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O-VERSUS *S*-PROTONATION IN DIARYL SULFOXIDES: A SEMI-EMPIRICAL MO INVESTIGATION: COMPARISON WITH SOLUTION STUDIES IN SUPERACIDS

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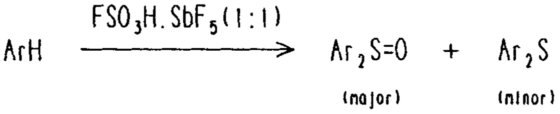
The protonation of diphenyl sulfoxide and several substituted diphenyl sulfoxides was probed by the MNDO-PM3 method to gain a theoretical insight into the experimentally observed preference for stable diphenyl sulfoxonium ion formation (*O*-protonation) in 1:1 FSO_3H-SbF_5 (Magic Acid)–SO_2. In agreement with solution studies, *O*-protonation is uniformly favored (by *ca* 17 kcal mol^{-1}) over *S*-protonation. The differences in the heats of formation of protonated and unprotonated diphenyl sulfoxides are increased by electron-withdrawing substituents (F, CF_3) and decreased by electron-donating groups (Me, OMe). Variations in the SO bond length and bond order in the onium ions are compatible with simple resonance arguments and the oxonium/sulfonium character of both the *O*- and *S*-protonated onium ions. Surprisingly, the *O*- and *S*-protonated dibenzothiophene *S*-oxides are predicted to have identical energetics as compared with the corresponding protonated diphenyl sulfoxides. On structure optimization dibenzothiophene *S*-oxide itself, if the initial geometry is somewhat twisted, rearranges by ring expansion to give a new heterocycle with lower energy. A rotational barrier study on the parent *O*-protonated diphenyl sulfoxide showed two minima, separated by 1.3 kcal mol^{-1}, at HOSC dihedral angles of 60° and 240°. The two conformations correspond to *syn* and *anti* orientations of the OH proton relative to the aromatic rings, and support the low-temperature solution observations of the presence of two distinct sulfoxonium ions in solution. The rotational barriers for diphenyl sulfoxonium cation are compared with those of *O*-protonated dimethyl sulfoxide.

INTRODUCTION

In a recent solution study,[1] we showed that a variety of simple arenes react with 1:1 FSO_3H-SbF_5 (Magic Acid)–SO_2 to give diaryl sulfoxides in good yields (Scheme 1). We proposed the following sequence of events to explain diaryl sulfoxide synthesis: sulfinylation of the arenium ions with SO_2, *O*-protonation of the resulting sulfinic acids and subsequent dehydration and arylation steps.



Scheme 1. Diaryl sulfoxide synthesis for simple arenes with Magic Acid–SO_2

An 'unusual' feature of this one-pot reaction was the presence of the corresponding sulfides in minor amounts, illustrating a reduction process in a highly oxidizing superacid! Probing the reaction progress with time showed that diaryl sulfides were indeed formed from the sulfoxides by *in situ* reduction. Finally, to confirm that sulfoxides are the precursors of the sulfides, independent reaction of the diaryl sulfoxide products with Magic Acid–SO_2 or $HF-SbF_5-SO_2$ led to substantial amounts of diaryl sulfides on work-up.

Detailed studies have been made of *O*- versus *S*-protonation for dimethyl sulfoxide (DMSO). Low-temperature NMR studies by Olah *et al.*[2], and Raman studies by Speikermann and Shrader[3] pointed to a sulfoxonium ion (*O*-protonation). MINDO/3[2] predicted the *S*-protonated onium ion to be significantly less stable (*ca* 70 kcal mol^{-1}); a hydrogen-bridged

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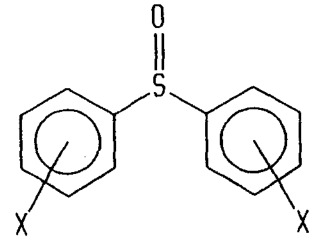
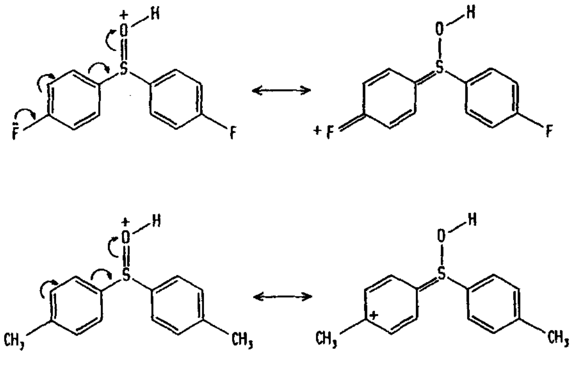


