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Why are dimethyl sulfoxide and dimethyl sulfone such good solvents?

Timothy Clark · Jane S. Murray · Pat Lane · Peter Politzer

Abstract We have carried out B3PW91 and MP2-FC computational studies of dimethyl sulfoxide, $(CH_3)_2SO$, and dimethyl sulfone, $(CH_3)_2SO_2$. The objective was to establish quantitatively the basis for their high polarities and boiling points, and their strong solvent powers for a variety of solutes. Natural bond order analyses show that the sulfur–oxygen linkages are not double bonds, as widely believed, but rather are coordinate covalent single $S^+ \rightarrow O^-$ bonds. The calculated electrostatic potentials on the molecular surfaces reveal several strongly positive and negative sites (the former including σ-holes on the sulfurs) through which a variety of simultaneous intermolecular electrostatic interactions can occur. A series of examples is given. In terms of these features the striking properties of dimethyl sulfoxide and dimethyl sulfone, their large dipole moments and dielectric constants, their high boiling points and why they are such good solvents, can readily be understood.

T. Clark
Computer-Chemie-Centrum,
Friedrich-Alexander-Universität Erlangen-Nürnberg,
Nägelsbachstraße 25,
91052 Erlangen, Germany

T. Clark
Interdiscplinary Center for Molecular Materials,
Friedrich-Alexander-Universität Erlangen-Nürnberg,
Nägelsbachstraße 25,
91052 Erlangen, Germany

J. S. Murray · P. Lane · P. Politzer (✉)
Department of Chemistry, University of New Orleans,
New Orleans, LA 70148, USA
e-mail: ppolitze@uno.edu

J. S. Murray · P. Politzer
Department of Chemistry, Cleveland State University,
Cleveland, OH 44115, USA

Background

Dimethyl sulfoxide, $(CH_3)_2SO$ (DMSO), and dimethylsulfone, $(CH_3)_2SO_2$ (DMSO2), have some interesting physical properties, as can be seen in Table 1. To provide perspective, several other compounds with some structural similarity to DMSO and DMSO2 are included in the table: dimethyl sulfide, $(CH_3)_2S$ (DMS), acetone, $(CH_3)_2CO$, and carbon disulfide, CS_2.

The dipole moments and especially the dielectric constants of DMSO and DMSO2 indicate that they are quite polar, which suggests strong intermolecular interactions in the liquid phase. This can be used to account for the very high boiling points of DMSO and DMSO2 (compare DMSO and DMSO2 to the other three compounds in Table 1).

DMSO and DMSO2 are important and widely used solvents [2, 4], the latter being especially valuable for high-temperature reactions. They can dissolve a wide range of solutes and are miscible with many other solvents; this is true not only for polar compounds but also for some of low polarity, e.g., naphthalene and toluene. Being aprotic, DMSO and DMSO2 can tolerate relatively strong bases.

Why are the DMSO and DMSO2 molecules so polar? Oxygens certainly have the capacity to become highly negative, but sulfur (which is of intermediate electronegativity) and methyl groups are not normally expected to become highly positive. Acetone, $(CH_3)_2CO$, is similar to DMSO, except that carbon (also of intermediate electronegativity) replaces sulfur; however, the dipole moments

Table 1 Experimental physical properties of some organic solvents[a]

Compound	Dielectric constant	Dipole moment, D	Melting point, °C	Boiling point, °C
Dimethyl sulfoxide, $(CH_3)_2SO$	47.24	3.96	17.89	189
Dimethyl sulfone, $(CH_3)_2SO_2$	47.39	4.44	108.9	238
Dimethyl sulfide, $(CH_3)_2S$	6.70	1.554	−98.24	37.33
Acetone, $(CH_3)_2CO$	21.01	2.88	−94.7	56.05
Carbon disulfide, CS_2	2.6320	0	−112.1	46

[a] Most of the data are from Reference [1]. Other sources are references [2, 3, 4]

and dielectric constants in Table 1 show acetone to be much less polar than DMSO, and its boiling point accordingly much lower.

In this paper, we will explore the issue of DMSO and DMSO2 polarities in terms of their computed structures, electronic properties and electrostatic potentials. We will also look at some of their intermolecular interactions, as a means of addressing their very high boiling points and their notable solvent capabilities. Since both DMSO and DMSO2 can be prepared by the oxidation of dimethyl sulfide, DMS [2, 4], we shall include the latter in our computational analysis as a reference point.

Electrostatic potential: definitions

The electrostatic potential $V(\mathbf{r})$ that the nuclei and electrons of a molecule create at any point $\mathbf{r}$ in the surrounding space is given by

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \qquad (1)$$

in which Z_A is the charge on nucleus A, located at R_A, and $\rho(\mathbf{r})$ is the molecule's electronic density. $V(\mathbf{r})$ is a physical observable, which can be determined experimentally [5, 6] as well as computationally. It can be positive or negative in a given region, depending upon whether the effect of the nuclei or that of the electrons is dominant in that region.

The electrostatic potential has been found to be a particularly effective tool for analyzing and predicting noncovalent interactions. For this purpose, we generally compute $V(\mathbf{r})$ on the surface of the molecule, labeling it $V_S(\mathbf{r})$. We take the surface to be the 0.001 au (electrons/Bohr^3) contour of the electronic density, as suggested by Bader et al. [7]. The most positive and most negative values of $V_S(\mathbf{r})$ on a given molecular surface are designated as $V_{S,max}$ and $V_{S,min}$, respectively; there may be several such local maxima and minima. The magnitudes of $V_{S,max}$ and $V_{S,min}$ have been shown to correlate well with empirical measures of hydrogen bond donating and accepting tendencies [8].

