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Polar Covalent Bonds: An AIM Analysis of S,O Bonds

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The electron distribution for S,O bonds in a wide range of molecules is analyzed using Bader's atoms in molecules theory (AIM) and measures of bond order. It is shown that the electron density and other derived parameters at the bond critical point correlate very well with bond length. Measures of bond order show a more complex behavior, but a combination of bond order and polarity correlates well with bond length. The trends shown in the properties of derived parameters demonstrate clear characteristics for polar covalent bonds and for recognition of multiple bonding in many of the molecules.

Introduction

Bonds between oxygen and sulfur are expected to be quite polar because of the electronegativity difference between the atoms (3.4 and 2.6, respectively, on the Pauling scale). There have been several studies of the bonding of molecules with S,O bonds, but attention has largely focused on sulfoxide R_2SO and sulfone R_2SO_2 molecules (R = H, CH_3, F, and Cl)[1–4] with some study of the bonding in SO_4^{2-}, SO_2, and SO_3.[4–6] However, sulfur can bond in a variety of ways in molecules which include S,O bonds and with a variety of atoms also attached to an O atom, for example, $(HS)_2O$ and $(CH_3O)_2S$. It is therefore of interest to widen the range of S,O bonds in the molecules studied to elucidate general trends and behavior.

While there is general agreement that these S,O bonds are very polar, there is disagreement as to the significance of any π-bonding. Dobado et al.[2] considered that each S,O bond was best considered as a single polar bond similar to the P,O bonds they had studied previously.[7] The other groups found some double bond character particularly for SO_2 and SO_3. The groups utilizing the Cioslowski localization procedure found that the oxygen "lone pairs" contribute to the bonding significantly. This is variously described as back-bonding,[3] ionic (π-) bonding,[1] and π-bonding,[5] and this gives the bonds double bond character. Fradera et al.[6] concluded that the bond orders in the oxides are consistent with two pairs of electrons for each bond. Cunningham et al. in their spin-coupled valence bond (VB) study of sulfur di- and trioxides and oxofluorides[4] concluded that all six valence electrons of sulfur were involved in two-center two-electron polar covalent bonds. They found that the bonding from sulfur to each oxygen involved both a sigma and a π bond, with the latter being the more polar, comparable to that of a S−F bond. Bader et al. considered that the ellipticity of the electron distribution in the S,O bonds of SO_2 and SO_3 also indicated significant double bond character.[8]

Chesnut and Quin[3] found for the four pairs of sulfoxide and sulfone molecules studied that the mean sulfoxide bond order (1.45) was higher than that for the sufones (1.27) but with a greater bond length (1.50 Å compared to 1.45 Å). By examining localized molecular orbitals (MOs) for dimethyl sulfoxide and sulfone, they found that the S lone pair did not contribute much to the Cioslowski bond order (6%), unlike the O lone pairs, which for dimethyl sulfoxide and sulfone contributed, respectively, 34% and 41% of the bond order despite being over 80% ionic. They pointed out that the sulfones had about twice the charge on the sulfur atom compared to sulfoxides thus making the bonds more polarized and hence reducing the bond order of the sulfones.

In this study, we have extended the range of molecules with sulfur−oxygen bonds to include many that are neither sulfoxide (R_2SO) nor sulfone (R_2SO_2) and have investigated the properties of their electron densities, Laplacians, and bond orders so that their nature can be elucidated more fully.

Molecular Electron Density, Its Laplacian, and Bond Orders. Bader's atoms in molecules theory[9] (AIM) provides invaluable tools in analyzing the electron density in a molecule. The molecule is partitioned into atomic basins, whose boundary surfaces are ones of zero flux in the gradient vector field of the electron density. The sum of the three curvatures (or eigenvalues of the Hessian) of the electron density (λ_1, λ_2, and λ_3) defines its Laplacian, $\nabla^2\rho(r)$. Two bonded atoms are linked by a bond path, which is the line of maximum electron density between their nuclei, and its minimum is the bond critical point (bcp) which lies on the boundary surfaces of the atomic basins. There is one positive curvature, λ_3, along the bond path and two negative curvatures, λ_1 and λ_2, perpendicular to it, and the bcp is a (3, −1) critical point in ρ.

Bader points out that the sign of the Laplacian of the electron density is the outcome of two competing processes: the compression of electron density perpendicularly toward the bond path (giving negative eigenvalues λ_1 and λ_2) and its expansion along the bond path (giving the positive eigenvalue λ_3). The ellipticity $\varepsilon = \lambda_1/\lambda_2 - 1$ indicates any elliptical nature of the electron density, which for CC bonds can be related to π bonding.[10] For a homopolar covalent bond, the sum of the negative eigenvalues is greater in magnitude than the positive one, making the Laplacian negative at the bond critical point. In closed shell bonding interactions (ionic, hydrogen bonding, etc.), the Pauli exclusion principle operates to remove electron density from the interatomic surface[11] resulting in a positive Laplacian and low electron density at the bond critical point. Highly polar covalent bonds combine a positive Laplacian with high electron density: Bader[9] found that C,O and C,S bonds in carbon oxides and sulfides had large positive values for $\nabla^2\rho_b$ indicating both a substantial accumulation of charge density near the interatomic surface and a transfer of charge density to the

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more electronegative atom's basin resulting in concentration there and depletion in the other atomic basin.