1 X = H
2 X = 4-CH_3
3 X = 4-F
4 X = 3-CF_3
5 X = 2,4-$(CH_3)_2$
6 X = 2,4,6-F_3
7 X = 4-OCH_3
8 X = 4-CF_3

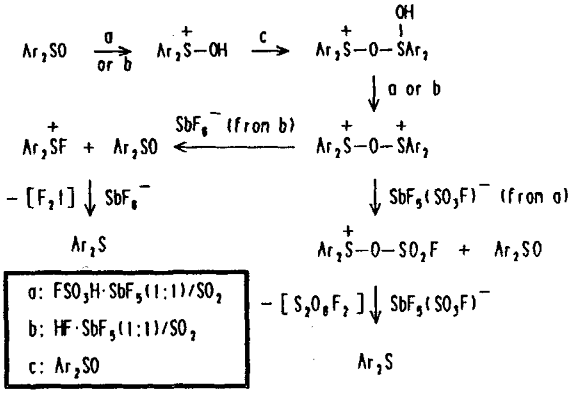
Scheme 2. Diaryl sulfoxide substrates

structure was an additional 30 kcal mol^{-1} higher in energy.[2] Two minima, separated by 3.1 kcal mol^{-1}, were located for the *syn* and *anti* forms of *O*-protonated DMSO.

In contrast to the situation with DMSO, previous work on the stable ion chemistry of diaryl sulfoxides has been limited; the parent diphenyl sulfoxide is *S*-protonated with HF–SbF_5, but with Magic Acid competing ring fluorosulfonation occurs.[4] We showed that substituted diaryl sulfoxides **2**, **3**, **4** and **5** (Scheme 2) are all *O*-protonated under persistent ion conditions (Magic Acid–SO_2) to give their corresponding sulfoxonium ions, whereas **6** is *S*-protonated. Our solution NMR data on persistent diaryl sufoxonium ions indicated that π-electron delocalization into the sulfoxonium ion is fairly extensive (pπ-dπ overlap), resulting in enhanced double bond character of the CS bond (Scheme 3). Another notable feature was that the sulfoxonium ions were in several instances present in two conformations at low temperature.



Scheme 3. Extended conjugation in *O*-protonated diaryl sulfoxides



Scheme 4. Proposed mechanism of sulfoxide reduction via *O*-protonated diaryl sulfoxides

Having established the key role of the sulfoxonium ions in the reduction chemistry, we proposed the mechanism outlined in Scheme 4 for the reduction process.

This study was undertaken in order to address the following specific issues: (a) why is *O*-protonation preferred over *S*-protonation?; (b) does the nature of the substituents play a role in the protonation outcome?; (c) are pπ–dπ overlap (higher CS bond order) and extended conjugation involving the *para* substituent, e.g. pπ back-bonding with F and OMe in a simple resonance model, reflected in the calculated charges and bond lengths?; and (d) why are diaryl sulfoxonium ions present in two conformations, and what is the difference in their relative stability?

RESULTS AND DISCUSSION

X-ray diffraction data on diaryl sulfoxides are surprisingly limited. The parent diphenyl sulfoxide, **1**, has been studied, and the phenyl rings are nearly orthogonal to the CSC plane.[5] Table 1 provides a comparison between the x-ray data on diphenyl sulfoxide and calculated (MNDO and PM3) geometries. AM1 parameters for sulfur have only recently been published[6] and are

Table 1. Calculated and experimental geometry of diphenyl sulfoxide

Parameter	Bonds	Exptl	PM3	MNDO
Bond length (Å)	C—C	1·400(3)	1·392(2)	1·407(3)
	C—H	1·100(11)	1·096(2)	1·091(1)
	S—C	1·804(6)	1·803(1)	1·749(0)
	S=O	1·489(5)	1·554	1·514
Bond angle (°)	C—S—C	103·(9)	99·3	102·4
	C—S=O	111·(4)	105·4	

not included in MOPAC 5.0. With the exception of the exaggerated SO bond length, the agreement between experimental and PM3 calculated parameters is acceptable.

We have calculated the heats of formation, ΔH_f° (gas phase), geometries and charge densities for seven diaryl sulfoxides and their *O*- and *S*-protonated onium ions (Table 2), utilizing the MNDO-PM3 method,[7] which has been shown to give heats of formation data closer to experimental values than MNDO and AM1, particularly with hypervalent compounds of N, S, P and the halogens. The only geometrical constraint imposed on the molecules during the calculations was to keep each ring and the atoms directly attached to it coplanar. This was done to ensure an 'average' geometry for the phenyl rings and to reduce the calculation time.

We found that with the exception of **6** and **7** the nature and location of the substituent has only a minor effect on the stability differences between the *O*- and *S*-protonated cations. A *para*-methoxy substituent stabilizes the *S*-protonated isomer more than the other substituents do. In agreement with stable ion studies,[1] the PM3 method predicts that the sulfoxonium ions are uniformly more stable than the sulfonium ions by *ca* 17 kcal mol^{-1}. The difference in stability between the two onium ions is, however, much less than that for the conjugate acids of DMSO. The substituent effect on the stability of both the *S*- and *O*-protonated diaryl sulfoxides is in the expected direction. Plotting $\Delta\Delta H_{ni}$, the difference in ΔH_f° between the protonated and unprotonated diaryl sulfoxides, versus the normal σ constants (Figure 1) shows that the electron-withdrawing F and CF_3 groups increase ΔH_f° for both onium ions by the same amount, whereas Me and OMe groups decrease this difference. The effects of substituents on the geometries, bond orders on charge distributions of the protonated and unprotonated diaryl sulfoxides are given in Table 3 (Scheme 5 identifies the coding).