$V_S(\mathbf{r})$ can be characterized further by means of several statistically defined quantities, such as its average positive and negative values, and its positive and negative variances. In terms of these and related quantities, it has been found possible to develop analytical expressions for a variety of condensed phase physical properties that depend upon noncovalent interactions: heats of phase transitions, solubilities, boiling points and critical constants, viscosities, surface tensions, diffusion constants, etc. For reviews, see Murray and Politzer [9, 10].

Computational approach

The computational procedures were the same as in our earlier studies of σ-hole-bonded systems [19–21, 35]. To obtain the electrostatic potentials $V_S(\mathbf{r})$ on the surfaces of the molecules of interest, we used the density functional B3PW91/6–31G(d,p)//B3PW91/6–31G(d,p) method. For natural bond orbital (NBO) analyses [11], and to compute interaction energies ΔE, we used higher computational levels. We optimized geometries at B3PW91/6–311G (3df,2p) and used these for NBO and ΔE at B3PW91/6–311G(3df,2p) and for just ΔE at MP2-FC/6–311++G (3df,2p). Energy minima were confirmed by the absence of imaginary vibration frequencies. With such large basis sets, any errors in ΔE due to basis set superposition should be minimal [12] and were accordingly not evaluated. The ΔE are the differences between the energy minima at 0 K, products minus reactants.

Structures and NBO analyses

The structures of DMS, DMSO and DMSO2 are shown in Fig. 1. Table 2 shows some key features of their optimized geometries. The agreement with the corresponding experimental values, given in brackets, is excellent. As can be seen from Fig. 1 and the bond angles in Table 2, the configuration of sulfur is pyramidal in DMSO and distorted tetrahedral in DMSO2; in the latter, repulsion between the oxygens is presumably the reason for the large O–S–O angle.
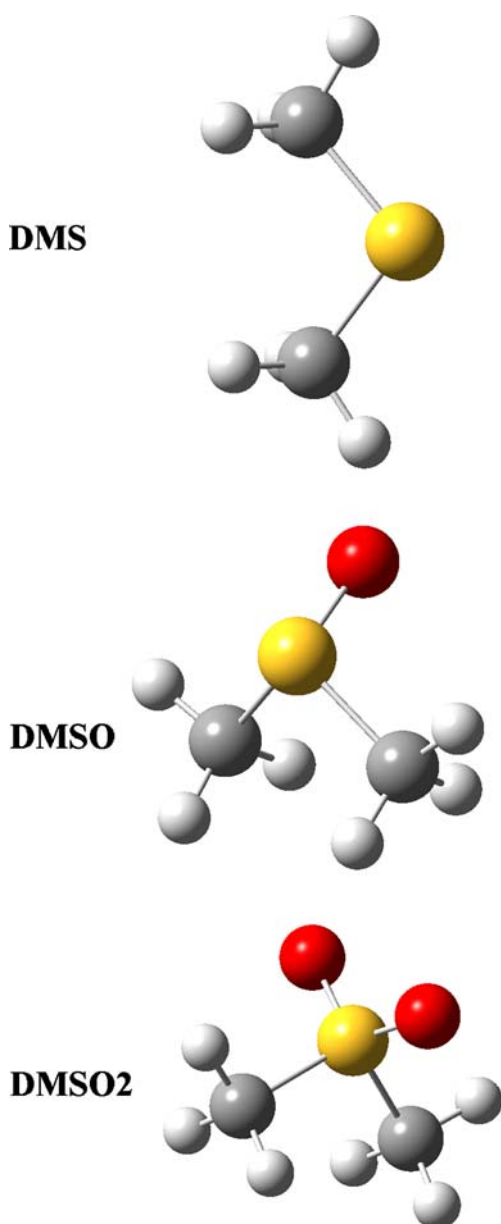
Fig. 1 Optimized structures of dimethyl sulfide, (CH₃)₂S (DMS), dimethyl sulfoxide, (CH₃)₂SO (DMSO), and dimethylsulfone, (CH₃)₂SO₂ (DMSO2). Sulfur atoms are *yellow*, oxygens are *red*, carbons are *gray* and hydrogens are *white*

The nature of the sulfur–oxygen bonding in DMSO and DMSO2 has, in the past, been a matter of some disagreement [13–16]. It is now commonly described as involving S=O double bonds, with sulfur $3d$ orbitals having important roles. Indeed, the sulfur–oxygen bond lengths in Table 2 are very similar to our calculated value for the SO molecule (1.484 Å), which is certainly expected to have a double bond. However, it has also been argued that DMSO and DMSO2 have coordinate covalent single bonds between the sulfur and oxygen, in which both electrons are provided by the sulfur: $S^+ \rightarrow O^-$.

In order to better understand the electronic structures of DMS, DMSO and DMSO2, we carried out NBO analyses [11]. The results are shown in Table 3, which lists, for each sulfur bond (BD) and sulfur or oxygen lone pair (LP), the % contributions of the s, p, d and f orbitals that are involved.

