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Protonated and Methylated Dimethyl Sulfoxide Cations and Dications. DFT/GIAO-MP2 NMR Studies and Comparison with Experimental Data[1]

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Energies, electronic structures, and thermodynamics of protonated and methylated dimethyl sulfoxide (DMSO) cations and dications were calculated using the density functional theory (DFT) method. The O-protonated structure **2** was found to be 37.0 kcal/mol more stable than the S-protonated **3**. For diprotonated DMSO dication, the O,O-diprotonated form **6** was found to be the global minimum, more stable by 20.8 kcal/mol than O,S-diprotonated **7**. Interestingly, for dimethylated DMSO dication, O,O-dimethylated **11** and O,S-dimethylated **12** are isoenergetic. ^{13}C, ^{17}O, and ^{33}S NMR chemical shifts of the cations and dications were calculated using the GIAO-MP2 method and compared with the available experimental data.

Introduction

In 1978, Olah et al. studied[2] protonation and methylation of dimethyl sulfoxide in superacid media. When dimethyl sulfoxide was dissolved in $HSO_3F-SbF_5-SO_2$ at −100 °C, a broad singlet peak at δ ^1H 6.53 was observed that indicated the formation of long-lived protonated dimethyl sulfoxide. However, the site of protonation was difficult to ascertain on the basis of ^1H and ^{13}C NMR chemical shifts. Also, since the absorption at δ ^1H 6.53 is broadened, it could indicate the possibility of an exchanging system in $HSO_3F-SbF_5-SO_2$ media involving diprotonated dimethyl sulfoxide. Similarly, when dimethyl sulfoxide was treated with an equimolar amount of CH_3F-SbF_5 in SO_2 at −30 °C, O-methylated dimethyl sulfoxide was observed.[2] Olah et al. also calculated the possible protonated and diprotonated dimethyl sulfoxide structures by the semiempirical MINDO/3 method.[2] Recently, Turecek reported[3] a theoretical study on the relative stabilities of several C_2H_6OS molecules and protonated $C_2H_7OS^+$ ions. Among C_2H_6OS isomers dimethyl sulfoxide is the most stable species, followed by methyl methanesulfenate. Among $C_2H_7OS^+$ ions O-protonated dimethyl sulfoxide was found to be most stable, while S-protonated dimethyl sulfoxide is significantly less stable.

In the course of our continuing studies on the protosolvolytic activation of electrophiles to give superelectrophiles[4] we have previously shown that it is possible to protonate nonbonded electron pairs of onium ions. Moreover, even the parent hydronium ion (H_3O^+) can be further protonated to form the corresponding *gitonic* onium dication.[5] In the present study we report density functional theory (DFT)[6] calculational studies of protonated (methylated) and diprotonated (methylated) dimethyl sulfoxide ions to establish their structures and relative stabilities. We also report the calculated NMR chemical shifts of these ions by ab initio correalted GIAO-MP2 method and their comparison with the available experimental results.

Calculations

Calculations were performed by using the Gaussian 98 program.[7] The geometry optimizations were carried out using the DFT[6] method at the B3LYP[8]/6-311+G** level.[9a] Vibrational frequencies at the B3LYP/6-311+G**//B3LYP/6-311+G** level were used to characterize stationary points as minima (number of imaginary frequency (NIMAG) = 0) and to evaluate zero-point vibrational energies (ZPE), which were scaled by a factor of 0.96. Final energies were calculated at the B3LYP/6-311+G**//B3LYP/6-311+G** + ZPE level. Calculated energies are given in Table 1. B3LYP/6-311+G** geometrical parameters and final energies will be discussed throughout, unless stated otherwise. NMR chemical shifts were calculated by the GIAO method.[9b] GIAO-MP2[10] calcula-

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Table 1. Total Energies (−au), ZPE,[a] and Relative Energies (kcal/mol)[b]

no.	B3LYP/6-311+G**// B3LYP/6-311+G**	ZPE	rel energy (kcal/mol)
1	553.267 72	47.5	214.8
2	553.621 44	54.7	0.0
3	553.561 92	54.3	37.0
4	592.938 12	71.5	0.0
5	592.915 20	71.5	14.4
6	553.705 54	59.5	0.0
7	553.672 43	59.5	20.8
8	593.048 05	77.1	0.0
9	593.047 73	76.9	0.0
10	593.010 54	76.5	22.9
11	632.380 79	94.3	0.0
12	632.380 21	93.9	0.0

[a] Zero point vibrational energies (ZPE) at B3LYP/6-311+G**//B3LYP/6-311+G** scaled by a factor of 0.96. [b] Relative energies at the B3LYP/6-311+G**//B3LYP/6-311+G** + ZPE level.