Table 2. *PM3 heats of formation for diaryl sulfoxides*

X	Compound	L[a]	ΔH_f°	$\Delta\Delta H_{ni}$[b]	$\Delta\Delta H_{so}$[c]
H	**1**	—	+32·0		
		O	+175·1[d]	143·1	
		S	+192·4[d]	160·4	17·3
4-CH_3	**2**	—	+13·0		
		O	+153·5	140·5	
		S	+170·6[d]	157·6	17·1
4-OCH_3	**7**	—	−45·2[d]		
		O	+95·9	141·1	
		S	+110·1	155·3	14·2
4-F	**3**	—	−54·7[d]		
		O	+93·8[d]	147·9	
		S	+111·3[d]	165·4	17·5
2,4,6-F_3	**6**	—	−131·2		
		O	+21·0[d]	152·2	
		S	+37·5	168·7	16·5
4-CF_3	**8**	—	−281·1[d]		
		O	−125·1[d]	156·0	
		S	−107·6[d]	173·5	17·5
3-CF_3	**4**	—	−282·7[d]		
		O	−127·6[d]	155·1	
		S	−110·1[d]	172·6	17·5

[a] Location of proton in conjugate acid.
[b] Difference in ΔH_f° between neutral and ion (kcal mol^{-1}).
[c] Difference in ΔH_f° between *S*- and *O*-protonated ions (kcal mol^{-1}).
[d] SCF achieved but geometry test not passed.

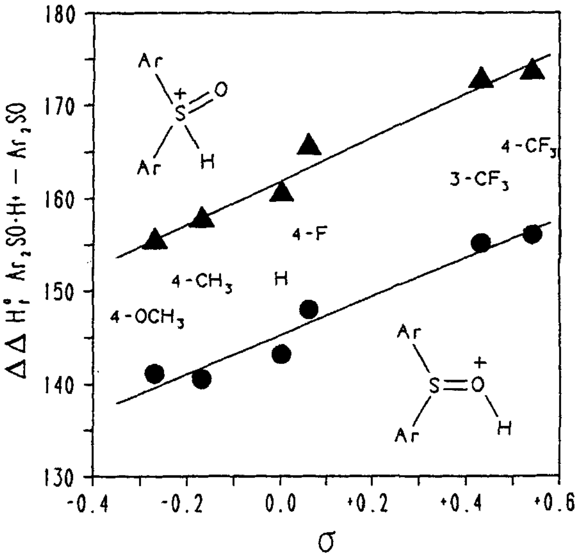


Figure 1. Plot of differences in heats of formation between the protonated and unprotonated diaryl sulfoxides against normal σ constants

The following generalizations can be made concerning the protonation of diaryl sulfoxides:

1. The SO bond length (and bond order, in parentheses) go from an average of 1.55 Å (1.27) in the unprotonated sulfoxides to 1.70 Å (0.97) and 1.45 Å (1.30) in the *O*- and *S*-protonated onium ions respectively. This is consistent with a simple resonance picture for the stabilization of the two conjugate acids:

   $Ar_2S{=}O^+H \leftrightarrow Ar_2S^+{-}OH$

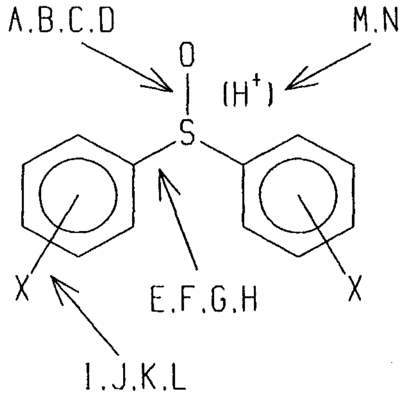
   and $Ar_2SH^+{=}O \leftrightarrow Ar_2SH{\equiv}O^+$

2. The S charge (and O charge, in parentheses) go from an average of +1·06 (−0·70) in the precursor to +1.07 (−0.37) and +2.24 (−0.74) in the *O*- and *S*-protonated cations respectively, in agreement with the results for protonated DMSO.[2]

Table 3. Geometries, bond orders and charge distributions for diaryl sulfoxides and their *S*- and *O*-protonated conjugate acids[a]