In DMS, the situation is fairly straightforward. The sulfur's contribution to the S–C bonds is primarily its half-filled $3p$ orbitals; the $3s$ character is only 17%. Sulfur also has two unshared pairs of electrons, one in a pure $3p$ orbital and the other in what is mainly the $3s$, although with 33% $3p$. Thus the sulfur in DMS approximates its valence electron configuration in the free state, $3s^2 3p^2 3p^1 3p^1$, with relatively little hybridization.

The above description of the S–C bonds also applies to DMSO, but in DMSO2, the sulfur is providing sp^3 hybrids rather than essentially $3p$ orbitals. However, what is important in both DMSO and DMSO2, in light of the earlier discussion, is that they contain only *single* sulfur–oxygen bonds. These can be described roughly as composed of sp^3 hybrid orbitals on the sulfurs and oxygens. Each oxygen also has *three* unshared pairs of electrons, two being in pure $2p$ orbitals and one in a primarily $2s$. Table 3 shows no significant participation of d or f electrons in any bond or lone pair.

The fact that there is only one bond between sulfur and each oxygen, and that the oxygens have three unshared pairs of electrons, strongly indicates coordinate covalent single S–O bonds, in which both shared electrons come from the sulfur, $S^+ \rightarrow O^-$. In contrast, our NBO analysis of the SO molecule showed both a σ- and a π-bond between the sulfur and oxygen.

Electrostatic potential analyses

How do the structural and electronic features that have been discussed translate into the molecules' polarities and intermolecular noncovalent interactions? We shall begin to

Table 2 Some optimized bond lengths and bond angles in (CH₃)₂S, (CH₃)₂SO and (CH₃)₂SO₂, at the B3PW91/6–311G(3df,2p) level. When two or more bond lengths or bond angles in the molecule have the same magnitudes, this is indicated in parentheses. Experimental values are given in brackets[a]

Molecule	Bond length, A	Bond angle, degree
(CH₃)₂S	S–C: 1.801 (2) [1.802 (2)]	C–S–C: 100.0 [98.9]
(CH₃)₂SO	S–C: 1.807 (2) [1.799 (2)]	C–S–C: 96.4 [96.6]
	S–O: 1.481 [1.485]	C–S–O: 106.9 (2) [106.5 (2)]
(CH₃)₂SO₂	S–C: 1.778 (2) [1.777 (2)]	C–S–C: 103.8 [103.3]
	S–O: 1.437 (2) [1.431 (2)]	C–S–O: 107.9 (4) [107.8 (4)]
		O–S–O: 120.3 [121]

[a] Data taken from Reference [3]

Table 3 Natural bond orbital (NBO) analyses of $(CH_3)_2S$, $(CH_3)_2SO$ and $(CH_3)_2SO_2$, at the B3PW91/6–311G(3df,2p) level. When the results are the same for two bonds or two lone pairs in a molecule, this is indicated in parentheses

Molecule	Bond (BD) or lone pair (LP)	Atom, percent contribution	% s	% p	% d	% f
$(CH_3)_2S$	BD: S−C (2)	S: 47.47	16.80	82.52	0.67	0.01
		C: 52.53	23.15	76.64	0.19	0.02
	LP: S	S: 100.00	67.31	32.67	0.02	0.00
	LP: S	S: 100.00	0.00	99.95	0.03	0.02
$(CH_3)_2SO$	BD: S−C (2)	S: 46.88	15.79	82.66	1.54	0.01
		C: 53.12	21.54	78.39	0.07	0.00
	BD: S−O	S: 35.77	20.67	77.92	1.34	0.06
		O: 64.23	22.73	76.01	1.25	0.02
	LP: S	S: 100.00	49.23	50.63	0.13	0.00
	LP: O	O: 100.00	76.25	23.67	0.08	0.00
	LP: O	O: 100.00	0.94	98.32	0.74	0.01
	LP: O	O: 100.00	0.00	99.30	0.69	0.01
$(CH_3)_2SO_2$	BD: S−C (2)	S: 47.32	23.13	75.04	1.83	0.00
		C: 52.68	21.95	77.76	0.29	0.00
	BD: S−O (2)	S: 33.97	26.94	71.13	1.89	0.04
		O: 66.03	27.65	71.32	1.02	0.01
	LP: O (2)	O: 100.00	72.25	27.65	0.09	0.00
	LP: O (2)	O: 100.00	0.00	99.32	0.67	0.01
	LP: O (2)	O: 100.00	0.02	99.31	0.65	0.01

address these questions by examining the computed electrostatic potentials $V_S(r)$ on the molecular surfaces of DMS, DMSO and DMSO2. These are shown in Figs. 2, 3 and 4, and the most positive and most negative values, $V_{S,max}$ and $V_{S,min}$, are listed in Table 4.

Looking first at the potential on the surface of DMS (Fig. 2), the sulfur is seen to be entirely negative, with two $V_{S,min}$ of −25.4 kcal mol^{-1} (Table 4). These are located above and below the C–S–C plane and can be attributed to the overlapping electronic densities of the two unshared pairs of sulfur electrons (Table 3). The methyl hydrogens are just weakly positive, with $V_{S,max}$ between 14 and 15 kcal mol^{-1}. The overall picture is consistent with relatively low polarity, and this is reflected in the dipole moment (Table 1).

