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MM3 CALCULATIONS ON SULFOXIDES

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The structures of several sulfoxides, including dimethyl sulfoxide and pentamethylene sulfoxide, were fitted with the MM3 force field to existing experimental data from electron diffraction and microwave spectroscopy. The vibrational spectra were also fitted for dimethyl sulfoxide. The torsional parameters could not be determined from existing experimental data, so the torsional profile for methyl ethyl sulfoxide was fitted to *ab initio* values.

INTRODUCTION

Earlier papers have described the MM3 force field which was used for calculations on hydrocarbons and for several kinds of functionalized molecules including alcohols and ethers,[2] amines,[3] sulfides,[4] alkenes,[5] aromatic hydrocarbons,[6] nitro compounds,[7] aldehydes and ketones,[8] carboxylic acids and esters[9] and additional functional groups.[10] It seemed desirable to extend these calculations to sulfoxides, and this extension is the subject of the present paper.

RESULTS AND DISCUSSION

The procedure used began with the MM2 force field as a starting point.[11,12] Sulfoxides were previously treated with MM2 in a somewhat cursory fashion.[11–13] Because of various changes in the potential functions and in the hydrocarbon parameters on going from MM2 to MM3, preliminary structures were initially calculated using the MM3 force field but with the MM2 parameters, and these were only fair. Systematic adjustments were then made to the various parameters so as to improve the structures and vibrational spectra.

The parameters required to define the force field for these compounds are given in Table 1. They must be added to those given previously for hydrocarbons to obtain the full force field. These parameters supersede the preliminary set that was included in MM3(90) and MM3(94), and were marked with ** to indicate that they were preliminary.[14]

Vibrational spectra

The vibrational spectra were calculated for the simple model compounds methyl sulfoxide, dimethyl sulfoxide and methyl ethyl sulfoxide. Since there are not enough experimental vibrational data available to define all of the force parameters, *ab initio* calculations with full geometry optimization at the MP2/6–31G* level were carried out for methyl sulfoxide and methyl ethyl sulfoxide. The scale factors (0·93–0·95) were determined based on a comparison of the experimental and MP2/6–31G*-calculated vibrational frequencies of dimethyl sulfoxide, and were used to scale all spectra calculated by *ab initio* methods. The MM3-calculated vibrational frequencies for the three molecules are given in Tables 2–4, and they have an overall rms error of 25 cm^{-1} with an average error of 0 cm^{-1}, compared with the experimental/*ab initio* spectra.

Structures and energies of sulfoxides

The molecular structures of five compounds, some in several conformers, were examined and are presented in Tables 5–9, together with the corresponding experimental or *ab initio* values. The conformational equilibria of 4-substituted thiane-1-oxides were also studied.

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Table 1. MM3 force field for sulfoxides

Torsional parameters (kcal mol^{-1})			
Type	V_1	V_2	V_3
1–17–1–5	0·000	0·000	0·600
5–1–17–7	0·000	0·000	0·175
5–1–17–5	0·000	0·000	0·700
1–1–17–7	−1·100	−0·150	0·175
1–1–17–1	−0·800	0·000	1·200
1–1–17–5	−0·800	−0·700	0·100
5–1–1–17	0·000	0·000	0·125
17–1–1–17	0·000	0·000	0·125
1–1–1–17	1·500	−0·800	0·100
6–1–1–17	−0·800	−1·200	−0·700

Bond stretching parameters			
Bond	K_s(mdyn Å^{-1})	l_0(Å)	Bond moment
1–17	2·95	1·800	0·600
7–17	7·10	1·487	−3·550
5–17	3·17	1·372	0·400

Electronegativity effect parameters (Å)				
Bond	Type	Atom type	Attached atom type	Correction
1	17	17	5	0·0050
7	17	17	5	0·0080
1	1	1	17	−0·0100

Angle bending parameters			
Angle	K_θ(mdyn Å rad^{-2}	θ_0(°)	Type
1–17–7	0·800	105·6	1
1–17–7	0·800	107·8	2
1–17–1	1·200	94·4	
1–17–5	0·860	90·0	1
7–17–5	0·860	109·6	1
5–1–17	0·715	107·7	3
5–1–17	0·715	105·0	2
5–1–17	0·715	105·0	1
1–1–17	0·650	106·0	3
1–1–17	0·650	104·7	2

Methyl sulfoxide

Since no experimental data could be found for this molecule (it is the unstable tautomer of methyl sulfenate[28]), *ab initio* calculations were employed to give the both vibrational spectrum and the molecular structure. The *ab initio* and MM3-calculated results are given in Table 5, and they are very consistent with each other, except for the the S=O bond length. This bond appeared longer in the MP2/6–31G* calculation. It is common that bond lengths, especially those for double bonds, are overestimated by *ab initio* calculations when electron correlation is included at the MP2 level.