X	A	B	C	D	E	F	G	H	I	J	K	L	M	N
H	—	1·551	1·262	+1·05	−0·69	1·801	0·831	−0·37	99·0	1·095	0·966	−0·06	+0·10	—
H	O	1·699	0·954	+1·04	−0·38	1·759	0·963	−0·40	106·9	1·098	0·961	+0·00	+0·13	+0·27
H	S	1·456	1·297	+2·23	−0·74	1·729	0·846	−0·62	107·0	1·098	0·961	+0·01	+0·13	−0·17
4-CH_3	—	1·554	1·257	+1·05	−0·69	1·801	0·834	−0·37	99·4	1·485	1·003	−0·04	−0·07	–
4-CH_3	O	1·699	0·949	+1·05	−0·38	1·755	0·966	−0·41	107·1	1·482	1·007	+0·04	−0·10	+0·27
4-CH_3	S	1·457	1·294	+2·23	−0·75	1·725	0·849	−0·64	107·2	1·482	1·008	+0·05	−0·10	−0·17
4-OCH_3	—	1·555	1·256	+1·05	−0·69	1·798	0·835	−0·41	99·6	1·377	1·045	+0·12	−0·18	—
4-OCH_3	O	1·691	0·958	+1·14	−0·36	1·743	0·960	−0·50	105·2	1·359	1·111	+0·20	−0·16	+0·25
4-OCH_3	S	1·459	1·290	+2·25	−0·75	1·719	0·853	−0·69	107·5	1·358	1·114	+0·21	−0·16	−0·17
4-F	—	1·551	1·267	+1·06	−0·68	1·802	0·829	−0·39	99·3	1·342	1·009	+0·10	−0·09	—
4-F	O	1·698	0·955	+1·06	−0·38	1·756	0·965	−0·43	106·6	1·334	1·037	+0·18	−0·05	+0·27
4-F	S	1·453	1·302	+2·24	−0·74	1·728	0·844	−0·65	106·9	1·333	1·039	+0·19	−0·05	−0·17
2,4,6-F_3	—	1·537	1·305	+1·10	−0·66	1·822	0·784	−0·45	98·8	1·339	1·017	+0·16	−0·08	—
2,4,6-F_3	O	1·693	0·986	+1·09	−0·36	1·771	0·939	−0·50	105·8	1·332	1·044	+0·23	−0·05	+0·28
2,4,6-F_3	S	1·444	1·326	+2·27	−0·73	1·753	0·805	−0·71	106·0	1·331	1·047	+0·23	−0·04	−0·16
4-CF_3	—	1·547	1·279	+1·06	−0·67	1·802	0·823	−0·35	98·9	1·530	0·938	−0·14	+0·40	—
4-CF_3	O	1·695	0·981	+1·05	−0·37	1·765	0·952	−0·37	104·8	1·539	0·927	−0·09	+0·40	+0·28
4-CF_3	S	1·450	1·311	+2·23	−0·73	1·735	0·838	−0·60	106·2	1·539	0·927	−0·08	+0·40	−0·16
3-CF_3	—	1·547	1·279	+1·07	−0·68	1·804	0·824	−0·38	99·0	1·528	0·940	−0·20	+0·40	—
3-CF_3	O	1·695	0·975	+1·06	−0·37	1·762	0·955	−0·41	105·5	1·536	0·930	−0·18	+0·41	+0·28
3-CF_3	S	1·450	1·312	+2·24	−0·74	1·733	0·837	−0·63	106·4	1·537	0·929	−0·19	+0·41	−0·16

[a] X = substituent; A = location of H^+: O, S or —(none); B = S—O bond length (Å); C = S—O bond order; D = total charge on S; E = total charge on O; F = C—S bond length (Å); G = C—S bond order; H = total charge on C—S carbon; I = C—S—C angle (°); J = C—X bond length (Å); K = C—X bond order; L = total charge on C—X carbon; M = total charge on X; N = total charge on added proton.



Scheme 5. Abbreviations used in Table 3

3. The CS bond length (and bond order, in parentheses) go from an average of 1·80 Å (0·82) in the unprotonated sulfoxides to 1·76 Å (0·96) and 1·73 Å (0·84) in the *O*- and *S*-protonated forms respectively. The bond shortenings, although small, suggest increased phenyl participation in stabilizing both onium ions.
4. The CS carbon charge goes from an average of −0·39 in the unprotonated sulfoxides to −0·43 and −0·64 in the *O*- and *S*-protonated cations respectively. These changes taken together with the accompanying changes in the sulfur charges illustrate the increased bond polarization which helps to stabilize ions in the gas phase.
5. The CSC bond angle goes from 99° in the precursor sulfoxide to 106° and 107° in the *O*- and *S*-protonated onium ions respectively, suggesting that the sulfur atom is largely unhybridized in the precursors and approaches sp^3 hybridization in the two conjugate acids.

Compared with the role of polarization and resonance interactions of the SO and the CS bonds in stabilizing the protonated sulfoxides, the effects of single substituents are for the most part relatively insignificant. In **6**, however, the effect is noticeable in the individual columns in Table 3, although when the differences between the protonated and unprotonated forms are compared, the effects of all of the substituents tend to be leveled (Table 4). The substituents in Table 4 are listed in increasing order of their normal σ values. In no case do we observe a smooth progression in the property with the inductive effect of the substituents, although there often is a difference between the extremes of the *para*-methoxy and 2,4,6-trifluoro substituents, particularly in the SO bond length, when protonation occurs an oxygen and in the charge of the atom being protonated. The lack of a clear pattern in

Table 4. Substituent effects on changes in SO bond length and C, S and O charges for diaryl sulfoxides on protonation at S and at O

