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Bonding between Nonbonded Sulfur and Oxygen Atoms in Selected Organic Molecules (A Quantum Chemical Study)

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Abstract: A series of model compounds capable of intramolecular sulfur(II)–oxygen interaction of the 1,5-type was investigated by the ab initio SCF–MO method. Compounds of the type $X{-}S{-}A{=}B{-}Y(Z){=}O$ with cis configuration about $A{=}B$, containing X = F, OH, NH_2, CH_3, and SH; A = CH; B = CH and N; and Z = H, O, as well as lone pair, were studied. This resulted in four families containing a total of twenty compounds. The geometries of two basic planar conformations of these compounds, s-cis/s-trans (CT) and s-trans/s-trans (TT), obtained by internal rotations about the B–Y and S–C bonds, respectively, were optimized by using three different basis sets. These energy minimum conformations represent optimum geometries with and without S$\cdots$O interactions, respectively. Four quantities were used to measure the extent of S$\cdots$O interactions. These included the lengthening of the $Y{=}O$ bond on going from TT to CT [$\Delta R(Y{=}O)$], the shortening of the S$\cdots$O distance [$\Delta R(S\cdots O)$], the energy change between TT and CT [$\Delta E(S\cdots O)$], and the Mayer type bond order in the CT conformations [$B(S\cdots O)$]. The linear interdependence of these four quantities indicated that each of these four parameters was about equally good measure of the extent of S$\cdots$O interaction. With the aid of these numerical measures earlier qualitative principles may now be evaluated quantitatively. Depending on the constitution of the individual compounds studied, the covalent character of the S$\cdots$O "bond" was found to be 10–30% of a usual single bond when sulfur d orbitals were included in the split-valence basis set. In compounds with X = OH, the O—S$\cdots$O moiety can be related to the nonequivalent O–S—O hypervalent bond of unsymmetrical sulfuranes.

Intramolecular interactions between a pair of nonbonded fragments of a molecule have an important role in governing properties like conformation, spectroscopic behavior, or chemical reactivity. Moreover, after the pioneering work of Bürgi and Dunitz,[1] it has also been pointed out[2] that the relative positions of reactive moieties in the crystalline state are in fact along the direction that one expects from reactants in the early stage of a given reaction. This of course offers an invaluable tool for the study of the initial part of a chemical reaction and yields important pieces of information about the reaction coordinate itself.

An extremely interesting case, which is not yet fully understood, is the interaction of nonbonded S and O atoms, since these atoms do not escape from a very close contact. In fact a large number of organosulfur compounds are known, where the actual conformation is controlled by intramolecular sulfur–oxygen (S$\cdots$O) interactions.[2,3] In these molecules the S$\cdots$O nonbonded distances are significantly shorter (2.03–3.00 Å) than the sum of the corresponding van der Waals radii (3.25 Å). The interest in these kinds of compounds is at least twofold. First, the stability of S$\cdots$O close contact conformations in crystalline[2,3] and gas[4] phase may explain the unusual spectroscopic and physicochemical properties of these compounds as well as their behavior in chemical reactions.[5] Secondly, understanding the electronic structure of these molecules may add important information to the nature of S–O bonding. Typically, S–O single and double bonds are shorter than 1.65 Å, while the sum of the van der Waals radii is 3.25 Å. The remaining gap of 1.60 Å (from 1.65 to 3.25 Å) is partially covered by hypervalent S–O bonds that may be as long as 2.25 Å. The nonbonded S$\cdots$O interactions fall in the critical region between 2.0 and 3.0 Å, which is not covered by any other known type of S–O bonding. Since the region of nonbonded interactions overlaps with that of the hypervalent bonds, it would be interesting to know what the difference is, if there is any, between these "covalent" and "nonbonded" type of contacts. Compounds exhibiting S$\cdots$O

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(5) Givens, E. N.; Kwart, H. *J. Am. Chem. Soc.* **1968**, *90*, 378–386. Kwart, H.; Omura, H. *Ibid.* **1971**, *93*, 7250–7256. Kapovits, I.; Ruff, F.; Gulyás, J.; Kucsman, Á. *Tetrahedron* **1976**, *32*, 1811–1818. Ruff, F.; Kapovits, I.; Rábai, J.; Kucsman, Á. *Ibid.* **1978**, *34*, 2767–2773.

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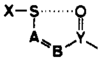
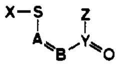
close contact together with geometrical data have been reviewed recently in ref 2. The empirical rules about S···O interaction which have been established by the analysis of X-ray data collected from Cambridge Crystallographic Database are also summarized.