Cremer and Kraka[12,13] found that the electronic energy density $H(\mathbf{r})$, which is the sum of the local kinetic and potential energy densities, $H(\mathbf{r}) = G(\mathbf{r}) + V(\mathbf{r})$, is always negative at the bond critical point for a covalent bond corresponding to the electron density at the bond critical point being a stabilizing influence. Consequently, it is necessary to consider several parameters at the bond critical point (ρ_b, $\nabla^2\rho_b$, H, or G) to characterize the type of bonding.[11,14]

Using the more intuitive function $L(\rho) = -\nabla^2\rho(\mathrm{r})$, the maxima of $L(\rho)$ can be found and can correspond to points where the value of ρ is more than that of its average in the neighborhood. These "shoulders" in ρ are called valence shell charge concentrations (VSCCs) and are (3, −3) critical points in $L(\rho)$.[15] The VSCCs show a notable correspondence to the hypothetical electron pairs in the VSEPR model of molecular geometry.[16]

The delocalization index defined by Fradera et al. from the pair density[6] measures the electrons shared (exchanged) between the two atoms. In polar bonds (with classically unequal sharing of electron pairs), the transfer of electron density results in the reduction of the delocalization index, and it loses its parallel with the number of bonding pairs in the Lewis model. For this reason, it is sometimes called the covalent bond order. Ponec and Cooper[17] arrived at the same quantity from consideration of the correlation function and call it the shared electron distribution index (SEDI) to differentiate it from other definitions of a delocalization index.

Within the single determinant (Hartree−Fock or Kohn−Sham) approximations, it is identical to the earlier definition of bond order defined by Ángyán et al.[18] from the diatomic contribution to the electron number and the sharing index defined by Fulton:[19]

$$\delta(\mathrm{A,B}) = 4\sum_{i,j} S_{ij}(\mathrm{A})S_{ij}(\mathrm{B})$$

where i,j are the molecular orbitals, and $S_{ij}(\mathrm{A})$ is the molecular orbital overlap integral integrated over the atomic basin A and is an element of the topological atomic overlap matrix for atom A.

Cioslowski and Mixon[20] had earlier proposed an AIM-based bond order from the diatomic contributions to the electron number after an isopycnic localization scheme that maximizes the atomic contributions. This enables the contributions of the different localized orbitals to the bond order to be separately identified together with their ionicities: $(S_{ii}(\mathrm{A}) - S_{ii}(\mathrm{B}))/(S_{ii}(\mathrm{A}) + S_{ii}(\mathrm{B}))^5$, where $S_{ii}(\mathrm{A})$ is now the diagonal element for the ith localized orbital. The Cioslowski bond order is expected to be a close approximation to the SEDI as it differs only in the neglect of the off-diagonal elements of the atomic overlap matrix.[18]

Computational Details. All wave functions were obtained using the Gaussian98 package[21] using the B3LYP hybrid density functional[22] methods therein after geometry optimization at the 6−311++G(3df, 2dp) level. MORPHY98[23] provided a full analysis of all critical points in ρ and $L(\rho)$ and the graphical representations of the Laplacians of the wave functions.[24] Biegler-Konig et al.'s PROAIMV[25] was used to integrate over atomic basins to obtain the atomic charges and the atomic overlap matrix and hence the SEDI. Coding within Gaussian98 provided Cioslowski bond orders and atomic occupancies using Cioslowski's localization method but at the 6−311++G(2d, p) level as the localization procedure failed with the more flexible basis sets (which gave closer to the experimental geometries).

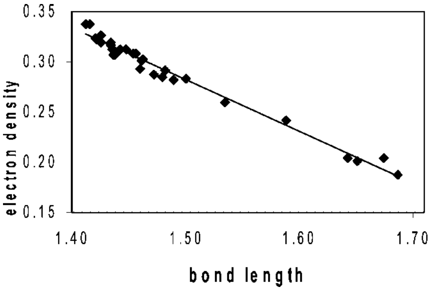

Figure 1. Variation of electron density at the bond critical point (atomic units) with bond length (Å).

Results and Discussion

1. Electron Density and the Laplacian. Figure 1 shows the excellent and essentially linear relationship between bond length and electron density at the bond critical point, ρ_b (see also Table 1).

A linear relationship was found for C,C bonds in hydrocarbons[10,26] and a similar, although slightly curved, relationship was found by Love for N,O bonds in a wide range of molecules.[27] Gillespie et al. found similar curved relationships for the bonds of Be, B, and C in oxo and hydroxo compounds.[28] For all the S,O bonds, the electron density ρ_b at the bond critical point is substantial, and so indicative of covalent bonding. It is noticeable that bonds which are invariably considered single (HO−S, etc.) occupy a range of the graph (from 1.59 to 1.69 Å) quite different from that of most examples (1.41−1.49 Å) with only the oxoanions $\mathrm{SO_3}^{2-}$ and $\mathrm{SO_4}^{2-}$ between them.