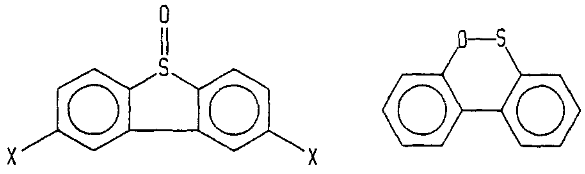
X	Δd_{SO}^{a}	Δd_{SO}^{b}	$\Delta q_{C}^{a,c}$	$\Delta q_{C}^{b,c}$	Δq_{S}^{a}	Δq_{S}^{b}	Δq_{O}^{a}	Δq_{O}^{b}
4-OCH_3	+0·136	−0·096	−0·09	−0·22	+0·09	+1·20	+0·33	−0·06
4-CH_3	+0·145	−0·097	−0·04	−0·27	0·0	+1·18	+0·31	−0·06
H	+0·148	−0·096	−0·03	−0·25	−0·01	+1·18	+0·31	−0·05
4-F	+0·147	−0·098	−0·04	−0·26	0·0	+1·18	+0·30	−0·05
3-CF_3	+0·148	−0·097	−0·03	−0·25	−0·01	+1·16	+0·37	+0·01
4-CF_3	+0·148	−0·097	−0·02	−0·25	−0·01	+1·17	+0·36	0·0
2,4,6-F_3	+0·156	−0·093	−0·05	−0·26	−0·01	+1·17	+0·30	+0·07

[a] Change in property between unprotonated and *O*-protonated forms.
[b] Change in property between unprotonated and *S*-protonated forms.
[c] C—S carbon.

the Δq_C columns in Table 4 and in the CS bond length and bond order columns in Table 3 argue against a significant resonance stablization of either the *O*- or the *S*-protonated diaryl sulfoxides by the phenyl rings in apparent contrast with solution NMR-based conclusions.[1] We note, however, that d orbitals are not included in the MOPAC basis sets, although it is generally assumed that their effects are to some extent incorporated via the parameters.

Dibenzothiophene *S*-oxide

To test further the effect of ring conjugation with the SO system, we carried out PM3 calculations on dibenzothiophene *S*-oxides **9–11** (Scheme 6) and their *S*- and *O*-protonated onium ions. The results, which are given in Table 5, are essentially indistinguishable from those reported in Table 2 for the diaryl sulfoxides. An intriguing aspect of the dibenzothiophene *S*-oxide calculations is that when the geometry optimization was first carried out on the parent compound, the initial geometry was twisted. This structure then converged to **12**, which is predicted to be 8·6 kcal mol^{-1} more stable than dibenzothiophene *S*-oxide. To our knowledge, such a rearrangement, which could be synthetically valuable in heterocyclic chemistry, has not been reported.



9 X = H
10 X = F
11 X = CF_3

12

Scheme 6. Dibenzothiophene *S*-oxide and its rearrangement to **12**

Table 5. PM3 heats of formation for bis(disubstituted)-benzothiophene *S*-oxides

X	Compound	L[a]	ΔH_f°	$\Delta\Delta H_{ni}^{b}$	$\Delta\Delta H_{SO}^{c}$
H	**9**	—	+32·6		
		O	+176·0	143·5	
		S	+192·5	160·0	16·5
4-F	**10**	—	−54·1		
		O	+94·6	148·7	
		S	+111·5	165·5	16·8
4-CF_3	**11**	—	−281·1		
		O	−125·1	156·0	
		S	−107·6	173·5	17·5

[a] Location of proton in conjugate acid.
[b] Difference in ΔH_f° between neutral and ion (kcal mole^{-1}).
[c] Difference in ΔH_f° between *S*- and *O*-protonated ions (kcal mol^{-1}).

Geometrical isomers of diphenylsulfoxonium ions

We previously suggested that the presence of two conformations in low-temperature solution NMR studies of diaryl sulfoxides was related to the near orthogonal relationship of the phenyl rings with the CSC plane and formation of *syn* and *anti* conformers. The exact structures of those conformations and their relative stability differences were unknown. To shed light on this issue, we performed PM3 and MINDO/3 calculations on the *O*-protonated ion Ph_2SOH^+ to determine the rotational barrier about the SO bond while the dihedral angle between the phenyl rings is allowed to float. Initially the ring planes were made perpendicular to the CSC plane so that a 90° rotation of the two rings would make then coplanar.

Figure 2 shows for the two computational methods the effects of the HOSC dihedral angle on the heat of formation, on the angle of rotation of the phenyl rings about the C—S bond and on the OSC angle. The differences are striking. MINDO/3 gives the more easily