The surface potential of DMSO shows considerably more variation than that of DMS, as can be seen by comparing Figs. 2 and 3. The three pairs of unshared electrons of the oxygen combine to produce a strongly negative $V_{S,min}$ of −46.0 kcal mol^{-1} on its outer tip, and the oxygen's electron-withdrawing power causes the methyl hydrogens to be more positive than in DMS. However, the most interesting is the sulfur. While it has a distinct negative region, which overlaps with that of the oxygen and therefore does not have a separate $V_{S,min}$, we wish to focus upon the positive region centered between two hydrogens of the two methyl groups. It is shown in red in the top and middle portions of Fig. 3, and reaches a $V_{S,max}$ of 26.2 kcal mol^{-1}. Such a positive center is not found between other pairs of hydrogens (see bottom portion of Fig. 3), which have separate weaker $V_{S,max}$ of 18.4 or

19.8 kcal mol^{-1} for each hydrogen. The stronger $V_{S,max}$ of 26.2 kcal mol^{-1} is on the extension of the O–S bond and is due to what has come to be called a σ-hole [17, 18], as will now be explained.

When a half-filled p or hybridized p orbital interacts to form a covalent bond, or a filled one forms a coordinate covalent bond, some degree of electronic charge deficiency in its other, noninvolved lobe normally results. This "σ-
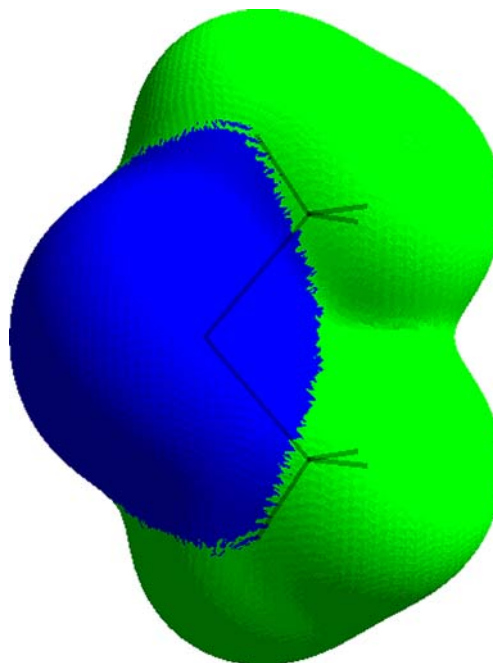

Fig. 2 Calculated electrostatic potential on the molecular surface of DMS. The sulfur is at the left. Color ranges (in kcal mol^{-1}): *blue* between −30 and 0, *green* between 0 and 15
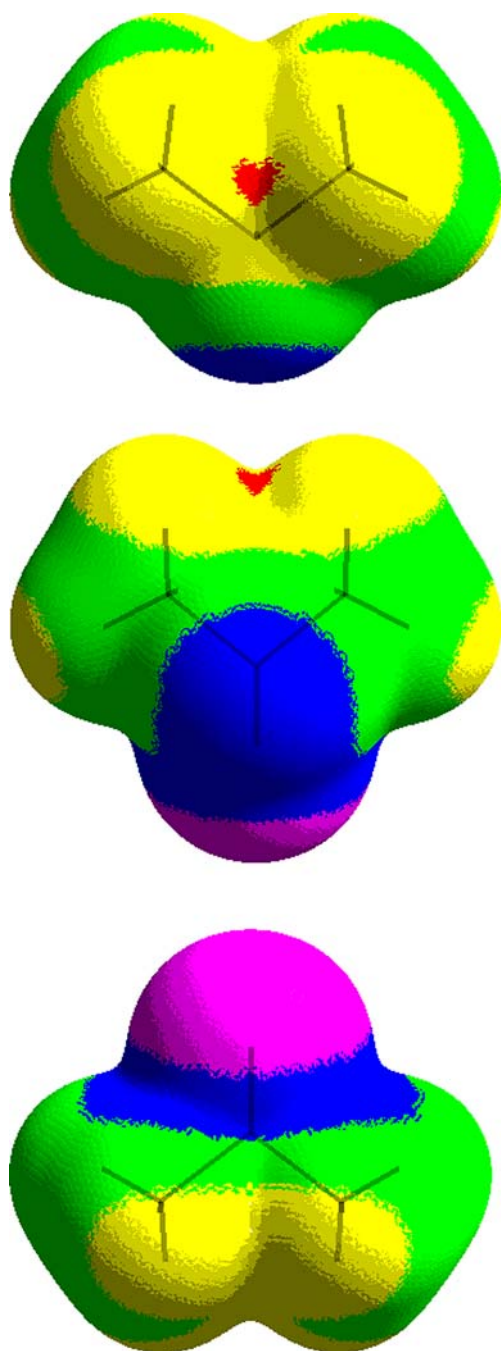
polarizable, and as there is less mixing of s character into the p orbital. For these reasons, the σ-hole is typically enhanced in going from the lighter to the heavier elements in a given column of the periodic table. Thus the phosphorus atom in $(CH_3)_3P$ is completely negative, whereas the arsenic in $(CH_3)_3As$ has a $V_{S,max}$ of 7.7 kcal mol^{-1} along the extension of each C–As bond [19]. The σ-holes also become more positive as the remainder of the molecule is more electron-withdrawing; in $(CH_3)_2PF$, there is a $V_{S,max}$ of 25.4 kcal mol^{-1} on the extension of the F–P bond, but still none along the C–P. Positive σ-holes have now been found computationally for covalently-bonded atoms of Groups V [19], VI [20] and VII [17, 18, 21], although only infrequently for the lightest members of these Groups (N, O and F).