The Laplacian at the bond critical point, $\nabla^2\rho_b$, is positive for most of the molecules (Table 1), increasingly so as bond length decreases and ρ_b increases, and is only negative for the longer bonds. Figure 2 shows that there is a marked correlation for most molecules with only three of those of the lowest electron density showing significant deviation. These are the molecules where the S atom is bonded to only two atoms (instead of three or four). A similar decrease in positive values of $\nabla^2\rho_b$ with increasing bond length was found by Boily[29] for most of the X,O bonds in the oxyacids he studied and by Henn et al.[30] for a series of S,N bonds.

The general trend in the Laplacian found for S,O bonds contrasts with the behavior of C,C bonds[26] and with that of N,O bonds,[27] where the Laplacian is negative and becomes more negative as bond length decreases and ρ_b increases. A second contrast is that the curvature along the bond path, λ_3, increases more rapidly than that perpendicular to it (λ_1) for the S,O bonds, whereas the opposite is true of relatively nonpolar bonds (Figure 3). Again, it can be observed that the three molecules with dicoordinate sulfur deviate a little from the trend lines of all the other molecules; this, as is detailed later, is probably because of the lower polarity of the S,O bonds in those molecules.

A further contrast is the kinetic energy density per electron G/ρ_b, which is greater than unity for all but the longest bonds; typically, this is expected to be less than unity for covalent bonds[11] (Figure 4).

However, for all the S,O bonds, the electron density at the bond critical point, ρ_b, is substantial, and its electronic energy density, H_b, is negative, decreasing with decrease in ρ_b, indicative of covalent bonding.[12,13] This suggests that the trends found here are general properties of polar covalent bonds having a positive Laplacian: the Laplacian increases with increasing electron density at the bond critical point, and consequently so does the ratio λ_3/λ_1. Both of these again are the opposite of the behavior found for relatively nonpolar covalent bonds. However,

TABLE 1: AIM Analysis of S,O Bonds at Bond Critical Points[a]

	r	ρ	$\nabla^2(\rho)$	$-H_b$	G/ρ	$-\lambda_1$	λ_3	ε
SF_4O	1.4119	0.337	0.903	0.674	2.000	0.655	2.102	0.202
SO_2F_2	1.4160	0.337	0.980	0.686	2.036	0.630	2.211	0.049
SO_2Cl_2	1.4206	0.324	0.949	0.650	2.006	0.599	2.116	0.055
SOF_2	1.4218	0.322	1.035	0.664	2.062	0.596	2.215	0.021
SO_3	1.4253	0.319	0.897	0.565	1.771	0.627	2.023	0.254
$(HO)_2S{-}O_2$	1.4256	0.326	0.837	0.632	1.939	0.622	2.043	0.065
H_2SO_2	1.4345	0.316	0.840	0.610	1.930	0.591	2.000	0.039
$(NH_2)_2SO_2$	1.4349	0.319	0.793	0.607	1.903	0.600	1.983	0.016
CH_2SO_2	1.4354	0.312	0.852	0.605	1.939	0.596	1.953	0.180
SO_2	1.4367	0.307	1.001	0.623	2.029	0.612	2.156	0.129
$SOCl_2$	1.4380	0.307	0.957	0.617	2.010	0.538	2.032	0.002
Me_2SO_2	1.4430	0.312	0.766	0.586	1.878	0.582	1.909	0.038
$HOS{-}O_3^-$	1.4481	0.312	0.653	0.563	1.804	0.604	1.835	0.046
$NH_2SO_3^-$	1.4539	0.308	0.625	0.549	1.782	0.595	1.790	0.045
$HOS{-}O_3^-$	1.4567	0.308	0.590	0.540	1.753	0.594	1.747	0.055
$S(NSO)_2$	1.4604	0.293	0.802	0.555	1.894	0.541	1.830	0.109
HSO_3^-	1.4611	0.302	0.607	0.533	1.765	0.585	1.754	0.040
$NH_2SO_3^-$	1.4627	0.303	0.565	0.526	1.736	0.582	1.704	0.049
CH_2SO	1.4720	0.287	0.687	0.520	1.812	0.507	1.655	0.097
H_2SO	1.4802	0.285	0.549	0.487	1.709	0.458	1.463	0.006
$S_2O_3^{2-}$	1.4818	0.291	0.457	0.479	1.646	0.550	1.529	0.052
Me_2SO	1.4891	0.282	0.500	0.471	1.670	0.463	1.420	0.010
SO_4^{2-}	1.5005	0.284	0.302	0.433	1.525	0.529	1.359	0.000
SO_3^{2-}	1.5353	0.260	0.220	0.369	1.419	0.463	1.117	0.069
$(HO{-})_2SO_2$	1.5886	0.241	−0.060	0.272	1.129	0.461	0.823	0.091
$(MeO)_2S$	1.6420	0.204	0.012	0.223	1.093	0.317	0.562	0.359
$(HO)_2S$	1.6508	0.201	−0.003	0.213	1.060	0.313	0.534	0.397
$HO{-}SO_3^-$	1.6747	0.204	−0.238	0.164	0.804	0.338	0.422	0.050
$(HS)_2O$	1.6869	0.188	−0.106	0.167	0.888	0.267	0.372	0.268

[a] Theoretical bond length in Å, electron density, its Laplacian, energy density, kinetic energy per electron, curvatures, ellipticity, all in au.