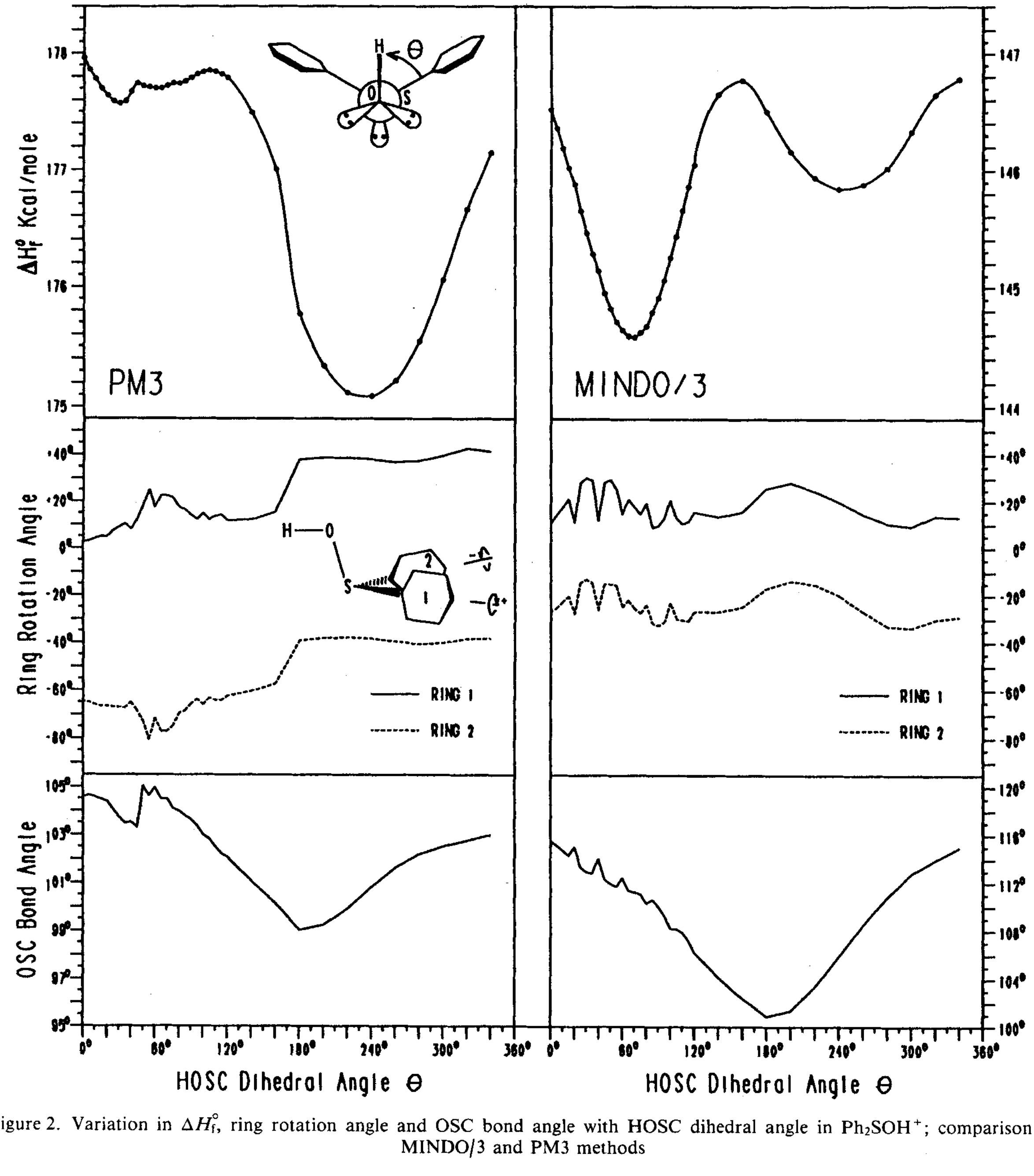


Figure 2. Variation in ΔH_f°, ring rotation angle and OSC bond angle with HOSC dihedral angle in Ph_2SOH^+; comparison of MINDO/3 and PM3 methods

rationalized data which agree with the DMSO results reported by Olah *et al.*[2] The two minima at 60° and 240° correspond to the *syn* and *anti* arrangement of the OH proton with the phenyl rings, the *syn* form being more stable by 1.3 kcal mol^{-1} in the gas phase. This geometry gives minimum overlap between the oxygen and sulfur lone pairs and between the oxygen lone pairs and the CS bonds. Maxima occur when one oxygen lone pair eclipses the sulfur lone pair and the other eclipses a CS bond. At an HOSC dihedral angle of 0°, the two phenyl rings, designated arbitrarily rings 1 and 2, have rotated $+10°$ and $-25°$ respectively, about the CS bond from their original positions. Thereafter, as the HOSC angle is varied from 0° to 340°, the rings undergo an in-phase oscillation with an amplitude of about 20° about their bonds to sulfur, and a period of about 140° in the HOSC angle. During the rotation, the sulfur atom undergoes what amounts to a change in hybridization, as the OSC bond angle changes by about 15° from a low of 101°, when the oxygen lone pairs flank one of the CS bonds, to a high of 116°, when one oxygen lone pair eclipses a CS bond and the other eclipses the sulfur lone pair.

The PM3 results are harder to explain. The basic pattern of minima at 60° and 240° is repeated, but the very shallow 'minimum' at 60° (*ca* 0·3 kcal mol^{-1}) also contains a small maximum which, by changing the rotation angles of the phenyl rings, we have been able to raise or lower but not completely eliminate, and the 240° minimum is now lower by 2.5 kcal mol^{-1}. The minimum energy structure corresponding to the deeper minimum (240°) is shown in Figure 3.