Dimethyl sulfoxide

The various force and structural parameters were optimized based on the available experimental data for dimethyl sulfoxide, including the determination of the scale factors for the vibrational frequencies of other sulfoxides when calculated by the MP2/6–31G* method.

The MM3 structure of dimethyl sulfoxide is summarized in Table 6, together with the corresponding the microwave and x-ray data, including the dipole moments and the methyl group rotational barrier. The moments of inertia in MM3 are calculated as r_g values. Normally, when we go from an r_z geometry (MW structure) to an r_g geometry, the moments of inertia increase by about 1%. Here the calculated values are in this range as expected (see Table 6).

Methyl ethyl sulfoxide

Methyl ethyl sulfoxide is one of the simple molecules used to define the parameters such as the CCS bond angle and the CCSC torsional constants. The rotational energy profile for CCSC in methyl ethyl sulfoxide is not known experimentally, and was calculated using a 6–31G* basis set at the MP2 level. The central C—S bond of this molecule was rotated from 0 to 360° in 30° increments, and the full potential function was obtained. The MM3-calculated rotational curve is in good agreement with that obtained by MP2/6–31G* calculation. While the agreement could be improved, it was desirable to fit well the equilibrium data on thiane oxide (see later), and the parameters chosen were a compromise.

The optimized geometries of the three stable conformations of methyl ethyl sulfoxide are presented in Table 7, along with the relative conformational energies. The structural parameters do not vary much among the different conformers, except for the CCS angles. We could not accurately fit the CCS angles for the different conformers all at the same time, so compromised values were used here. A torsion–bend interaction could be used to reduce this error, but this is beyond the scope of MM3. The MP2/6–31G* calculation gave a longer S=O bond length than that from MM3, as discussed previously. In fact, the HF method calculated the length of this bond as 1·487 Å, which is closer to the MM3 result. The experimental bond length is usually between the HF calculated value and the one calculated by inclusion of electron correlation at the MP2 level. Hence the S=O bond parameters defined in the MM3 force field appear reasonable.

Table 2. Vibrational frequencies of methyl sulfoxide (C_1) (cm^{-1})

MP2/6–31G*[a]	MM3	Difference (MM3 – *ab initio*)	Assignment
3014	3009	−5	CH asym. stretch
3000	3007	7	CH asym. stretch
2899	2900	1	CH sym. stretch
2337	2335	−2	SH stretch
1462	1430	−32	CH_3 def.
1433	1421	−12	CH_3 def.
1345	1339	−6	CH_3 def.
1126	1138	12	CH_3 rock., OSH bend.
1099	1044	−55	SO stretch
1036	1003	−33	CH_3 rock.
942	984	42	CH_3 rock.
802	776	−26	CH_3 rock., OSH bend.
685	691	6	CS stretch
293	302	9	CSO bend.
235	225	−10	CH_3 torsion
Rms		23	
Av.		−7	

[a] The frequencies for CH stretching were scaled down to 93% of the original values and the others are scaled to 95%.

Table 3. Vibrational frequencies of dimethyl sulfoxide (C_s) (cm^{-1})