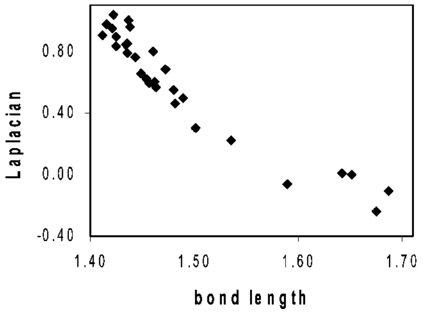

Figure 2. Variation of the Laplacian at the bond critical point (atomic units) with bond length (Å).

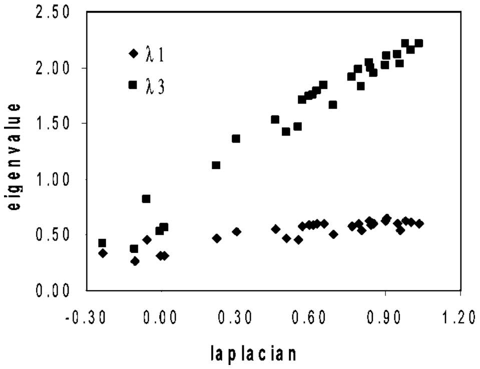

Figure 3. Variation of the curvatures with the Laplacian at the bond critical point.

generally for covalent bonds, the results indicate that the magnitude of the Laplacian increases with electron density at the bond critical point whether the Laplacian is negative or positive. This can be expected as a consequence of the electron density at the bond critical point increasing with decreasing bond length as the electron density along the bond path between the nuclei is necessarily becoming more constricted. Consequently, the curvatures λ_1, λ_2, and λ_3 will all increase in magnitude, and hence also the magnitude of the Laplacian can be expected to increase. The differences in behavior of the Laplacian comparing very polar and relatively nonpolar covalent bonds are associated with the large charge transfer between the atomic basins for the former and the consequent large values of λ_3 at the bond critical point.

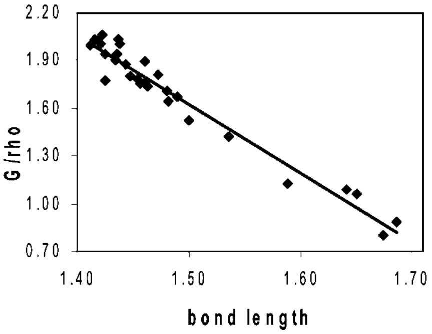

Figure 4. Variation of the kinetic energy density per electron at the bond critical point (atomic units) with bond length (Å).

Figure 5 shows the plots of the Laplacian for SO_2F_2 and $(HO)_2S$ molecules at the opposite ends of the electron density and bond length ranges. The plot for SO_2F_2 shows that the VSCC zone of its sulfur has essentially disappeared unlike the plot of $(HO)_2S$ which has a substantial VSCC zone for the sulfur: a contrast arising as a consequence of the much greater transfer of electron density from the sulfur for SO_2F_2 than for $(HO)_2S$.

The atomic basin for sulfur lost 3.9 electrons in SO_2F_2 but only 1.1 in $(HO)_2S$ although the oxygen atoms gained similar amounts: 1.28 for SO_2F_2 and 1.1 for $(HO)_2S$ (the latter oxygen gained some of its electron density from its hydrogen atom).

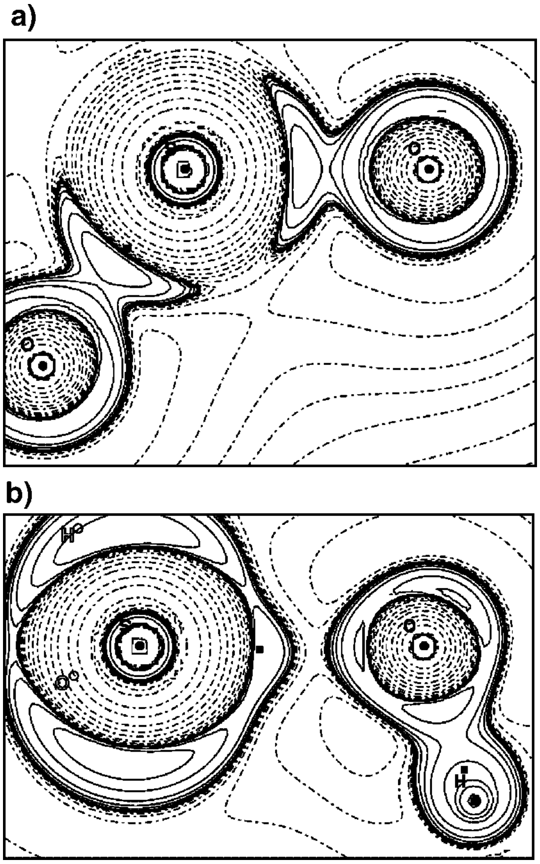

Figure 5. Laplacian of (a) SO_2F_2 and (b) $(HO)_2S$ in S,O plane. ■ indicates the bond critical points; dotted contours are positive.