In DMSO, the positive potential of the σ-hole merges with those of the neighboring hydrogens, but its presence is clearly evident in Fig. 3 by the single $V_{S,max}$ (red) between those hydrogens. In contrast, the other four methyl hydrogens have separate $V_{S,max}$ (Table 4). Overall, as Fig. 3 shows, there is an extended negative region on one side of the molecule, arising from the oxygen and sulfur, and an
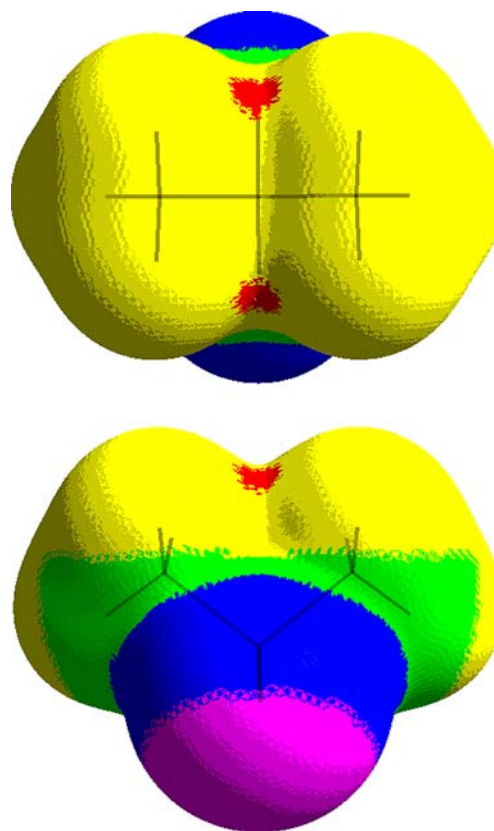

Fig. 3 Calculated electrostatic potential on the molecular surface of DMSO. Color ranges (in kcal mol^{-1}): *purple* more negative than −30, *blue* between −30 and 0, *green* between 0 and 15, *yellow* between 15 and 26, *red* more positive than 26. The *top view* shows the two methyl groups with the sulfur between them. The *small red region* is the center of the sulfur σ-hole, on the extension of the O–S bond. The *middle view* has the oxygen at the bottom, methyl groups at the top and sulfur negative region (*blue*) in the middle. The *bottom view* has the oxygen at the top and the methyl groups below; there is no σ-hole positive center between the hydrogens

Fig. 4 Calculated electrostatic potential on the molecular surface of DMSO2. Color ranges (in kcal mol^{-1}): *purple* more negative than −30, *blue* between −30 and 0, green between 0 and 15, *yellow* between 15 and 29.7, *red* more positive than 29.7. The *top view* shows the two methyl groups with the sulfur between them. The *small red regions* are the centers of the two σ-holes, on the extensions of the two O–S bonds. The *bottom view* has the two methyl groups at the top and one of the oxygens at the bottom, and shows one of the two σ-holes

hole" (the electron-deficient outer lobe of a bonding orbital) may result in a positive electrostatic potential, centered approximately along the extension of the covalent bond. The σ-hole becomes more positive as the atom becomes more

Table 4 Most negative and most positive electrostatic potentials, $V_{S,min}$ and $V_{S,max}$, on molecular surfaces of $(CH_3)_2S$, $(CH_3)_2SO$ and $(CH_3)_2SO_2$, computed at the B3PW91/6–31G** level. When the $V_{S,min}$ or $V_{S,max}$ occurs two or more times in the molecule, this is indicated in parentheses. Values are in kcal mol^{-1}

Property	$(CH_3)_2S$	$(CH_3)_2SO$	$(CH_3)_2SO_2$
$V_{S,min}$	S: −25.4 (2)	O: −46.0 S: negative region but no $V_{S,min}$	O: −38.5 (2)
$V_{S,max}$	H's: 14.2 (4), 14.5 (2)	S: 26.2 H's: 18.4 (2), 19.8 (2)	S: 30.2 (2) H's: 23.2 (2)

extended positive one on the other, due to the sulfur σ-hole and the adjoining two methyl hydrogens. The $V_{S,min}$ and $V_{S,max}$, −46.0 and 26.2 kcal mol^{-1}, are quite similar to those of the ammonia molecule, −46.3 and 25.5 kcal mol^{-1}. The other methyl hydrogens also represent significant positive centers. The polarity seen in Fig. 3 readily explains the high dipole moment of DMSO.

In DMSO2, the sulfur has two distinct positive σ-holes (Fig. 4), on the extensions of the two O–S bonds, with $V_{S,max}=30.2$ kcal mol^{-1}. As in DMSO, each of these σ-hole potentials merges with those of the two nearest hydrogens, creating an extended positive region with just a single $V_{S,max}$. The two oxygens have $V_{S,min}$ of −38.5 kcal mol^{-1}, not quite as strong as in DMSO because they have to share the electronic charge withdrawn from the remainder of the molecule. On the other hand, the two hydrogens of DMSO2 that have separate $V_{S,max}$ are more positive than those of DMSO. Thus, DMSO2 has two strong negative centers and four strong positive ones, accounting for its having the largest dipole moment in Table 1.

