxygen atoms in a sulfone in terms of LIS interactions. Our results also confirm that the formation of lanthanide–sulfone complexes is extremely sensitive to steric factors. Finally, our data show that LIS effects on oxygen chemical shifts are a fine and very useful analytical tool. Applications to functional groups such as the "soft" (from the point of view of the interactions of the oxygen atom with the rest of the molecular skeleton[8]) sulfinyl group, -SO-, where sulfur may be chiral, appear particularly promising.

Experimental Section

Materials. ***trans*-2-Thiabicyclo[4.3.0]nonane 2,2-dioxide (I)** was prepared (95%) by MCPBA oxidation of *trans*-2-thiabicyclo[4.3.0]nonane 2-oxide[12] and crystallized from hexane: mp 67–68 °C; ^1H NMR ($CDCl_3$) δ 2.4–3.1 (m, 3 H), 1.5–2.1 (m, 9 H), 1.0–1.4 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 65.6 (C_1), 52.0 (C_3), 45.4 (C_6), 31.1, 29.5, 24.5, 21.1, 20.3. Anal. Calcd for $C_8H_{14}O_2S$: C, 55.14; H, 8.10. Found: C, 54.93; H, 8.08.

***cis*-2-Thiabicyclo[4.3.0]nonane 2,2-dioxide (II)** was obtained (98%) by MCPBA oxidation of *cis*-2-thiabicyclo[4.3.0]-nonane 2-oxide[12] and crystallized from hexane: mp 70–71 °C; ^1H NMR ($CDCl_3$) δ 3.2 (m, 1 H), 2.9 (m, 2 H), 2.5 (m, 1 H), 1.3–2.1 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 63.6 (C_1), 48.4 (C_3), 41.1 (C_6), 30.1, 25.1, 24.1, 21.8, 21.4. Anal. Calcd for $C_8H_{14}O_2S$: C, 55.14; H, 8.10. Found: C, 55.10; H, 8.13.

***trans*-8-Thiabicyclo[4.3.0]nonane 8,8-dioxide (III)** was prepared (97%) by MCPBA oxidation[13,15] of *trans*-8-thiabicyclo-[4.3.0]nonane[17] and crystallized from cyclohexane: mp 70–71 °C; ^1H NMR ($CDCl_3$) δ 3.2 (dd, 1 $H7_{eq}$ and 1 $H9_{eq}$), 2.6 (t, 1 $H7_{ax}$ and 1 $H9_{ax}$), 1.8 (m, 6 H), 1.2 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 58.9 (C_7 and C_9), 42.1 (C_1 and C_6), 30.1, 25.3. Anal. Calcd for $C_8H_{14}O_2S$: C, 55.14; H, 8.10. Found: C, 55.21; H, 8.09.

NMR. ^{17}O NMR spectra were obtained at the probe temperature with a Bruker CXP-300 spectrometer (working frequency 40.06 MHz), using the high power probe equipped with a solenoid insert and a home-made 15-mm horizontal tube. A spin–echo pulse sequence with alternate phase of the first pulse was employed. **I**, **II**, and **III** were stored over P_2O_5 for several days before use as were the shift reagents. Solutions were 200 mM in anhydrous CH_2Cl_2 and the chemical shifts were measured with respect to deionized water as external reference. Weighed increments of tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato)europium, [$Eu(fod)_3$], or tris[3-((heptafluorpropyl)-hydroxymethylene)-*d*-camphorato]praseodymium(III) were added to the solution of sulfones **I–III**.

Computational Details. All calculations were carried out with a Microvax 3500, using the MOPAC 6.0[18] and the Gaussian 86[19] programs for semiempirical and *ab initio* calculations, respectively, and the N. L. Allinger MM2(87)[18] program for molecular mechanics calculations.

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(19) Gaussian 86. Frisch, M. G.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; DeFrees, D. J., Fox, D. J.; Whiteside, R. A.; Seeger, R. C.; Melius, C. F.; Baker, J.; Martin, L. R.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. *Gaussian Inc.*, Pittsburgh PA.