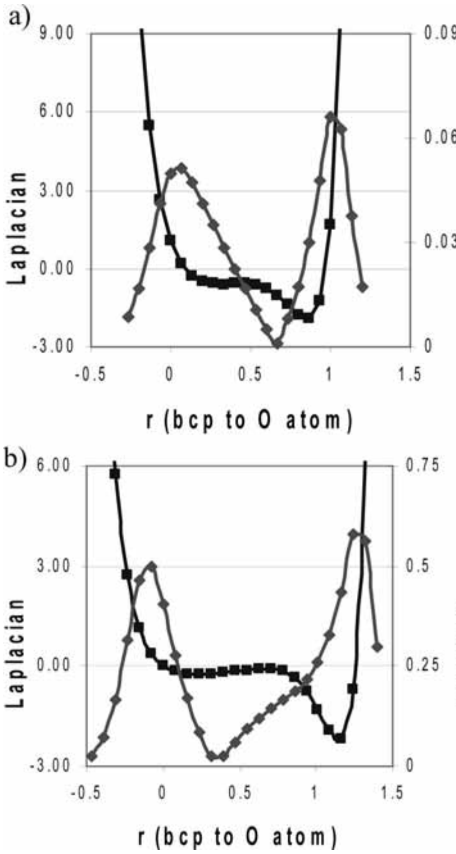

Figure 6. Plot of Laplacian (■) and ellipticity (◆) along bond path from bcp to O atom for (a) SO_2F_2 and (b) $(HO)_2S$.

Despite the large difference in transfer of electron density, the variation of the Laplacian along the bond path shows one crucial similarity: the characteristic double dip in the Laplacian for a covalent bond[14] is evident in both cases (Figure 6). The dip nearer to the S atom is flattened because of the charge transfer. For SO_2F_2, both dips are in the oxygen atomic basin with the bcp in the VSCD (valence shell charge depletion) zone of sulfur, whereas for $(HO)_2S$, one peak is within each atom's VSCC zone, and the bcp is within the VSCC zone of the sulfur atomic basin.

Analysis of the Laplacian also shows the number and location of the VSCCs. The dicoordinate O atoms (HO−S and MeO−S) all have two nonbonded VSCCs giving an approximate tetrahedral arrangement of VSCCs as expected from the VSEPR model. The two oxyanions SO_4^{2-} and SO_3^{2-} have three nonbonded VSCCs, but as SO_4^{2-} ion has 3-fold symmetry about each S,O bond, this precludes it having only two VSCCs; no such restriction applies to the SO_3^{2-} ion, so in the latter case the VSCCs imply single bonds between S and O. All other molecules with the O atoms bonded only to the S atom have only two nonbonded VSCCs on the O atoms coplanar with the S and O atoms. By analogy with the VSEPR model, this is taken to imply multiple bonding between the S and O atoms. The S,O bond lengths are consistent with this conclusion: those with dicoordinate O are 1.59−1.69 Å, the bond lengths for SO_4^{2-} and SO_3^{2-} are 1.50 and 1.54 Å, respectively, and all other molecules with monocoordinate O atoms have bond lengths of 1.41−1.49 Å (Table 1).

The ellipticity of the S,O bonds at the bond critical point is generally very small, only greater than 0.1 for eight of the bonds (Table 1). The highest values are for $(HO)_2S$ and $(CH_3O)_2S$ at 0.40 and 0.36, respectively, with $(HS)_2O$ and SO_3 next at 0.27 and 0.25. Thus, the ellipticity does not relate to expected multiple bonding and indicates generally an approximately cylindrical symmetry at the bond critical point as is also found for N,O bonds.[27] The ellipticity of the Laplacian at the bonding VSCCs is also generally low except for SF_4O and SO_3 with 1.27 and 1.01, respectively. However, the ellipticity is not at all constant for polar bonds (see also refs 31 and 32). Generally, for the S,O bonds, it diminishes toward zero when moving away from the bond critical point in both directions along the bond path and toward the O atom flipping orientation and rising again to another (small) maximum before diminishing back toward zero (Figure 6).

2. Delocalization Index and Electron Density. For most bonds, the delocalization index (SEDI) is between 1 and 1.5 with the HO−S bonds of H_2SO_4 and HSO_4^- much lower at 0.680 and 0.628, respectively (Table 2), clearly showing the reduction in delocalization index expected for polar bonds.