tions using the tzp/dz basis set[10,11] have been performed with the ACES II program.[12] The ^{13}C, ^{17}O, and ^{33}S NMR chemical shifts were referenced to TMS [calculated absolute shift i.e σ(C) = 198.7], H_2O [σ(O) = 349.2], and CS_2 [σ(S) = 564.5]. For comparison, GIAO−SCF calculations using the tzp/dz basis set have also been performed with the ACES II program. The ^{13}C, ^{17}O, and ^{33}S NMR chemical shifts were referenced to TMS [calculated absolute shift i.e σ(C) = 192.9], H_2O [σ(O) = 3324.8], and CS_2 [σ(S) = 496.9]. Calculated chemical shifts are listed in Table 2.

Results and Discussion

Calculated structures of dimethyl sulfoxide **1** and O- and S-protonated dimethyl sulfoxide (DMSO) **2** and **3** (Figure 1) agree well with those recently reported.[2] The O-protonated structure **2** is 37.0 kcal/mol more stable than S-protonated **3**. Deprotonation of **2** was found unfavorable by 214.8 kcal/mol (Table 3). We also calculated O- and S-methylated DMSO **4** and **5**, respectively (Figure 1). Again the O-methylated form **4** is more stable than the S-methylated form **5**. However, the difference of 14.4 kcal/mol is significantly less than that of between **2** and **3**. Dissociation of **4** into DMSO and CH_3^+ is also calculated to be endothermic by 107.1 kcal/mol (Table 3). Ion **4** has been prepared by Olah et al. by treating DMSO with an equimolecular solution of $CH_3F{-}SbF_5$ in SO_2 at −30° C. Ion **5** also has been experimentally observed.[13]

The ^{13}C, ^{17}O, and ^{33}S NMR chemical shifts of **1**-**5** were calculated at the correlated GIAO-MP2 method using DFT optimized geometries (Table 2). Calculated δ^{13}C of neutral DMSO **1** is 43.5 and matches with the experimental value of 37.1 ppm. The calculated δ^{13}C of O-protonated DMSO **2** (40.0) also matches well with the experimental value of 34.3.[2] On the other hand, the calculated δ^{13}C of S-protonated DMSO **3** is slightly deshielded at δ^{13}C 43.4 compared to that of O-protonated DMSO **2**. The calculated δ^{13}C of $-SCH_3$ and $-OCH_3$ carbons of methylated DMSO **4** are 39.0 and 70.0, respectively, and can be compared with experimental values of 32.7 and 60.4. Similarly, the calculated δ^{13}C of **5** (45.8) compares well with the experimental value of 39.8.[2,13]

Table 2. Experimental and Calculated NMR Chemical Shifts[a]

no.	atom	GIAO-SCF	GIAO-MP2	expt
1	^{13}C	37.4	43.5	37.1
	^{17}O	17.5	54.5	
	^{33}S	222.3	332.0	
2	^{13}C	35.0	40.0	34.3
	^{17}O	30.1	42.4	
	^{33}S	253.6	356.9	
3	^{13}C	36.9	43.4	
	^{17}O	50.2	83.5	
	^{33}S	204.7	275.9	
4	^{13}C (SCH_3)	33.9	39.0	32.7
	^{13}C (OCH_3)	63.9	70.7	60.4
	^{17}O	24.3	47.9	
	^{33}S	262.6	373.5	
5	^{13}C	38.6	45.8	39.8
	^{17}O	61.3	102.5	
	^{33}S	226.0	311.6	
6	^{13}C	49.7	56.0	
	^{17}O	30.5	53.2	
	^{33}S	814.7	856.2	
7	^{13}C	42.2[b]	47.8[b]	
	^{17}O	41.9	55.9	
	^{33}S	251.7	342.5	
8	^{13}C (SCH_3)	43.6[b]	49.6[b]	
	^{13}C (OCH_3)	105.6	113.4	
	^{17}O	30.7	59.6	
	^{33}S	586.6	672.1	
9	^{13}C	42.0[c]	49.0[c]	
	^{17}O	59.5	81.6	
	^{33}S	287.7	395.4	
10	^{13}C (SCH_3)	39.3[b]	45.2[b]	
	^{13}C (OCH_3)	91.5	98.8	
	^{17}O	31.8	57.3	
	^{33}S	251.8	346.2	
11	^{13}C (SCH_3)	38.7[b]	44.4[b]	
	^{13}C (OCH_3)	89.6	98.2[c]	
	^{17}O	21.6	58.2	
	^{33}S	532.5	640.2	
12	^{13}C (SCH_3)	38.9[c]	45.6[c]	
	^{13}C (OCH_3)	78.9	85.5	
	^{17}O	45.7	138.7	
	^{33}S	281.3	393.4	

[a] Experimental and calculated ^{13}C, ^{17}O, and ^{33}S NMR chemical shifts were referenced to TMS, H_2O, and CS_2, respectively. [b] Average of the two carbons. [c] Average of the three carbons.