The behavior of the phenyl rings is likewise different from the MINDO/3 case. At an HOSC angle of 0°, ring 2 has rotated by about 60° toward ring 1, which in turn has rotated only about 2° toward ring 2. From here the rings rotate an additional 20° away from each other until an HOSC angle of 60° is reached. From 60° to 180°, where one oxygen lone pair eclipses that of sulfur, the rings rotate back toward each other about 15–25°. Thereafter both rings continue to rotate an additional 25° in the same direction, and the resulting angle is approximately maintained until the HOSC angle is 340°. Unlike the MINDO/3 case, the ring rotation pattern does not appear to repeat, and the pattern seen in Figure 2 must depend on the initial rotation angle of the rings. As before, the OSC bond angle changes with rotation about the SO bond. Here, however, the change is much less, going from about 105° to a low of about 99°. The discontinuities in this curve, as in the corresponding MINDO/3 curve, parallel similar events in the phenyl rotation curves. These spikes probably result from the fact that at each value of the HOSC dihedral angle the gradient search algorithm fails to search all of the possible ring orientations, thus allowing the energy

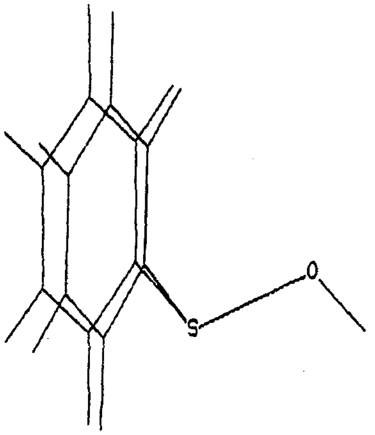


Figure 3. Minimum energy structure of Ph_2SOH^+ at an HOSC dihedral angle of 240°

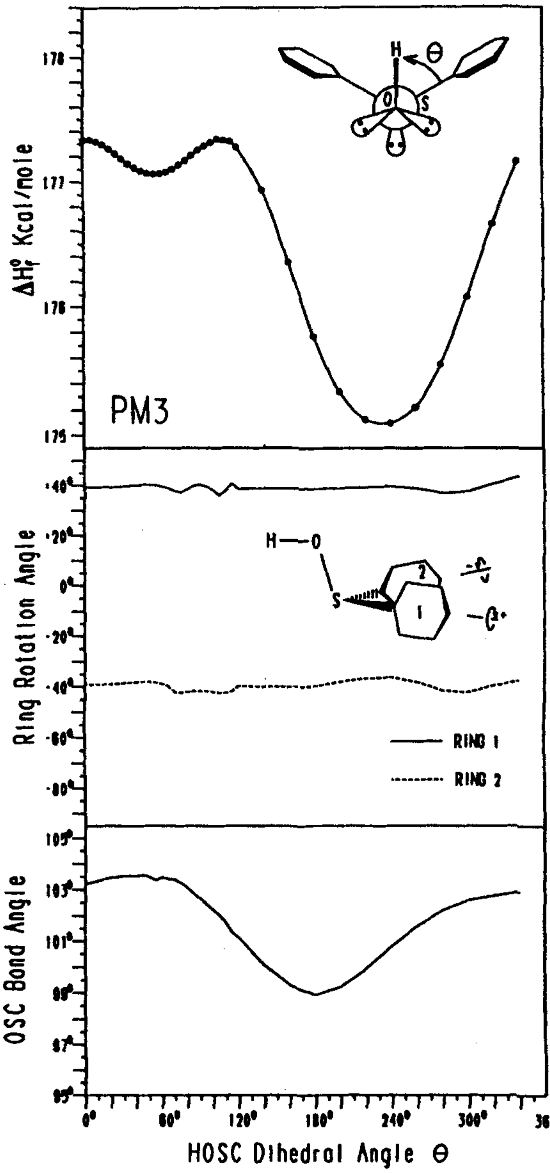


Figure 4. Variation in ΔH_f°, ring rotation angle and OSC bond angle with HOSC dihedral angle in Ph_2SOH^+ with the rings rotated by +40° and −40°; PM3 method

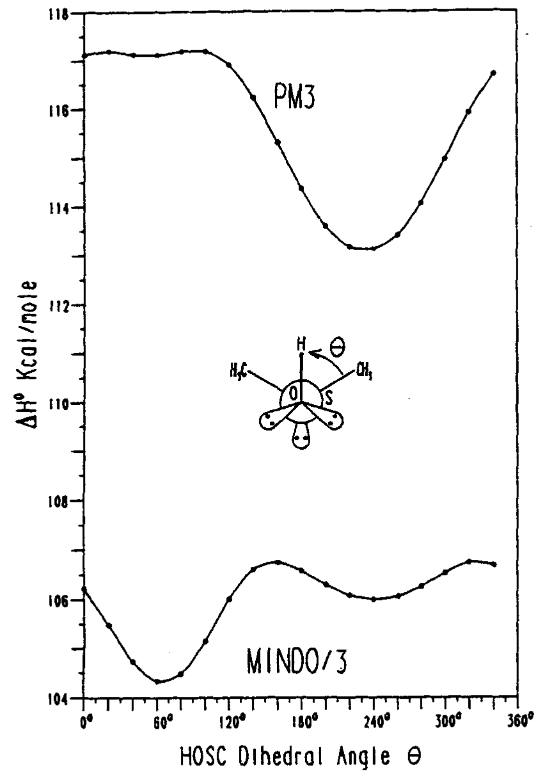


Figure 5. Rotational barrier study for DMSO; comparison of MINDO/3 and PM3 methods

to rise until with a further slight change in the dihedral angle, the rings 'snap' to a new position.