Noncovalent interactions

The $V_S(\mathbf{r})$ analyses have shown that DMSO and DMSO2 offer a remarkable array of possible sites for intermolecular

Table 5 Computed properties of $(CH_3)_2SO$ (DMSO) and $(CH_3)_2SO_2$ (DMSO2) complexes. All geometry optimizations at B3PW91/6–311G (3df,2p) level. When the same separation occurs two or more times in the complex, this is indicated in parentheses

| Complex	Separation, A	Angle, degrees	ΔE (kcal mol^{-1})	
			B3PW91/6–311G (3df,2p)	MP2-FC/6–311++G (3df,2p)
DMSO---DMSO, **1**	H---O: 2.39 (2) H---O: 2.40(2)		−8.9	−11.7
DMSO---DMSO, **2**	S---O: 3.54 H---O: 2.50 H---O: 2.51	O–S---O: 177	−5.2	−7.7
DMSO---DMSO, **3**	S---O: 3.56 H---O: 2.46 H---O: 2.49	O–S---O: 175	−4.9	−7.4
DMSO2---DMSO2, **4**	S---O: 3.60 (2) H---O: 2.40 (4)	O–S---O: 173 (2)	−6.9	−11.8
DMSO---H$_2$O, **5**	S---O: 3.23 H---O: 2.77 (2) H---S: 2.64	O–S---O: 167	−4.5	−4.2
DMSO---H$_2$O, **6**	H---O: 1.85 H---O: 2.42 H---O: 2.42		−10.4	−10.2
DMSO---H$_2$O, **7**	H---O: 1.91 H---O: 2.44		−8.5	−8.3
DMSO2---H$_2$O, **8**	S---O: 3.34 H---O: 1.99 H---O: 2.44 (2)	O–S---O: 177	−8.3	−8.8
DMSO2---H$_2$O, **9**	H---O: 2.03 H---O: 2.40		−6.5	−6.2
DMSO---acetone, **10**	H---O$_{acetone}$: 2.56 (2)		−3.3	−4.5
DMSO2---acetone, **11**	S---O: 3.65 H---O$_{acetone}$: 2.48 (2) H---O$_{DMSO}$: 2.85 (2)	O–S---O: 174	−5.3	−9.4
Sums of van der Waals radii:[a]	H---O: 2.69; S---O: 3.35; H---S: 3.00.			

[a] Reference [36]
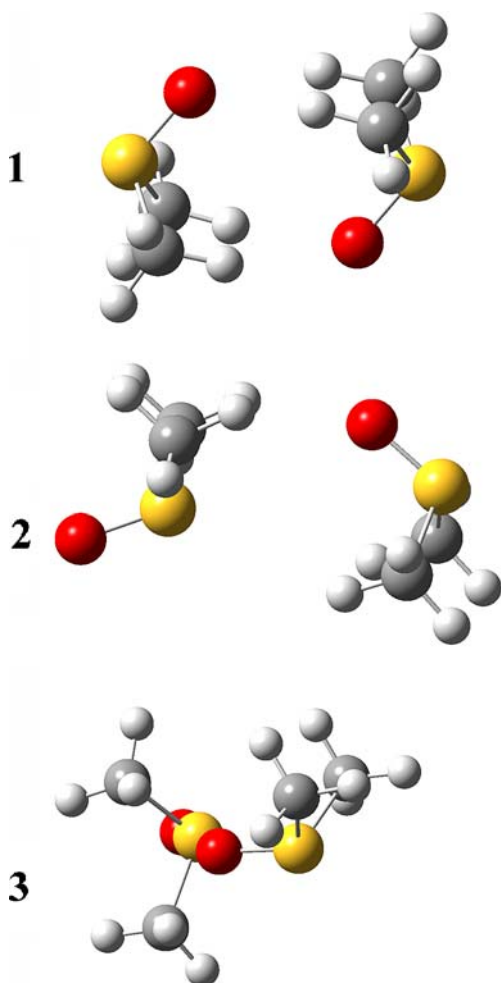
Fig. 5 DMSO---DMSO complexes **1**–**3**. Sulfur atoms are *yellow*, oxygens are *red*, carbons are *gray* and hydrogens are *white*

The resulting noncovalent bonding is highly directional, approximately along the extensions of the bonds that produced the σ-holes. These interactions, which are often called "halogen bonding" when the σ-hole is on a Group VII atom, are competitive with hydrogen bonding [22, 23, 34, 35].

With this variety of positive and negative sites, it follows that DMSO and DMSO2 can easily interact electrostatically with other molecules in several different ways, some of them simultaneously. We shall now look at some specific examples.

Table 5 shows our computed results for 11 complexes of DMSO and DMSO2 interacting with themselves, water or acetone. For each one is given the overall interaction energy ΔE, at both B3PW91 and MP2-FC levels, and the separations of the atoms participating in the key interactions. For those involving the sulfur σ-holes, the O–S---O angles are also listed, to confirm the expected directionality. Finally, the table presents, for each pair of interacting atoms, the sum of their van der Waals radii, to serve as a reference point. It should be kept in mind that these are only rough indicators of noncovalent interactions, not strict cutoffs.