A particular class of compounds exhibiting S···O close contact can be characterized by a planar, conjugated five-membered "ring", closed by the nonbonded sulfur(II) and oxygen atoms, as it is represented by **1**-CT. In both structures X = halogen, O, N, C, or S; A = C(sp^2); B and Y = C(sp^2), N(sp^2); Z = O, N, C, H, or lone pair. CT and TT symbolize the s-cis-s-trans (synperiplanar–antiperiplanar) and s-trans-s-trans (antiperiplanar–antiperiplanar) arrangements around the Y–B and A–S single bonds. Such 1,5-type interactions produce the shortest S···O nonbonded distances known. An essential structural feature of these molecules is the presence of a nearly linear X—S···O sequence, where the O(sp^2) atom belongs to a carbonyl, nitroso, or nitro group and X is an electronegative or polarizable "counteratom".

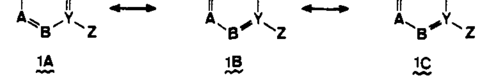

1-CT


1-TT

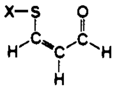
The quantum chemical interpretation of the nature of the S···O interaction has already been attempted by several authors using qualitative arguments[6] and/or semiempirical (extended Hückel[7,8] or CNDO/2[9]) calculations.

On qualitative grounds one can argue that the X—S···O sequence is nothing but an example of a "four-electron three-center bond", which has been discussed recently.[10] However, one must not forget that the presence of the central sulfur atom, by its ability to extend its valence shell, lends some special feature to the S···O interaction. If this were not the case then the situation could be explained fully as a four-electron three-center bond and similar interactions, such as O···O interactions, could also be expected to the same degree. The following concepts that describe the numerous factors which are suspected to govern, or at least influence, the nature of S···O interaction are worth mentioning: (a) electrostatic (dipole–dipole) forces acting between the X—S and Y=O moieties; (b) the inherent rigidity (or softness) of the "SABYO ring" skeleton; (c) extension of the sulfur valence shell accompanied by a change of its hybridization from sp^3 to sp^{3}d; (d) delocalization of the oxygen lone pair (n_O) to the σ^*_{S-X} antibonding orbital; and (e) formation of a six-electron delocalized π-system in the "SABYO ring".

When a qualitative VB language is used, the concepts c, d, and e may be summarized as a "no-bond single-bond resonance", **1A** ↔ **1C** (cf. the classical paper dealing with S···S interaction[6]), while **1A** ↔ **1B** resonance may be correlated with electrostatic interaction a. Alternatively, qualitative MO-theoretical considerations point out the possibility of an n_O–σ^*_{S-X} orbital interaction as well as a π-conjugative stabilization in the planar five-membered "SABYO ring". Various semiempirical quantum chemical methods may overemphasize one or more of these factors. Consequently the unambiguous characterization of the S···O interaction needs more sophisticated quantum chemical approaches.


1A 1B 1C

A systematic ab initio study was carried out on the series of model compounds of type **2**–**5** which were expected to be capable of more or less effective S···O interaction, i.e., to exhibit S···O contact with relatively short nonbonded distances. As "counteratoms" X = F, O(H), S(H), N(H$_2$), or C(H$_3$) were chosen, which allowed us to investigate how the S···O interaction is influenced by the nature (e.g., electronegativity and polarizability) of X.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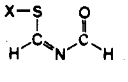
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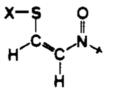
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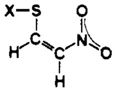
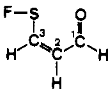
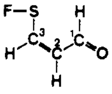

5

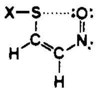
In a previous paper[11] a detailed conformational analysis of one of the model compounds, the (*Z*)-3-fluorothio-2-propenal (**2a**), was reported. It was found that the planar conformations **2a**-CT and **2a**-TT represent the most stable structures of this molecule.

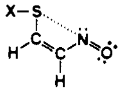

2a-CT


2a-TT

In light of the results of this conformational study, it seemed to be a reasonable choice to restrict our investigation to only these two planar conformers, denoted by TT and CT.

Compounds of type **2** (**2a**–**2e**) and type **3** (**3a**–**3e**) are very similar, the only difference being that in type **3** a more electronegative N is substituting the central C–H unit in the "SABYO ring". For nitro compounds (**5**) the conformations **5**-CT and **5**-TT are identical, due to the local symmetry of the NO$_2$ group. On the other hand, the basic conformations of nitroso compounds (**4**) differ significantly and in an unusual way. While **4**-CT exhibits the expected 1,5-type S···O close contact, **4**-TT is associated with 1,4-type S···N interaction, owing to the nitrogen lone pair.


4-CT


4-TT

Methodology

Since our aim is to characterize the S···O interaction in a series of compounds, we have to define what criteria are to be used to measure the "strength" of the interaction. Three types of parameters have been applied: geometric, energetic, and electronic. The conventional geometrical parameters are the S···O distance and the X—S···O angle in the CT conformations. The energetic criterium can be defined as the energy difference between the optimum TT and CT conformations. Finally, as an electronic parameter, Mayer's[12,13] bond orders B_{AB}

$$B_{AB} = \sum_{\mu\in A}\sum_{\nu\in B} (PS)_{\mu\nu}(PS)_{\nu\mu}$$

and atomic valences V_A

$$V_A = \sum_{B\neq A} B_{AB}$$

have been computed from the ab initio wave functions, where **P** and S are the density and overlap matrices, respectively.