In order to determine the extent to which the ring rotations were responsible for the different appearances of the PM3 and the MINDO/3 energy curves, we repeated the PM3 calculations with the phenyls initially rotated +40° and −40°, respectively, out of the 'vertical' (Figure 4). Now the rings undergo almost no further oscillations over the complete range of HOSC angles, the ΔH_f° curve is much more symmetrical and it appears to repeat at 360°. The gap between the two minima is now 2·0 kcal mol^{-1}, and the barrier to conversion from one rotamer to the other is less than 0·2 kcal mol^{-1}. The OSC bond angle variation is nearly identical with that in the previous case, but the curve is free from discontinuities.

We also repeated Olah's *et al.* calculation[2] on *O*-protonated DMSO using both methods (Figure 5), Clearly, the basic features of the protonated diphenyl sulfoxide curves have been maintained. In our case, the two minima in the MINDO/3 calculation are separated by only 1·7 kcal mol^{-1}, rather than the 3.1 kcal mol^{-1} found previously. The earlier work, however, used a version of the program which had been parameterized by those authors for the SO bond. The MINDO/3 routine contained in MOPAC 5·0 has different parameters for this bond. Whereas it is not certain which of the two methods, if either, is correct, the NMR data on protonated **2** and **4** clearly showed the presence of two OH resonances. A recent communication[8] notes a flaw in the PM3 treatment of non-bonding interactions involving phenyl rings. This flaw produces an abnormal stabilization for the H–H interactions at short distances, leading, for example, to unexpected ring orientations in the conformational analysis of diphenyl-

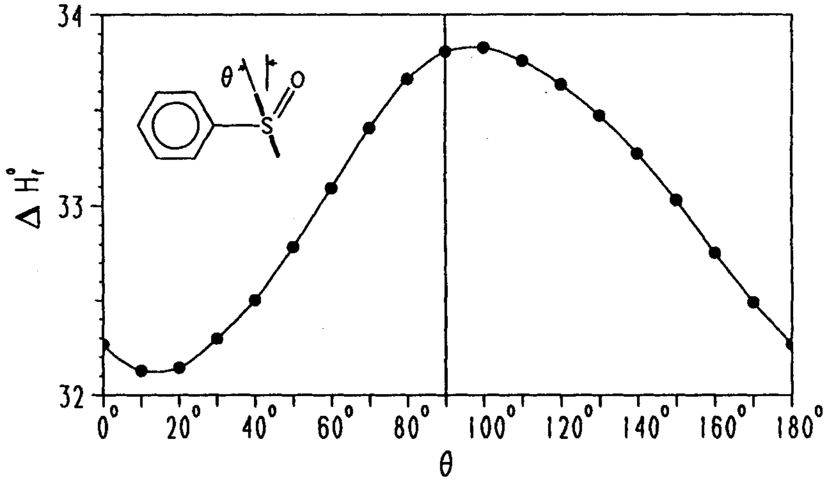


Figure 6. Rotational barrier measurement for diphenyl sulfoxide

methanes. It is likely that this at least partly explains our PM3 results.

An SC rotational calculation carried out on the parent Ph_2SO (Figure 6) showed a barrier of only $1 \cdot 8$ kcal mol^{-1}, with a maximum at a dihedral angle of 100° between the rings and a minimum at about 15°. At 100° there is steric interaction of one phenyl ring both with the other ring and with the oxygen.

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REFERENCES

1. K. K. Laali and D. S. Nagvekar, *J. Org. Chem.* **56**, 1867–1874 (1991).
2. G. A. Olah, D. J. Donovan, H. C. Lin, H. Mayr, P. Andreozzi and G. Klopman, *J. Org. Chem.* **43**, 2268–2272 (1978).
3. M. Speikermann and B. Shrader, *Angew. Chem., Int. Ed. Engl.* **16**, 197–198 (1977).
4. G. A. Olah, A. T. Ku and J. A. Olah, *J. Org. Chem.* **35**, 3904–3908 (1970).
5. (a) J. Drabowics, P. Kielbasinski and M. Mikolajczyk, in *The Chemistry of Sulfones and Sulfoxides*, edited by S. Patai, Z. Rappoport and C. J. M. Stirling, Chapt. 8. Wiley, Chichester (1988); (b) B. Rozsondai, J. H. Moore, D. C. Gregory and I. Hargettai, *J. Mol. Struct.* **51**, 69–76 (1979).
6. M. J. S. Dewar and Y. C. Yuan, *Inorg. Chem.* **29**, 3881–3890 (1990).
7. J. J. P. Stewart, *MOPAC—A Semiempirical Molecular Orbital Program*, pp. 67–69. ESCOM Science, Leiden (1990).
8. V. Buss, J. Messinger and N. Heuser, *QCPE Bull.* **11**(1), 5–6 (1991).