IR[15]	IR[16] (gas)	IR[17] (gas)	IR[18] (gas)	MM3	Difference (MM3 – IR[a])	Symmetry	Assignment
3010	2973	3001	3001	3011	1	*A′*	CH stretch
3010	2973	3001	3001	3011	1	*A″*	CH stretch
3010	2973	3001	3001	3011	1	*A″*	CH stretch
3010	2973	3001	3001	3009	−1	*A″*	CH stretch
2933	2908	2922	2922	2902	−31	*A′*	CH stretch
2933	2908	2922	2922	2902	−31	*A″*	CH stretch
1419	1419	1440	1440	1439	20	*A′*	CH_3 def.
1455	1455	1419	1419	1430	−25	*A″*	CH_3 def.
1405	1405	1419	1419	1422	17	*A′*	CH_3 def.
1440	1440	1404	1404	1418	−22	*A″*	CH_3 def.
1304	1304	1310	1310	1343	39	*A″*	CH_3 def.
1319	1319	1293	1293	1339	20	*A″*	CH_3 def.
1102	1102	1101	1101	1104	2	*A′*	SO stretch
1016	1006	1004	1004	1020	4	*A′*	CH_3 rock.
953	1016	915	915	1000	47	*A″*	CH_3 rock.
1006	915	926	930	992	−14	*A′*	CH_3 rock.
933	929	881	881	977	44	*A″*	CH_3 rock.
695	689	692	685	700	5	*A″*	CS asym. stretch
672	672	661	661	672	0	*A*	'CS sym. stretch
333	333	329	—	333	0	*A″*	CSO sym. def.
382	382	376	376	309	−73	*A′*	CSO asym. def.
308	308	—	—	297	−11	*A′*	CSC def.
—	—	—	231	229	−2	*A′*	CH_3 torsion
—	—	—	207	206	−1	*A″*	CH_3 torsion
Rms					25		
Av.					0		

[a] The rms calculation is based on the observed vibrational frequencies from Ref. 15, except the CH_3 torsional frequencies, which were obtained from Ref. 18.

Table 4. Vibrational frequencies of methyl ethyl sulfoxide (C_1) (cm^{-1})

MP2/6–31G*[a]	MM3	Difference(MM3 – *ab initio*)	Assignment
3001	3011	10	CH_3 asym. stretch
2997	3010	13	CH_3 asym. stretch
2993	2979	−14	C–CH_3 asym. stretch
2977	2977	0	C–CH_3 asym. stretch
2951	2975	24	CH_2 asym. stretch
2895	2918	23	C–CH_3 sym. stretch
2892	2902	10	CH_3 sym. stretch
2887	2883	−4	CH_2 sym. stretch
1490	1466	−24	C–CH_3 asym. def.
1479	1452	−27	C–CH_3 asym. def.
1453	1436	−17	CH_3 asym. def.
1438	1441	3	CH_2 def.
1429	1420	−9	CH_3 asym. def.
1395	1386	−9	C–CH_3 sym. def.
1336	1346	10	CH_3 sym. def.
1284	1341	57	CH_2 wagging.
1249	1224	−25	CH_2 twisting.
1085	1090	5	SO stretch
1066	1023	−43	C–CH_3 rock., CH_3 rock.
1032	1015	−17	C–CH_3 rock.
975	982	7	C–C stretch
945	1004	59	CH_3 rock.
940	985	45	CH_3 rock.
769	813	44	CH_2 rock.
689	695	6	CS stretch
643	658	15	Cs stretch
379	354	−25	CCS bend.
358	305	−53	CSO bend.
280	294	14	CSO bend., CCSO torsion
229	233	4	CCS, CSC bend.
204	219	15	CH_3 torsion
194	207	13	CH_3 torsion
91	106	15	CCSC torsion
Rms		26	
Av.		4	

[a] The wavenumbers for CH stretching are scaled down to 93% of the original values and the others are scaled down to 95%.

Table 5. Structure of methyl sulfoxide

Parameter[a]	MP2/6–31G*	MM3
S—C	1·810	1·808
S—O	1·508	1·496
S—H	1·375	1·373
C—H (av.)	1·092	1·109
C—S—O	108·5	108·4
C—S—H	90·6	91·1
O—S—H	109·9	109·8

[a] Bond lengths in Å, angles in degrees.

Isopropyl sulfoxide

The structure of isopropyl sulfoxide was studied by both *ab initio* and molecular mechanics calculations. A total of three conformers were found. The calculated relative energies of the different conformations are presented in Table 8, along with the optimized geometries calculated by both methods.