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Table I. Sulfur–Oxygen Nonbonded Distances in the Optimized CT Conformations Calculated by STO-3G, 3-21G, and 3-21G+ Basis Sets

compd type	X	S···O distance (ΔR(S···O))[a] STO-3G	3-21G	3-21G+	expt[b]
2	F	2.8515 (+0.073)	2.5809 (+0.298)	2.3960 (+0.490)	
	OH	2.8623 (+0.069)	2.7041 (+0.195)	2.5404 (+0.361)	2.52 (**6**)
	NH_2			2.7250 (+0.169)	
	CH_3	2.9172 (−0.005)	2.8893 (−0.011)	2.7976 (+0.088)	2.70 (**7**)
	SH	2.8843 (+0.021)	2.7379 (+0.118)	2.6789 (+0.169)	
3	F	2.6810 (−0.036)	2.5686 (+0.225)	2.3790 (+0.385)	
	OH	2.6926 (−0.049)	2.6852 (+0.118)	2.5097 (+0.262)	2.24 (**8**)
	NH_2		2.7822 (+0.015)	2.6752 (+0.097)	
	CH_3	2.7527 (−0.125)	2.8594 (−0.083)	2.7500 (+0.015)	2.68 (**9**)
	SH	2.7229 (−0.101)	2.7350 (−0.037)	2.6508 (+0.103)	
4	F	2.7025 (−0.287)	2.4691 (−0.185)	2.1898 (+0.082)	
	OH	2.7128 (−0.283)	2.5848 (−0.234)	2.3718 (−0.036)	
	NH_2		2.6913 (−0.311)	2.5879 (−0.211)	
	CH_3	2.7707 (−0.339)	2.7709 (−0.363)	2.6652 (−0.268)	
	SH	2.7389 (−0.321)	2.6265 (−0.288)	2.5502 (−0.208)	
5	F	2.7200	2.5271	2.3656	
	OH	2.7365	2.6385	2.4868	2.44 (**10**)
	NH_2		2.7298	2.6407	
	CH_3	2.8062	2.7338	2.6797	2.64 (**11**)
	SH	2.7690	2.6756	2.6083	2.59 (**12**)

[a] Definition given in the text. [b] The boldfaced numbers in parentheses refer to the related compounds investigated by X-ray diffraction.[2] Molecular structures (**6–12**) are given in the text.

Table II. X—S···O Angles (degrees) for the STO-3G, 3-21G, and 3-21G+ Optimized CT Conformations[a]

compd type	X	X—S···O angle STO-3G	3-21G	3-21G+	bond lengths (3-21G+) X—S	Y=O
2	F	169.6	166.8	171.1	1.6308 (0.0169)	1.2288 (0.0189)
	OH	168.3	164.9	169.1	1.6851 (0.0074)	1.2252 (0.0140)
	NH_2			173.3	1.6728 (0.0156)	1.2200 (0.0075)
	SH	171.9	168.5	171.5	2.1163 (0.0131)	1.2194 (0.0083)
	CH_3	172.1	170.0	172.3	1.8192 (0.0010)	1.2179 (0.0054)
3	F	167.2	163.0	168.4	1.6261 (0.0142)	1.2216 (0.0258)
	OH	166.0	160.9	166.3	1.6792 (0.0048)	1.2181 (0.0210)
	NH_2		164.5	170.0	1.6710 (0.0130)	1.2134 (0.0145)
	SH	170.0	165.3	169.0	2.1140 (0.0122)	1.2122 (0.0148)
	CH_3	170.1	166.9	169.6	1.8196 (0.0004)	1.2111 (0.0122)
4	F	167.2	165.4	171.3	1.6334 (0.0172)	1.2647 (0.0411)
	OH	165.9	163.5	168.8	1.6797 (0.0015)	1.2525 (0.0267)
	NH_2		166.8	171.7	1.6715 (0.0065)	1.2393 (0.0124)
	SH	169.5	166.8	170.1	2.1189 (0.0117)	1.2379 (0.0132)
	CH_3	169.7	168.1	170.7	1.8202 (0.0016)	1.2358 (0.0092)
5	F	168.9	165.4	170.1	1.6259	1.2798 (0.0480)
	OH	167.5	163.3	167.9	1.6792	1.2715 (0.0333)
	NH_2			171.8	1.6679	1.2420 (0.0188)
	SH	171.1	166.9	170.2	2.1166	1.2612 (0.0214)
	CH_3	171.1	168.2	170.6	1.8195	1.2444 (0.0117)

[a] The numbers in parentheses are the change (increase) of the bond lengths with respect to the optimized values obtained for the TT conformations with the 3-21G+ basis set.