The second protonation of O-protonated DMSO **2** can take place either on oxygen or on sulfur. Both O,O-diprotonated DMSO dication **6** and O,S-diprotonated DMSO dication **7** are minima on the potential energy surface. Interestingly, the O,O-diprotonated structure **6** is significantly more stable than the O,S-diprotonated structure **7** by 20.8 kcal/mol. This shows that in cation **2** the oxygen atom is a much better electron donor than the sulfur atom. A significant increase of S−O bond length in **6** (1.817 Å) compared to **2** (1.641 Å) is observed on second protonation. Deprotonation of dication **6** is substantially endothermic by 48.0 kcal/mol. Similar to protonated dications when O-protonated, O-methylated dication **8** and O-protonated, S-methylated dication **9** were calculated, in contrast to diprotonated dications, methylated dications **8** and **9** are comparable energetically. Deprotonation of **8** is endothermic by 63.4 kcal/mol. Dissociation of **8** into **2** and CH_3^+ is also endothermic but by only 37.1 kcal/mol (Table 3). The isomeric O-methylated, S-protonated DMSO dication **10** was calculated to be 22.9 kcal/mol less stable than **8**.

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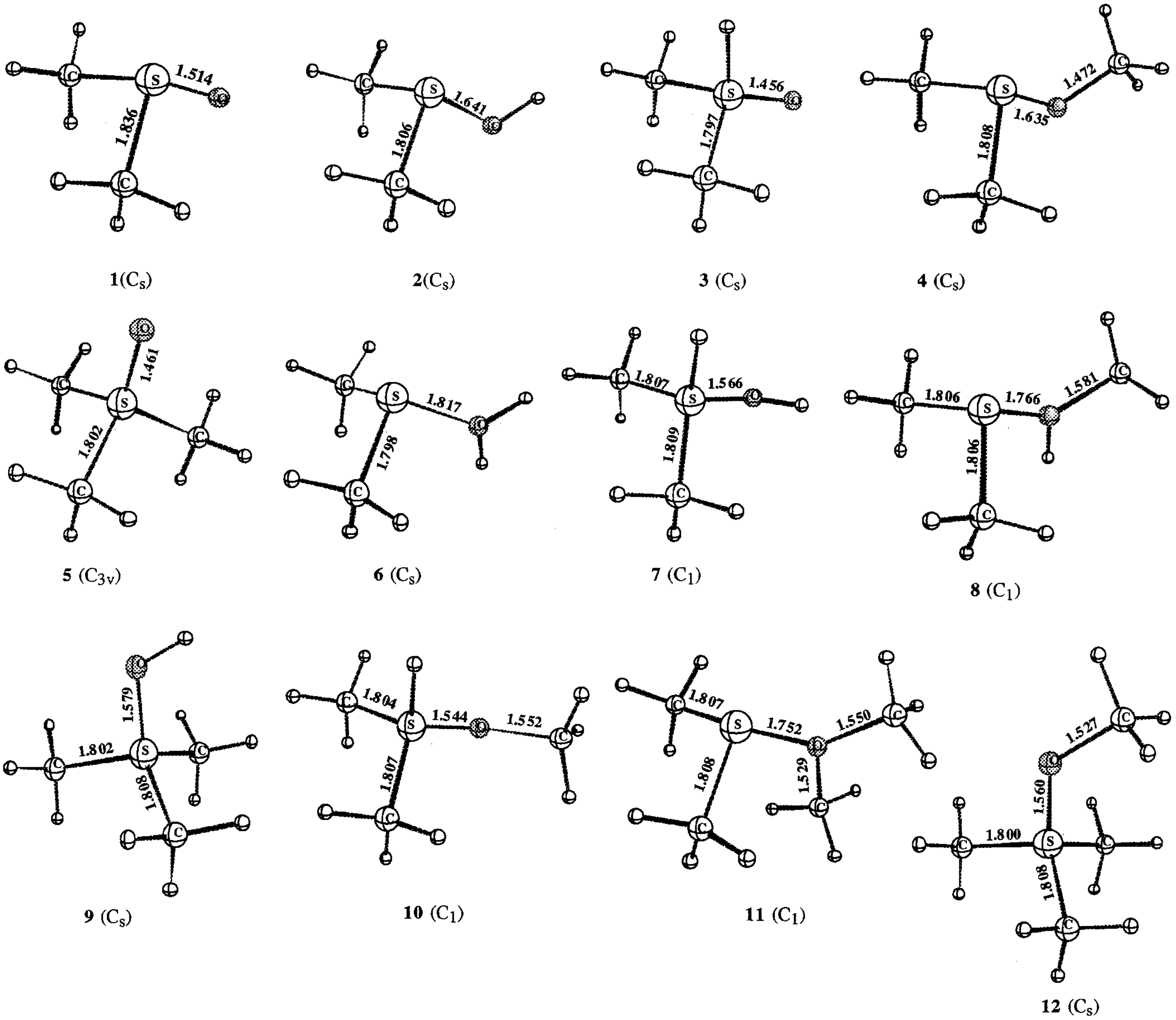