Thiane-1-oxides

In the parent thiane-1-oxide, and in the 4-substituted thiane-1-oxides, the isomer bearing the axial oxygen was found experimentally to be more stable.[22] There is some variation in the equilibrium composition, depending on the conditions and on the identity of the

Table 6. Structure of dimethyl sulfoxide

Parameter[a]	MW[19]	X-ray (−60 °C)[20]	MM3
S—C	1·799 (5)	1·812(14)	1·806
S—C	1·799 (5)	1·801(9)	1·806
S—O	1·485 (6)	1·471(8)	1·488
C—S—C	96·6 (3)	97·9(5)	96·4
C—S—O	106·6 (3)	107·0(6)	106·6
C—S—O	106·6 (3)	107·4(6)	106·6

	Rotational barrier (kcal mol^{-1})		
	Exp.[19]	MM3	Diff. (MM3 − Exp.)
CH_3 group	2·94	2·82	−0·12

	Dipole moment		
	Exp[21]	MM3	Diff. (MM3 − Exp.)
	3·9 ± 0·1	3·96	0·06

	Moments of inertia		
	Exp.[19]	MM3	Diff.
I_a	11·929	12·034	0·88%
I_b	12·146	12·245	0·82%
I_c	19·896	20·048	0·76%

[a] Bond lengths in Å, angles in degrees.

4-substituent (see Table 9). However, there is a general marked preference for the isomer with axial oxygen. The best value for the conformational free energy difference of the sulfoxide group within the six- membered ring is probably 1·3 kcal mol^{-1} (1 kcal = 4·184 kJ) favoring axial, as was obtained with the very bulky non-polar 4-*tert*-butyl group in both thermal and H^+-catalyzed equilibrations. A low-temperature (−90 °C) NMR study of unsubstituted thiane-3,3,5,5-d_4-oxide showed the conformational energy for the thiane oxide function to be 175 ± 30 cal mol^{-1} (62% axial isomer).[23] However, no experimental details, i.e. concentration, were provided. The conformational energy difference between the thiane-1-oxides (R = H) predicted by MM3 calculations was 1·55 kcal mol^{-1}, favoring the conformer with the axial oxygen. The 4-methylthiane-1-oxides (No. 3 in Table 9) also showed the same trend. The *cis* conformer is more stable than the *trans* conformer by about 1·57 kcal mol^{-1}.

There is a serious apparent anomaly here. On the one hand, equilibrium experiments have indicated that the energy difference between the axial and equatorial thiane-1-oxide is about 1·3 kcal mol^{-1}, whereas the NMR study indicates that it is only 0·2 kcal mol^{-1}, favoring the axial conformation in both cases. The *ab initio* value obtained from methyl ethyl sulfoxide is consistent with the higher but not with the lower value. Our interpretation of the results is that the 1·3 kcal mol^{-1} value is the correct value for the molecule in the gas phase, or under conditions which approximate that in terms of dilution (i.e. in a polar solvent, at high temperatures and at high dilution). Polar molecules often tend to dimerize (or form higher aggregates). Cyclohexanone has been shown[24] by freezing-point measurements to be a dimer in 0·01 M solution in cyclohexane, but it is a monomer in benzene or other polar solvents at this concentration, in the range of 0–10 °C. In the NMR work discussed here, the temperature is very low (−90 °C), and the concentration is probably substantial. Thiane-1-oxide has a geometry similar to that of cyclohexanone, with a single large dipole in an unhindered environment, and it should dimerize with a similar electrostatic energy and overall free energy. If so, the 1·3 kcal mol^{-1} value would appear to apply to the monomer, and the 0·2 kcal mol^{-1} would apply to the dimer (or perhaps to a mixture of monomer and dimer). Other NMR work (see below) indicates this 0·2 kcal mol^{-1} value is reasonably constant under 'NMR conditions', so it probably applies to

Table 7. Structure of methyl ethyl sulfoxide

Parameter[a]	Conformer	MP2/6–31G*	MM3
C_1—S	1	1·818	1·814
C_4—S		1·809	1·808
S—O		1·513	1·488
C—C		1·524	1·522
C—S—C		97·1	97·9
C—C—S		113·7	112·5
O—C—S		106·8	106·5
CSCC		67·4	68·9
OSCC		177·4	178·7
C_1—S	2	1·818	1·812
C_4—S		1·809	1·807
S—O		1·514	1·489
C—C		1·522	1·522
C—S—C		96·0	96·7
C—C—S		109·3	110·6
O—S—C		107·2	106·8
CSCC		187·8	181·6
OSCC		298·2	291·3
C_1—S	3	1·826	1·815
C_4—S		1·810	1·808
S—O		1·515	1·489
C—C		1·521	1·522
C—S—C		97·5	98·3
C—C—S		113·0	114·3
O—S—C		107·1	107·3
CSCC		291·7	295·5
OSCC		42·2	46·4

Relative energies of three conformers

Conformer	MP2/6–31G*	MM3
1	1·11	1·06
2	0·00	0·00
3	0·24	0·41

[a] Bond lengths in Å, angles in degrees.