The full geometry optimizations of the model compounds of type **2** to type **5** in their CT and TT planar conformations were carried out with the MONSTERGAUSS program.[14] Three basis sets were used: the standard minimal STO-3G basis,[15] the split-valence 3-21G basis,[16] and the 3-21G basis augmented with a sulfur d orbital with an exponent of 0.65 (3-21G+ basis).[17] The gradients of the SCF energy expression were calculated analytically with the subroutine FORCE written by Schlegel.[18] The geometries were optimized with the optimally conditioned algorithm of Davidon[19] and unless otherwise indicated satisfy the convergence criterion of reducing the gradient length to 5 × 10^{-4}.

Results and Discussion

(i) **Geometry Optimizations.** The relevant geometrical data characterizing the X—S···O(=Y) fragment in the CT conformation (S···O distances, X—S···O angles, X—S and O=Y bond lengths) are summarized in Tables I and II. The optimized STO-3G, 3-21G, and 3-21G+ geometries and the corresponding total SCF energies are available as supplementary material. The calculations using the largest (split valence) basis augmented by

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[14] MONSTERGAUSS: Peterson, M. R.; Poirier, R. A. Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1, and Chemistry Department, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7. The program is an extensively modified version of GAUSSIAN80: Binkley, J. S.; Whiteside, R.; Krishnan, R.; Schlegel, H. B.; Defrees, D. J.; Pople, J. A. *QCPE* **1981**, *13*, 406.

[15] Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657–2664.

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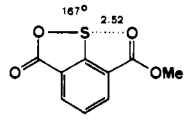
[18] Schlegel, H. B. Ph.D. Thesis, Queen's University, Kingston, Canada.

[19] Davidon, W. C.; Nazareth, L. Technical Memos 303 and 306, 1977, Applied Mathematics Division, Argonne National Laboratories, Argonne, IL. The algorithm is described in the following: Davidon, W. C. *Mathematical Programming* **1975**, *9*, 1.

sulfur d orbitals are generally in good agreement with the experimental S···O distances, which were obtained by X-ray diffraction for the solid-state compounds with related constitution (only the "SABYO ring" skeletons are identical). When judging the deviations in computed and observed distances one may not neglect the experimental fact that a simple change of substituent on the A-B part of the "SABYO ring" may induce a variation as large as 0.10–0.15 Å in the S···O distance. A pronounced change in the S···O distance occurs when substituents on S and Y atoms are replaced (see ref 2). The structures **6–12** used for comparison in Table I are given below.



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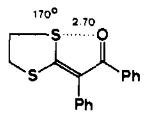

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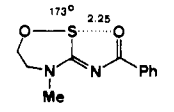

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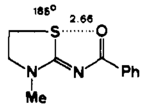

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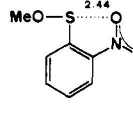

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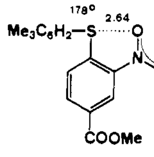

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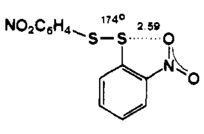

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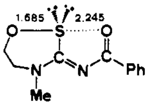
The omission of d orbitals from the basis leads to a lengthening of the S···O distance, and the poorest minimal STO-3G results show even weaker S···O interactions. However, in all the cases the S···O distances are significantly shorter (less than 3.0 Å) than the sum of van der Walls radii (3.25 Å).

As found generally for solid-state structures, the more electronegative the "counteratom" is in the X—S···O part the shorter the S···O nonbonded distance in a given family of compounds is. The experimentally observed trends are well reproduced in the calculations in all four series of compounds (**2–5**), both with and without d orbitals. As measured by the lengthening of the S···O nonbonded distance, the strength of the interaction decreases in the order of F > OH > NH$_2$ $\simeq$ SH > CH$_3$, corresponding to the order of electronegativities. However, the effect of the "counteratom" is much more pronounced in the calculations including d orbitals. In accordance with expectations based on X-ray data (see ref 2), on going from structure **2** to either structure **3**, **4**, or **5** by replacing a C(sp^2) atom in the position of B or Y (see **1**) by N(sp^2) atom, the S···O distance is decreased. In agreement with solid-state structures,[20] all nitroso compounds (**4**) excel in exhibiting very short S···O distances.

The X—S···O angles are in the range of 168–173° (3-21G+ calculations, Table II), which is consistent with the experimental findings. This indicates that the hybridization of the sulfur may be approaching the trigonal-bipyramidal state (180° bond angle). As known, such hybridization is expected by both symmetric and nonsymmetric hypervalent bonds about the central sulfur atom in sulfuranes. Since the axial bond angles about the sulfur in sulfuranes are analogous to the nearly linear X—S···O angles in systems exhibiting S···O nonbonded interaction, we feel that the sulfur-oxygen distances in the above two classes of compounds should be comparable. Atomic distances obtained experimentally provide strong indications that the structure of molecules exhibiting formally a sulfur-oxygen covalent bond and a sulfur-oxygen nonbonded contact (i.e., O—S···O in compound **8**[8]) may be closely related to that of sulfuranes with two nonequivalent O-S-O hypervalent bonds (e.g., O-S-O in **13**[21]).