The SEDI of S,O bonds with monocoordinate O atoms is about twice as large as these HO−S bonds of comparable polarity, which implies formal double bonds involving two unequally shared pairs of electrons (see further discussion of the SEDI ratios in ref 33). Figure 7 shows how the SEDI varies with electron density at the bond critical point: it is evident that there is no simple correlation although the trend that they decrease together is clear.

However, a detailed look reveals that bonds in most molecules with tetracoordinate sulfur generally lie on a lower trend line and that those with tri- and dicoordinate sulfur lie on an upper one. The SEDI values for a few molecules are between the two trend lines; notably, those for SO_3^{2-}, SO_3, CH_2SO_2, and SOF_2 are lower than expected for tricoordinate species, and those for Me_2SO_2, H_2SO_2, and SO_2Cl_2 are higher than expected for tetracoordinate species. Molecules whose S,O bonds are con-

TABLE 2: Electron Density, SEDI, and Charges on S and O Atoms[a]

	SEDI	ρ	qS	$-q$O	ρ (est)
SF_4O	1.102	0.337	3.829	1.240	0.337
SO_2F_2	1.096	0.337	3.897	1.278	0.327
SO_2Cl_2	1.200	0.324	2.869	1.246	0.302
SOF_2	1.360	0.322	2.554	1.254	0.320
SO_3	1.206	0.319	3.615	1.204	0.328
$(HO)_2S-O_2$	1.050	0.326	3.824	1.324	0.321
H_2SO_2	1.196	0.316	2.754	1.318	0.303
$(NH_2)_2SO_2$	1.038	0.319	3.613	1.357	0.314
CH_2SO_2	1.236	0.312	2.571	1.255	0.298
SO_2	1.468	0.307	2.401	1.200	0.331
$SOCl_2$	1.440	0.307	1.717	1.199	0.299
Me_2SO_2	1.134	0.312	2.612	1.347	0.288
$HOS\text{-}O_3^-$	0.974	0.312	3.806	1.393	0.314
$NH_2SO_3^-$	0.970	0.308	3.667	1.402	0.308
$HOS-O_3^-$	0.956	0.308	3.806	1.398	0.311
$S(NSO)_2$	1.386	0.293	2.061	1.223	0.304
HSO_3^-	1.004	0.302	3.408	1.408	0.304
$NH_2SO_3^-$	0.958	0.303	3.667	1.408	0.307
CH_2SO	1.400	0.287	1.703	1.236	0.293
H_2SO	1.416	0.285	1.453	1.263	0.287
$S_2O_3^{2-}$	0.993	0.291	3.096	1.416	0.288
Me_2SO	1.338	0.282	1.337	1.305	0.270
SO_4^{2-}	0.878	0.284	3.830	1.459	0.305
SO_3^{2-}	1.132	0.260	2.381	1.459	0.286
$(HO-)_2SO_2$	0.680	0.241	3.824	1.222	0.238
$(MeO)_2S$	1.090	0.204	1.094	1.104	0.205
$(HO)_2S$	1.126	0.201	1.077	1.133	0.213
$HO-SO_3^-$	0.628	0.204	3.806	1.183	0.223
$(HS)_2O$	1.108	0.188	0.578	1.040	0.189

[a] Shared electron delocalization index, electron density, AIM charges, and estimated electron density.

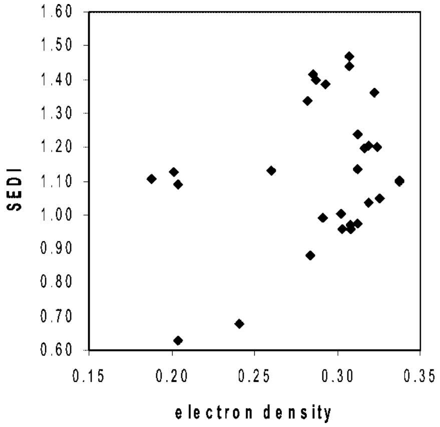

Figure 7. Variation of SEDI with electron density at the bond critical point.

ventionally described as single bonds are present in both major groups. It was pointed out by Chesnut and Quin[3] that sulfones, with sulfur bonded to two oxygens, will generally have bonds of greater polarity than sulfoxides when sulfur is bonded to only one oxygen, and so the corresponding SEDI will be smaller. The more general effect of the differing polarities of the bonds with two, three, and four coordinate sulfur is found here for the more extensive collection of molecules.

In contrast, the linear variation of the bond length with electron density suggests that the electron density at the bond critical point is determined almost completely by the bond length, which is itself a consequence of the attractive forces between the electrons and nuclei. Classically, bond order is the number of shared pairs of electrons, taking no account of the polarity of a bond, whereas the SEDI is reduced by the partial transfer of electrons in polar bonds.[6] Consequently, the attractive forces between the electrons and nuclei could be considered as a combination of the SEDI (the covalent part) and the polar (or ionic) part from the transfer of electrons.