Figure 1. B3LYP/6-311+G** structures of **1**−**12**.

Table 3. Thermodynamics of the Dissociation of 1−5b[a]

dissociation process	ΔH (kcal/mol)
2 → **1** + H^+	214.8
4 → **1** + CH_3^+	107.1
6 → **2** + H^+	48.0
8 → **4** + H^+	63.4
8 → **2** + CH_3^+	37.1
11 → **4** + CH_3^+	−34.6

[a] At the B3LYP/6-311+G**//B3LYP/6-311+G** + ZPE level.

^{13}C, ^{17}O, and ^{33}S NMR chemical shifts of **6-10** were also calculated (Table 2). The calculated $\delta^{13}C$ of dication **6** is 56.0, 16.0 ppm more deshielded than that of monocation **2**. The calculated $\delta^{13}C$ of the $-SCH_3$ and $-OCH_3$ carbons of **8** are 49.6 and 113.5, respectively. The calculated $\delta^{33}S$ of dication **6** was found to be extremely deshielded at 856.2 ppm.

Structures of O,O-dimethylated DMSO dication **11** and O,S-dimethylated DMSO dication **12** were calculated. The dications **11** and **12** were found to be energetrically similar. Unlike dissociation of other dications, dissociation of **11** into **4** and CH_3^+ is exothermic by 34.6 kcal/mol. Calculated ^{13}C, ^{17}O, and ^{33}S NMR chemical shifts of **11** and **12** are listed in Table 2. Structure **11** can also be considered a tetramethylthioperoxonium dication. The related tetramethylperoxonium dication $(CH_3)_2OO(CH_3)_2^{2+}$ was calculated to be a kinetically stable species at the MP2/6-31G* level but was not yet observed experimentally as a persistent ion.[14] The parent trimethylperoxonium ion, $CH_3OO(CH_3)_2^+$, has been prepared by the reaction of CH_3OOCH_3 and $CH_3F{-}SbF_5$ in SO_2 at −78 °C and characterized by ^1H and ^{13}C NMR spectroscopy.[14]

The present work helps to reveal the nature of interaction of DMSO, an important dipolar aprotic solvent, with acids, superacids, and electrophiles. Olah et al. in their studies reported[2] dimethyl sulfoxide in $HSO_3F{-}SbF_5{-}SO_2$ at −100 °C to give a broadened singlet peak at δ^1H 6.53. This broad peak indicates that either a proton exchange process is occurring at the NMR time scale between the protonated DMSO cation and the acid or, based on our present study, more probably an exchange involving a

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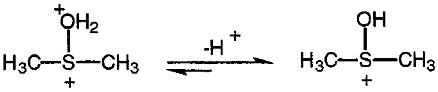
small equilibrium concentration of diprotonated DMSO dication (or protosolvated[4] dication) with the monocation is taking place. Similar monocationic intermediates are involved in DMSO-based oxidation chemistry (Moffatt, Swern, and related chemistry). The O,O-diprotonated DMSO dication **6** is the most probable candidate to be involved in such an equilibrium.



Conclusions

Structures and energies of protonated and methylated dimethyl sulfoxide cations and dications were calculated using the density functional theory method. The O-protonated structure **2** is 37.0 kcal/mol more stable than the S-protonated **3**. For dications, O,O-diprotonated DMSO **6** and O,S-diprotonated DMSO **7** were found to be energy minima. Structure **6** is 20.8 kcal/mol more stable than **7**. On the other hand, O,O-dimethylated DMSO dication **11** and O,S-dimethylated **12** are energetrically identical. ^{13}C, ^{17}O, and ^{33}S NMR chemical shifts of the studied ions were also calculated using the GIAO-MP2 method. Calculated ^{13}C NMR chemical shifts of DMSO **1**, protonated DMSO **2**, and methylated DMSO **4** and **5** agree well with the experimental data.

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