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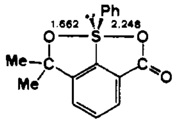
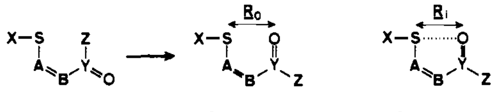


13

A further experimentally established characteristic feature of the S···O interaction is the slight elongation of the X—S and the marked lengthening of the O═Y bonds in structures like **1**-CT relative to bond lengths found in molecules exhibiting no S···O interaction (see ref 2). A more precise measure of the extent of this phenomenon is available if we compare the X—S and O═Y bond lengths of CT with those of TT conformations optimized for compounds **2–5**. The differences in these bond lengths of the CT and TT conformations, as obtained with the d orbital augmented basis set (3-21G+), are given in parentheses in Table II. The corresponding changes obtained without d orbitals are somewhat smaller. The maximum increase in X—S bond lengths is in the order of 0.01 Å for X = SH while the O═Y bond becomes longer by as much as 0.04 Å in certain cases, when X = F. The Y═O bond lengthenings, Δ*R*(Y═O), run roughly parallel with the "strengths of the interaction" governed by the electronegativity of the "counteratom".

In order to be able to use the S···O distance as a semiquantitative measure for the "strength of interaction", it would be important to know what would be the sulfur-oxygen nonbonded distance if no S···O interaction were present. To a first approximation, the S···O distance without S···O interaction can be obtained by taking the **1**-TT optimized geometry, rotating it to the **1**-CT conformation, and calculating the S···O distance in such a geometry. The difference between the two sulfur-oxygen distances, the one without interaction (R_0) and the one with interaction (R_i), yields a difference in distance (ΔR) associated with the S···O interaction.



1-TT geometry optimized

1-CT geometry without interaction

1-CT geometry optimized

$$\Delta R(\mathrm{S\cdots O}) = R_0 - R_i$$

Δ*R* may therefore be regarded in the first approximation as the geometry change due to the S···O interaction. The characteristic Δ*R*(S···O) values are listed in parentheses in Table I.

For compounds **2a–2d** Δ*R*(S···O) runs up to 0.50 Å while Δ*R*(Y═O) varies up to 0.02 Å. However, if both of these changes in distance are equally good measures of the "strength of interaction", then they should relate to each other linearly. This interdependence is illustrated in Figure 1. Similar plots may be obtained for the other two families of compounds (**3** and **4**).

(ii) Energy Differences. Since no experimental data are available on the energy difference between **1**-CT and **1**-TT conformers, only the S···O distance can be used as an experimental measure of the strength of the S···O interaction. Therefore it is interesting to compare the energies of the optimized CT and TT conformations, leading to an energy difference according to the following definition: Δ*E*(S···O) = *E*(TT) - *E*(CT). The calculated energy differences (if the d orbitals are taken into account) support the existence of S···O interaction in the sense that the CT con-

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(21) Lam, W. Y.; Duesler, E. N.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 127–135.

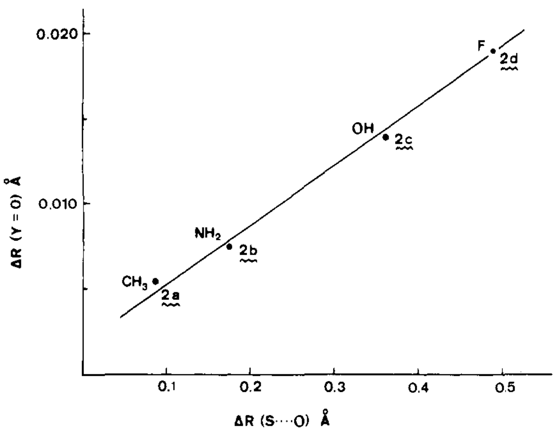

Figure 1. Interdependence of ΔR(Y=O) and ΔR(S···O) for compounds **2a–2d**.

Table III. Energy Difference (kcal/mol) between the TT and CT Conformations of the Model Compounds **2–4** Calculated by STO-3G, 3-21G, and 3-21G+ Basis Sets, with Full Geometry Optimization

compd type	X	ΔE(S···O) STO-3G	3-21G	3-21G+
2	F	1.24	7.80	11.23
	OH	1.18	5.38	8.23
	NH_2	0.86	3.03	4.30
	CH_3	0.13	0.89	2.86
	SH	0.54	3.50	4.94
3	F	3.28	10.97	15.45
	OH	3.12	8.41	12.25
	NH_2	2.67	6.19	8.37
	CH_3	1.70	4.02	6.58
	SH	2.21	6.22	8.48
4	F	−0.93	3.48	8.72
	OH	−0.88	1.88	5.96
	NH_2	−1.18	0.08	1.98
	CH_3	−1.49	−1.26	0.59
	SH	−1.27	0.35	2.11

formations with S···O close contact are of lower energy, by 0.6–15 kcal/mol as shown in Table III. Basis sets without d orbitals, at both minimal and split-valence level, yield much smaller energy differences, in most cases in favor of the CT conformation. For nitroso compounds (**4**) both the calculated (Table I) and experimental[20] S···O distances are very short, suggesting that S···O interaction is the strongest in compounds of type **4**. On the other hand the computed ΔE(S···O) energy differences are much less significant than expected. These results, however, do not imply a weak S···O interaction but, in fact, a difference between the energies of the 1,5 S···O and 1,4 S···N interactions as shown before by structures **4**-CT and **4**-TT. These small positive energy differences, ΔE(S···O), are shifted toward the small negative values when cruder basis sets are used.