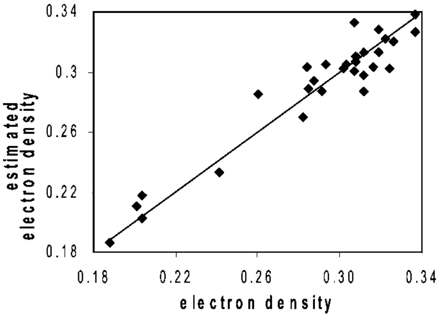

Figure 8. Correlation of estimated and actual electron density at the bond critical point.

The contribution to the forces from the attraction of a nucleus for the other atom's electrons (which could be called the ionic contribution) can be crudely approximated by considering the atoms as point charges. Here (Table 2), the charges of the AIM atoms are used, and they range for the sulfur atom from 0.58 for $(HS)_2O$ to 3.9 for SO_2F_2; the charges for the oxygen atom only vary from −1.04 to −1.46. The regression of the product of those charges and the SEDI (δ_{SO}) with the electron density gives a good correlation ($R^2 = 0.92$), Figure 8, with the equation

$$\rho_b = 0.201 \times \delta_{SO} + 0.0327 \times q_s \times (-q_o) - 0.055$$

Despite its limitations, the inclusion of AIM atomic charges compensates the reduction of the SEDI with polarity and adequately accounts for the variation in the electron density, ρ_b (contrast Figures 7 and 8, the latter having a single trend line with a mild scatter of points). Although the identical equation cannot be presumed to hold for polar bonds involving other atoms, similar empirical equations could be found, and comparison could be informative.

3. Localized Orbitals and Bond Orders. Cioslowski's orbital localization and bond order enables us to assess the contribution of localized orbitals to the bond order (Table 3).

Typically, the Cioslowski bond order is 10% greater than the SEDI for these molecules, which is not as negligible a difference as is often assumed. The SEDI values in this table are often larger than those in Table 1; they are from 6−311++G(2d,p) optimized wave functions as the localization procedure often did not converge with the more accurate 6−311++G(3df,2pd) wave functions. A further point is that only the main orbital contributions to the Cioslowski bond order are presented here; for example, with SO_2F_2, the other bonds and more localized orbitals each contribute small amounts (0.0085 and less) which make the given total of 1.325. For sulfoxides and sulfones (SO_aX_2, a = 1, 2; X = H, F, Cl, CH_3, NH_2), the S,O bond order is substantially increased because of back-bonding from the oxygen lone pairs, which is in line with Chesnut and Quinn's earlier results.[3] There is a σ orbital contributing typically 45−50% of the bond order with about 55% ionicity and two lone pairs each contributing 20−25% of the bond order and typically with ionicities of 75−85% (the third lone pair is essentially localized on the oxygen). Where present, the sulfur lone pair also contributes, but it contributes only about 6% of the total. The sulfoxides H_2SO and $(CH_3)_2SO$ are outside these ranges; their sigma type orbitals have lower ionicities (ca. 47%) with the oxygen lone pairs together only contributing ca. 37% of the total bond order. They also have significantly longer S,O

TABLE 3: SEDI and Contributions to Cioslowski Bond Order (BO)[a]

			contribution of σ		contribution of π		contribution of lone pair	
	SEDI	BO	to BO	*i*	to BO	*i*	to BO	*i*
SF_4O	1.216	1.349	0.684	52.9	0.404	75	0.210	88
SO_2F_2	1.204	1.325	0.658	55.6	0.338	80	0.280	83
SO_2Cl_2	1.288	1.417	0.663	54.9	0.358	79	0.312	82
SOF_2	1.452	1.544	0.635	59.1	0.440	73	0.337	80
SO_3	1.292	1.473	0.696	52.4	0.497	69	0.217	88
$(HO)_2S-O_2$	1.154	1.273	0.651	56.3	0.316	81	0.250	86
H_2SO_2	1.270	1.335	0.647	56.8	0.312	82	0.271	85
$(NH_2)_2SO_2$	1.150	1.243	0.639	57.5	0.281	84	0.252	86
CH_2SO_2	1.236	1.376	0.656	55.8	0.370	78	0.254	86
SO_2	1.532	1.676	0.637	61.5	0.609	58	0.270	85
$SOCl_2$	1.512	1.634	0.679	55.5	0.402	76	0.402	76
Me_2SO_2	1.210	1.268	0.640	57.2	0.281	84	0.252	86
$HOS-O_3^-$	1.070	1.165	0.639	57.2	0.265	85	0.209	88
$NH_2SO_3^-$	1.070	1.169	0.639	57.2	0.262	85	0.202	88
$HOS\text{-}O_3^-$	1.054	1.166	0.645	56.6	0.264	85	0.203	89
$S(NSO)_2$	1.448	1.572	0.664	56.6	0.491	69	0.262	85
HSO_3^-	1.090	1.174	0.625	58.4	0.214	85	0.259	88
$NH_2SO_3^-$	1.050	1.153	0.640	57.0	0.246	86	0.206	88
CH_2SO	1.400	1.486	0.700	53.5	0.376	76	0.231	87
H_2SO	1.466	1.482	0.763	46.8	0.313	82	0.232	87
$S_2O_3^{2-}$	1.078	1.159	0.640	56.4	0.237	86	0.207	88
Me_2SO	1.400	1.415	0.747	48.3	0.226	84	0.277	87
SO_4^{2-}	0.974	1.069	0.649	55.8	0.185	90	0.185	90
SO_3^{2-}	1.206	1.286	0.678	54.3	0.226	87	0.226	87
$(HO-)_2SO_4$	0.758	0.851	0.631	56.4	0.108	94	0.027	100
$(MeO)_2S$	1.116	1.166	0.717	49.9	0.180	90	0.185[b]	93
$(HO)_2S$	1.152	1.193	0.733	49.6	0.183	90	0.193[b]	93
$HO-SO_3^-$	0.690	0.790	0.622	56.5	0.082	96		
$(HS)_2O$	1.120	1.143	0.766	44.9	0.105	95	0.172[b]	94