Table 5 includes three different dimers of DMSO, one of DMSO2, three complexes of DMSO and H_2O, two of DMSO2 and H_2O, and finally one each of DMSO and DMSO2 with acetone. The structures of these 11 systems are shown in Figs. 5, 6, 7, 8 and 9. These certainly do not exhaust all of the possibilities for interaction between each
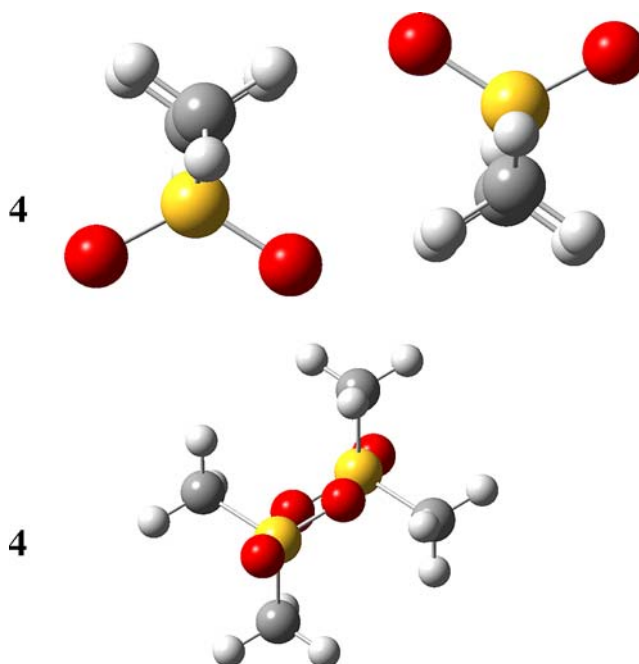
electrostatic interactions. Foremost are the strongly negative oxygens. The one in DMSO has a more negative $V_{S,min}$, −46.0 kcal mol^{-1} (Table 4), than the oxygen in H_2O, −39.6 kcal mol^{-1}, while those in DMSO2 are about the same. In addition, the sulfur in DMSO has a significant negative region (Fig. 3). On the positive side must be considered the methyl hydrogens. DMSO and DMSO2 are often described as aprotic solvents, because methyl hydrogens are normally not viewed as having significant acidity. However those in DMSO and DMSO2 are more positive than is typical; for example, the hydrogens in *n*-butane all have $V_{S,max} \leq 7$ kcal mol^{-1}, while in benzene the $V_{S,max}$ are 13.2 kcal mol^{-1}. In fact, the hydrogens in DMSO2 are nearly as positive as those in NH_3 (25.5 kcal mol^{-1}), a prototypical hydrogen bond donor. Finally, and very importantly, there are the positive σ-holes on the sulfurs in DMSO and DMSO2.

It is well established, both experimentally [22–28] and computationally [18–21, 29–33], that sufficiently strongly positive σ-holes can interact electrostatically with negative regions on other molecules, e.g., lone pairs of Lewis bases.

Fig. 6 Two views of DMSO2---DMSO2 complex **4**, each showing the two O–S---O interactions. Sulfur atoms are *yellow*, oxygens are *red*, carbons are *gray* and hydrogens are *white*
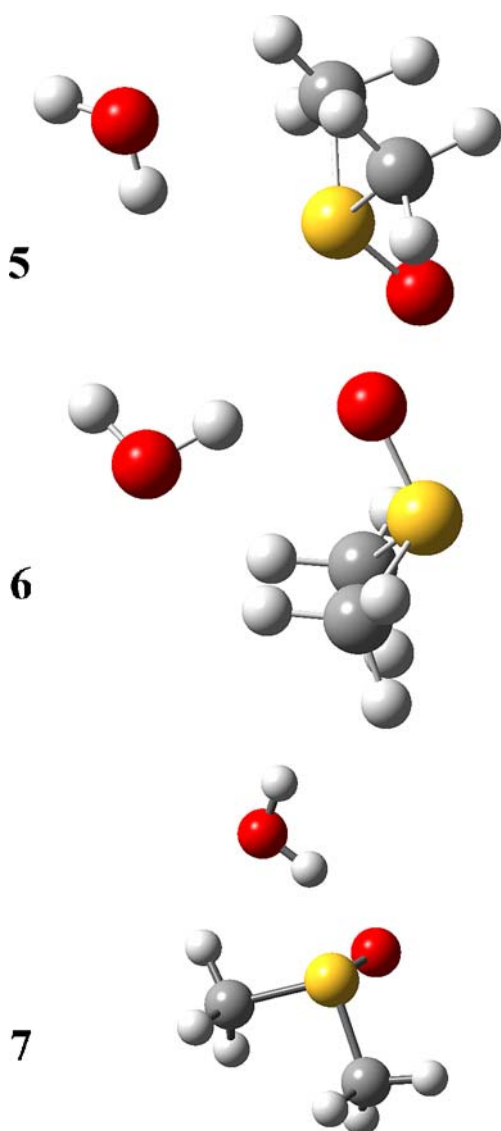
Fig. 7 DMSO---H₂O complexes **5**, **6** and **7**. Sulfur atoms are *yellow*, oxygens are *red*, carbons are *gray* and hydrogens are *white*

Fig. 8 DMSO2---H₂O complexes **8** and **9**. Sulfur atoms are *yellow*, oxygens are *red*, carbons are *gray* and hydrogens are *white*

The separations of the interacting atoms in complexes **1**–**11** are, for the most part, relatively large; many of them approach or even exceed the sum of the van der Waals radii (Table 5). Thus, it might be argued that there really is no significant σ-hole bonding in **2**, **3**, **4** and **11**, because the S---O distances are greater than the sum of the sulfur and oxygen van der Waals radii. To test this, we reoptimized the geometry of **2** (Fig. 5), starting with the DMSO molecule on the right in such a position that its oxygen could still interact with the two methyl hydrogens but not with the σ-hole of the sulfur on the left. In the reoptimization process, however, the

pair of molecules; our purpose is simply to give some examples. Thus, in an earlier computational study [37], Onthong et al. also considered three dimers of DMSO, one of which is unlike any of the three in Table 5. (They did not discuss σ-hole bonding).