It has been established in the previous section that not only the difference in the Y=O bond lengths, ΔR(Y=O), but also the calculated ΔR(S···O) distances can be used to characterize the "strength of the S···O interaction". Plots similar to Figure 1 in which ΔE(S···O) is plotted against ΔR(S···O) reveal linear interdependences in all three basis sets used, indicating that both ΔE(S···O) and ΔR(S···O) are equally good representations of the "strength of the S···O interaction". The three families of plots are shown in Figure 2. All nine straight lines have similar slopes, and for the 3-21G+ basis, the slopes range between 20 and 25 kcal/mol in ΔE(S···O) for 1.0 Å change in ΔR(S···O).

(iii) Analysis of the S···O Bond. The comparison of experimental sulfur(II)–oxygen distances in molecules, either with formally hypervalent covalent S—O bonds or with formally nonbonded S···O contact, shows an almost continuous transition between the two classes. The similar geometry of structures like **8** and **13** suggests the question of whether it is justified to attribute an at least partial covalent bonding character to the extremely short S···O contacts, although they are traditionally considered as linkages of nonbonded nature.

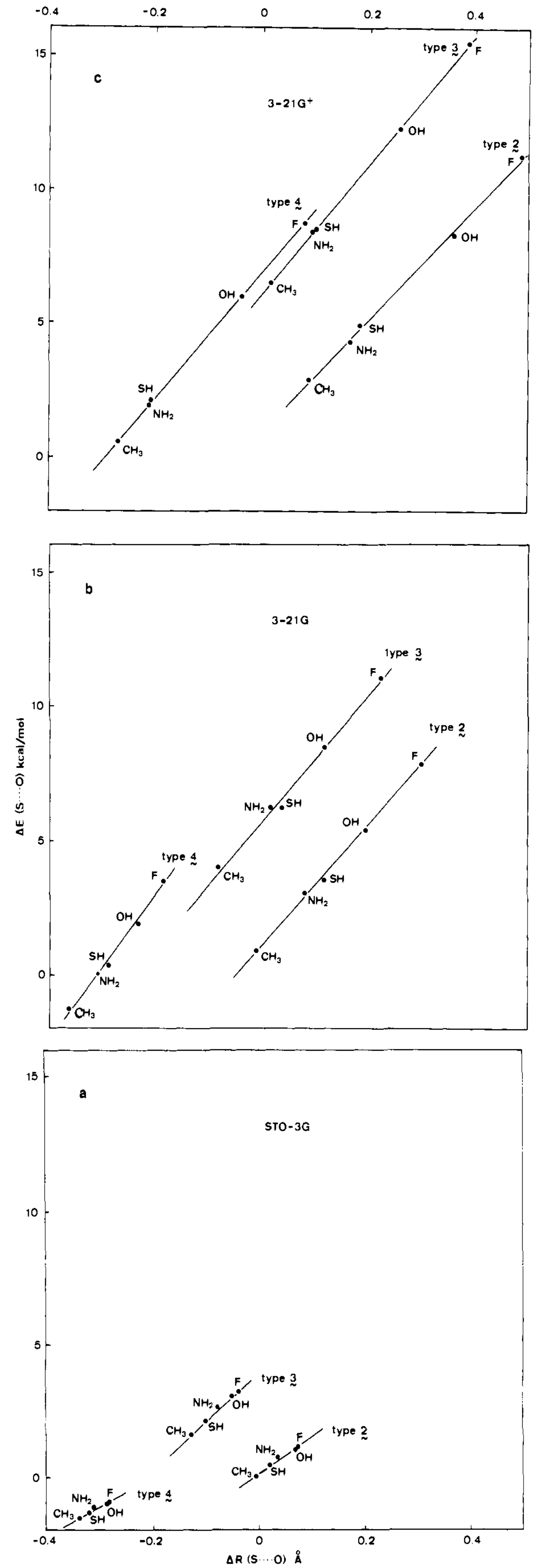

Figure 2. Interdependence of ΔE(S···O) and ΔR(S···O) for compounds **2–4** with use of three different basis sets.