[a] SEDI; Cioslowski bond order; contributions from localized orbitals and their ionicities using 6−311++G(2d, p) wave functions. [b] Indicates lone pair on S atom.

bonds than the others of this group. The monocoordinate S,O bonds in H_2SO_4 and the various singly charged substituted oxoanions XSO_3^- (X = H, HO, S, NH_2) have similar character to those of the sulfones, but with slightly lower contributions from the oxygen lone pairs to the total bond order.

Somewhat different properties characterize the planar oxides SO_2, SO_3, and $S(NSO)_2$: the sigma bonding orbitals have similar ionicities (52−62%) but contribute a lower fraction (38−47%) of the bond orders (1.473−1.676) with a pi bonding orbital of slightly greater ionicity (58−69%) contributing 31−36% of the bond order and one of the two oxygen lone pairs contributing about 16% of the bond order. For SO_2 and $S(NSO)_2$, the sulfur lone pair also contributes but only about 6% of the total.

The oxygen lone pairs of the binary oxoanions SO_4^{2-} and SO_3^{2-} all have slightly higher ionicities than the previous groups but together still contribute about one-third of the bond order with the S lone pair providing about 9% for the sulfite ion.

The S,O bonds with dicoordinate O have very localized oxygen and sulfur lone pairs (≥90%, where present) which nevertheless together contribute 25−35% of the bond order. The S,OH bonds in H_2SO_4 and its anion have a much lower bond order than the other three (which also have dicoordinate S) because of the much higher ionicity of the former bonds and the contributions from the S lone pairs in the latter (which comprise about 16% of their total bond orders).

A comparison of the bond order contributions and ionicities with those of the P,O bonds studied by Chesnut[34] is useful. The S,O bonds in the planar oxides have σ and π orbitals with similar characteristics to those of the formal double bond of HPO. Most of the other monocoordinate S,O bonds have similar characteristics to the phosphoryl bonds but with a lower ionicity especially for the lone pairs/π-bonds. A few (notably SF_4O and CH_2SO_2) are intermediate in character between these two groups.

Conclusion

Polar covalent bonds, as exemplified by the S,O bonds studied here, can be characterized in the AIM approach by substantial electron density at the bond critical point (ρ_b) together with a positive Laplacian ($\nabla^2\rho_b$). They are distinguished from closed shell (ionic) interactions by their high electron density and negative electronic energy density H_b at that point as well as by a substantial delocalization index (SEDI). The large charge transfer between the atomic basins of the atoms results in the positive Laplacian at the bond critical point, values of λ_1/λ_3 less than unity, and the kinetic energy density per electron G/ρ_b greater than unity; all of these are opposite to that found for homopolar covalent bonds.

When considering the variation of various properties at the bond critical point with S,O bond length, all of electron density, ρ_b, the kinetic energy density per electron G/ρ_b, and the negative of the electronic energy density H_b decrease with increasing bond length, which are characteristics shared with homopolar bonds. The Laplacian $\nabla^2\rho_b$, being positive, also decreases with increasing bond length. Plots of ρ_b and G/ρ_b with bond length show a clear distinction between formal single bonds and those that are often given double bond status.

The decrease of ρ_b with S,O bond length is modeled very well by combining the delocalization index (SEDI) with the product of the AIM ionic charges showing clearly the effect on the bond lengths of both shared electrons and polarity from partial electron transfer.

This study of S,O bonds has also shown that many S,O bonds can be considered to be double bonds. Generally, the location of the VSCCs on their oxygen atoms is trigonal, which accords with the classic view of lone pairs on double-bonded oxygen atoms. The relatively high values of their delocalization indices (contrasted with the low values found for comparably polar single bonds) corroborate this assessment as do the contributions from both sigma type and lone pair/pi-type Cioslowski localized orbitals. The ellipticity of very polar bonds cannot, however, be considered to be a useful indictor of the existence or otherwise of multiple bonding.

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