The results in Table 5 confirm that DMSO and DMSO2 do form stable complexes, both with their own kind and with other molecules, that typically involve two or more simultaneous σ-hole and/or hydrogen bonding interactions. O−S---O σ-hole bonding is found in six of the complexes: **2** and **3** (Fig. 5), **4** (two σ-hole bonds, Fig. 6), **5** (Fig. 7), **8** (Fig. 8) and **11** (Fig. 9). In each case the expected O−S---O near-linearity is observed; the angles average 174°. All of the complexes have at least one H---O hydrogen bond; **5** also has an H---S, between an H₂O hydrogen and the negative region on the sulfur in DMSO (Figs. 3 and 7).
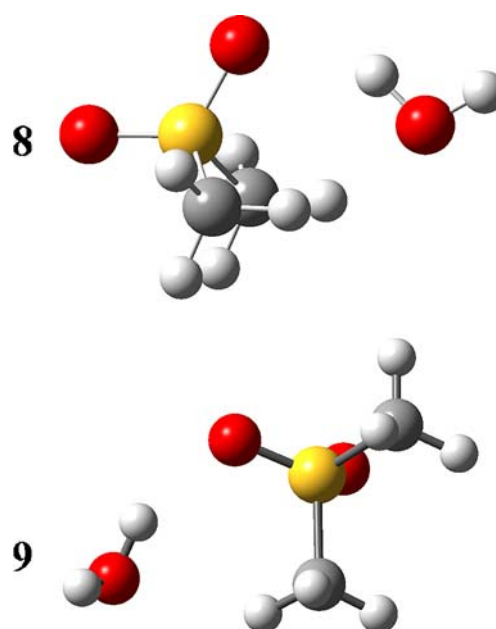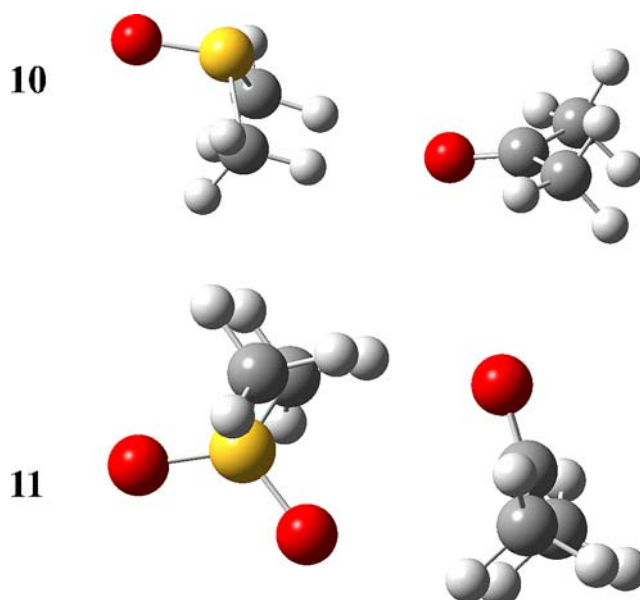

Fig. 9 DMSO---acetone complex **10** and DMSO2---acetone complex **11**. Sulfur atoms are *yellow*, oxygens are *red*, carbons are *gray* and hydrogens are *white*

system reverted to the structure shown for **2**, in which the oxygen in the molecule on the right is essentially on the extension of the O−S bond in the molecule on the left, as it would be in σ-hole bonding. Accordingly, the σ-hole interaction does play an important role. The large S---O separations in **2**, **3**, **4** and **11** may be due to steric factors and also because when there are several simultaneous interactions, the resulting structure is not likely to maximize any one of them.

Discussion and summary

The NBO analyses showed that the sulfur–oxygen linkages in DMSO and DMSO2 are coordinate covalent single $S^+ \rightarrow O^-$ bonds, with both of the shared electrons coming from the sulfur. The molecular surface electrostatic potentials confirm the highly negative characters of the oxygens, and also reveal positive σ-holes on the sulfurs, on the extensions of the O−S bonds. The σ-hole potentials merge with the unusually strongly positive ones of the neighboring methyl hydrogens to create extended regions of positive potential, with one local maximum, $V_{S,max}$, while the other hydrogens have their own $V_{S,max}$. These features account for the large dipole moments and high dielectric constants of DMSO and DMSO2 (Table 1).

The resulting arrays of positive and negative sites in DMSO and DMSO2 (which includes the weak negative region on the sulfur in DMSO) make possible a variety of simultaneous intermolecular electrostatic interactions to which can be attributed the high boiling points and notable solvent powers [2, 4] of DMSO and DMSO2. The fact that they are effective solvents not only for polar solutes but for aromatic compounds as well can be explained in terms of interactions between the extended positive regions of DMSO and DMSO2 and the pi electrons of, for example, naphthalene and biphenyl.

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