Table IV. Sulfur–Oxygen Bond Orders, $B(\mathrm{S}\cdots\mathrm{O})$, and the Valence of Sulfur, $V(\mathrm{S})$, Determined at the Optimized CT Geometries as Calculated with STO-3G, 3-21G, and 3-21G+ Basis Sets[a]

compd type	X	$B(\mathrm{S}\cdots\mathrm{O})$			$V(\mathrm{S})$		
		STO-3G	3-21G	3-21G+	STO-3G	3-21G	3-21G+
2	F	0.017	0.106	0.166	1.878 (0.020)	1.789 (0.067)	2.081 (0.202)
	OH	0.018	0.087	0.131	2.127 (0.016)	1.899 (0.074)	2.112 (0.167)
	NH_2	0.016		0.090	2.129 (0.014)		2.101 (0.104)
	CH_3	0.015	0.061	0.081	2.166 (0.016)	1.951 (0.064)	2.086 (0.108)
	SH	0.017	0.079	0.099	2.152 (0.019)	1.985 (0.073)	2.098 (0.056)
3	F	0.024	0.106	0.168	2.129 (0.024)	1.832 (0.094)	2.102 (0.216)
	OH	0.024	0.088	0.136	2.162 (0.026)	1.916 (0.078)	2.134 (0.176)
	NH_2	0.021	0.072	0.097	2.160 (0.022)	1.919 (0.064)	2.117 (0.117)
	CH_3	0.020	0.064	0.087	2.196 (0.023)	1.973 (0.067)	2.104 (0.119)
	SH	0.022	0.078	0.102	2.185 (0.028)	1.999 (0.077)	2.114 (0.132)
4	F	0.026	0.133	0.264	2.113 (0.024)	1.864 (0.117)	2.290 (0.365)
	OH	0.027	0.113	0.192	2.145 (0.024)	1.943 (0.095)	2.247 (0.250)
	NH_2	0.023	0.090	0.121	2.144 (0.020)	1.938 (0.072)	2.165 (0.129)
	CH_3	0.022	0.081	0.110	2.178 (0.019)	1.978 (0.066)	2.138 (0.118)
	SH	0.025	0.101	0.132	2.167 (0.022)	2.019 (0.083)	2.166 (0.146)
5	F	0.018	0.103	0.153	2.114	1.822	2.106
	OH	0.017	0.086	0.125	2.147	1.912	2.150
	NH_2	0.014	0.072	0.091	2.146	1.916	2.133
	CH_3	0.013	0.064	0.084	2.179	1.959	2.116
	SH	0.015	0.079	0.098	2.169	1.995	2.126

[a] The numbers in parentheses are the increase of the valence of sulfur, when changing the conformation from TT (without S···O close contact) to CT (with S···O close contact).

We attempted to analyze this problem using the definition of bond orders and atomic valences proposed by Mayer.[12,13] This bond-order definition is related to the exchange part of the second-order density matrix in the LCAO representation, and it offers a physically well-founded way of characterizing the multiplicity of chemical bonds on the basis of ab initio wave functions. Although the actual value of the bond orders may depend slightly on the quality of the basis set, it is a number close to 1, 2, and 3 for usual single, double, and triple bonds, respectively.

The bond orders of the S···O contact, $B(\mathrm{S}\cdots\mathrm{O})$, and the atomic valences of the sulfur, $V(\mathrm{S})$, for the optimized CT conformations of compounds **2**–**5** can be found in Table IV. The changes (increases) of the atomic valences coming from the TT conformation (without S···O close contact) to the CT conformation with S···O close contact are included in parentheses. Both the S···O bond orders and the changes in the atomic valences calculated with the 3-21G+ basis set with d orbitals on sulfur indicate that there is a small but significant amount of covalent interaction between the sulfur and the oxygen atoms. Smaller basis sets yielded significantly less covalency as measured by the S···O bond orders. Furthermore, the sulfur–oxygen 3-21G+ bond orders are by far the largest among the bond orders between any of the nonbonded atoms in the five-membered "SABYO ring" and reach a value of up to 25% of a usual single bond. There is a significant change in the valence of the sulfur when it occupies a position favorable for an interaction with the oxygen. In the case of an F—S···O(nitroso) close contact, **4a**, this increase in computed sulfur valence amounts to 0.37, pointing to a very strong sulfur–oxygen interaction. In effect the shortest S···O distance was found in this molecule. Even the relatively weak H_3C—S···O interactions induce changes of the order of 0.1 in the computed valence of sulfur.

An attempt to relate the two parameters, $\Delta E(\mathrm{S}\cdots\mathrm{O})$ and $B(\mathrm{S}\cdots\mathrm{O})$, that may both characterize the strength of the S···O nonbonded interaction is shown in Figure 3. The nearly linear nature of the plot indicates that both of these parameters are appropriate for a semiquantitative characterization of the strength of such close contacts. The similarity between the electronegativities of N and S manifests itself in the proximity of the points associated with compounds containing X = NH_2 and SH, respectively.

For compounds 2 and 3 the energy change is 10–11 kcal/mol per 0.1 bond order change, while for the nitroso compounds (**4**), where the conformational change involves 1,5 S···O and 1,4 S···N interactions, the slope is around 5 kcal/mol per 0.1 of bond order change.