Table 8. Structure of isopropyl sulfoxide

Parameter[a]	Conformer	MP2/6–31G*	MM3
C—S	1	1·830	1·824
S=O		1·513	1·496
C_1—C_4		1·522	1·526
C_1—C_5		1·524	1·526
C—H		1·099	1·112
S—H		1·377	1·373
C_4C_1S		109·9	110·0
C_5C_1S		107·5	108·0
CCS (av.)		108·7	109·0
CSO		107·5	109·5
CSH		90·9	91·7
C_4C_1SO		−50·0	−51·5
C_5C_1SO		72·3	71·1
C—S	2	1·828	1·823
S=O		1·511	1·496
C_1—C_4		1·521	1·526
C_1—C_5		1·523	1·526
C—H		1·096	1·112
S—H		1·376	1·373
C_4C_1S		107·6	108·5
C_5C_1S		109·1	108·5
CCS (av.)		108·4	108·5
CSO		108·5	109·0
CSH		90·6	91·4
C_4C_1SO		62·8	59·7
C_5C_1SO		−173·6	−178·4
C—S	3	1·829	1·823
S=O		1·511	1·496
C_1—C_4		1·523	1·526
C_1—C_5		1·519	1·526
C—H		1·097	1·112
S—H		1·379	1·372
C_4C_1S		108·9	108·6
C_5C_1S		110·0	110·2
CCS (av.)		109·5	109·4
CSO		108·7	109·2
CSH		90·1	91·8
C_4S_1SO		−168·3	−177·5
C_5S_1SO		−42·5	−53·9

Relative energies of three conformers

Conformer	MP2/6–31G*	MM3
1	0·322	0·242
2	0·853	0·970
3	0·000	0·000

[a] Bond length in Å, angles in degrees.

the dimer and not to a mixed aggregate. Accordingly, the MM3 parameterization has been carried out to give the results required for the monomer. If one is interested in properties of the dimer, one can apply an empirical correction (1·5 kcal mol^{-1}) to obtain the corresponding results from the monomer calculations. Unfortunately, the 'dimer' values apply only to a specific set of incompletely defined conditions.

The dimerization of dimethyl sulfoxide has been studied by Wolfe and Schlegel,[28] using HF 3–21G(d) calculations. They determined that the dimer is indeed stable, and has a geometry with C_2 symmetry in which the S—O bonds are anti-parallel, and with the methyl groups oriented such that one methyl on each molecule lies approximately in the plane of the four sulfur and oxygen atoms, while the other two methyls are approximately perpendicular to that plane, and on the same side of it. They calculated a separation between the non-bonded S—O atoms of 2·89 Å, and a dimerization energy of 17 kcal mol^{-1}. We repeated this calculation at the HF 6–31G* level, and found at that level the dimerization energy is 8·22 kcal mol^{-1}, while the S—O distance is 3·37 Å. We also calculated the basis set superposition error at that distance, which is

Table 9. Equilibration of 4-substituted thiane-1-oxides[22]

Compound No.	Method (°C)	Composition *cis*	Composition *trans*	ΔE (kcal mol^{-1}) *trans-cis*
1	HCl (25)	90	10	1·3
2	HCL (25)	80	20	0·8
3	HCL (25)	80	20	0·8
1	Decalin (190)	80	20	1·3
3	Decalin (190)	65	35	0·6
1	N_2O_4 (0)	81	19	0·8
3	N_2O_4 (0)	76	24	0·6

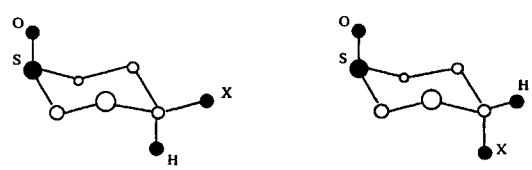
Table 10. Equilibrium data[25] on thiane-1-oxides (eq → ax)

Compound	Ax	Eq	MM3 ΔE(ax − eq) (gas phase)	MM3 ΔE(ax − eq) (dimers)	Exp (dimers)
Thiane-1-oxide	—	—	−1·55	−0·05	−0·18
4,4-Dimethyl-thiane-1-oxide	10·12	11·40	−1·57	−0·07	−0·30
3,3-Dimethyl-thiane-1-oxide	11·49	11·70	−0·50	+1·00	+1·30

cis *trans*

R= :1; R= :2; R= :3

1. $(CH_3)_3C$
2. p-ClC_6H_4
3. CH_3



4 5

X= Cl, OH, p-$SO_2C_6H_4CH_3$

Figure 1. Diagram of 4-substituted thiane-1-oxide

6·10 kcal mol^{-1}. Hence the corrected dimerization energy is calculated to be 2·12 kcal mol^{-1}. Clearly these results would be further changed by extending the basis set and including electron correlation, but this is the limit to which our present resources allow us to carry out the calculations. The MM3 calculations give the S—O distance in the dimer as 3·527 Å, with a dimerization energy of 3·78 kcal mol^{-1}. Our conclusion. however. is that if the *ab initio* calculations could be done at a sufficiently higher level, they would come into reasonable agreement with the MM3 values.

In Table 10 are shown equilibrium data on various thiane-1-oxides. First there is the parent compound, and the calculated values are given for the gas phase. The 'dimer' correction is applied, and the calculated NMR values are given, together with the experimental NMR values. If one considers the 4,4-dimethyl derivative, one would expect little change, since the oxygen on the sulfur is too far away from the methyls to interact with them in any significant way, and that is what is found. On the other hand, if one considers the 3,3-dimethyl derivative, the axial oxygen would be very much destabilized by a 1,3-diaxial interaction with the axial methyl group. Accordingly, one would expect that the oxygen would tend to be equatorial to a much greater extent in this compound than in either the parent, or the 4,4-dimethyl derivative. This is what is observed, and the experiment shows that the oxygen is in fact almost completely in the equatorial position, as is calculated for the 'dimer'.

Table 11. Structure of *trans*-1,4-Dithiane-1,4-dioxide (diaxial)

Parameter[a]	X-ray[27]	MM3
S—O	1·48 (1)	1·488
S—C	1·82 (2)	1·809
S—C	1·80 (2)	1·809
C—S—O	106·4 (8)	106·6
C—S—O	108·3 (8)	106·6
C—S—C	97·9 (8)	97·2
C—C—S	111·2 (13)	113·4
C—C—S	113·3 (12)	113·4

[a] Bond lengths in Å, angles in degrees.

Table 12. Dipole moments of some sulfoxides

	Dipole moment (D)		
Compound	MM3	Experiment	MP2/6–31G*
Methyl sulfoxide	3·93	—	4·45
Dimethyl sulfoxide	3·96	3·9 ± 0·1[21]	4·51
Methyl ethyl sulfoxide (2)	3·97	—	4·51

Dipole moment measurements in CCl_4 at 25 °C (high dilution, presumably monomers) show preferences for forms 4 and 5 in the conformations with the sulfoxide oxygen in the axial position (see Figure 1).[25] MM3 calculated the energy difference between the two isomers of 4-methylthiane-1-oxide with the axial S=O bond orientation as 1·57 kcal mol^{-1}, with the same preference.

Dimethylthiane-1-oxide

Low-temperature (−90 °C) NMR studies of 3,3-dimethylthiane-1-oxide showed more than 95% equatorial isomer ($\Delta G > 1·3$ kcal mol^{-1}), whereas 4,4-dimethylthiane-1-oxide is 70% axial ($\Delta G =$ 305 cal mol^{-1}).[26] MM3 calculates the axial conformer to be more stable in the gas phase than is observed in solution, but when the 'dimer' correction is applied. the agreement is reasonable (Table 10).

trans-1,4-Dithiane-1,4-dioxide (diaxial)

The structure of *trans*-1,4-dithiane-1,4-dioxide was determined by x-ray diffraction.[27] The experimental and MM3 calculated structures are summarized in Table 11. The MM3-calculated structural results are within the expected experimental errors, with the exception of the CCS and CSO angles that were not reproduced very well but appear to be distorted in the crystal by lattice forces.

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