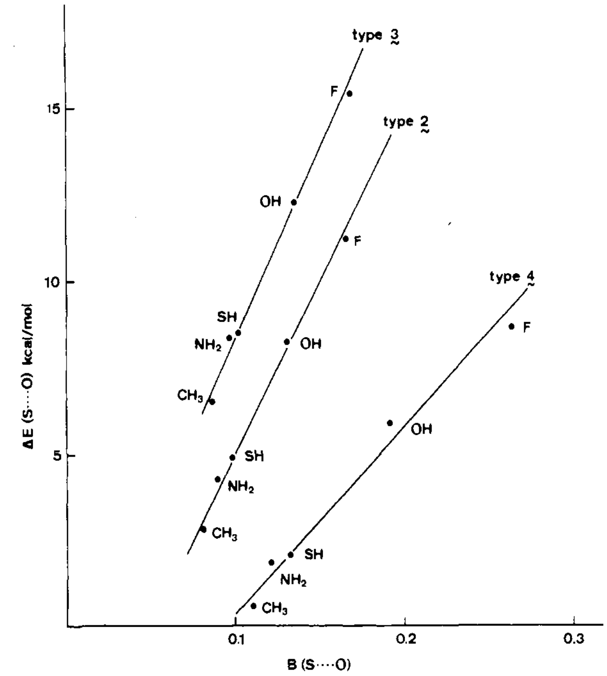

Figure 3. Interdependence of $\Delta E(\mathrm{S}\cdots\mathrm{O})$ and $B(\mathrm{S}\cdots\mathrm{O})$ for compounds **2**–**4** computed with the 3-21G+ basis set.

(iv) The Role of d Orbitals. It remains to be clarified whether the d orbitals on the sulfur atom participate in the S···O interaction in a chemically significant amount or whether their role is simply to improve mathematically the deficiencies of the sp basis set. The situation is far from being clear. One can argue that some of the qualitative features of the S···O interaction such as the S···O distance within the sum of van der Waals radii, the energetic preference of the CT conformation, the nearly linear X—S···O fragment, the lengthening of the Y=O bond, etc., are already present in the calculations with sp basis sets (STO-3G or 3-21G). Moreover, there are quite significant differences between the results obtained by the two sp basis sets (the interaction seems to be stronger with 3-21G basis), and the changes induced by the

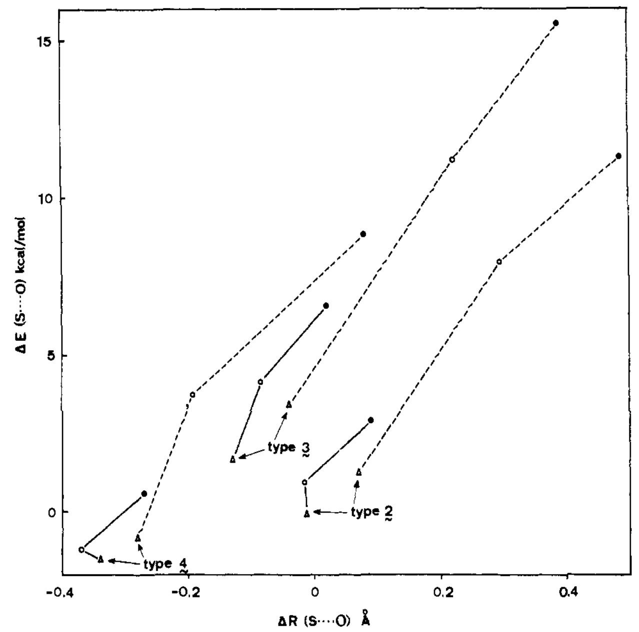

Figure 4. Basis set changes (STO-3G (Δ) → 3-21G (○) → 3-21G+ (●)) in the variation of ΔE(S···O) with ΔR(S···O) for three families of compounds (**2**, **3**, and **4**) with X = F (a, broken line) and X = CH_3 (d, solid line).

addition of d functions to the 3-21G set do not appear to be much more dramatic than those accompanying the improvement of the sp basis. One should also be aware of the fact that improvements in the sp basis may by themselves ensue important changes in the *local* geometrical parameters, independent of the S···O interaction. In principle these local variations of the bond lengths and bond angles in the "SABYO ring" when passing from STO-3G to 3-21G basis may cause the shortening (or lengthening) of the S···O distance in an indirect manner.

In order to evaluate the role of the different basis sets we compared the three families of compounds (**2**, **3**, **4**) for X = F (**a**) and X = CH_3 (**b**). These two "counteratoms" represent two extremes in enhancing the formation of hypervalent sulfur, which is, at least, partially created in an S···O interaction. The basis set changes are represented in Figure 4.

There are several points to note about this diagram. (1) The X = CH_3 curves are always to the left with respect to the X = F curve of all three types of compounds. (2) The X = OH, NH_2, as well as SH curves not shown in the figure fall between the pair of curves shown. (3) The extent, both horizontal and vertical, of the X = CH_3 curves is substantially smaller than the X = F curves, indicating a weaker interaction for X = CH_3 than X = F.

This latter point leads to the discussion of basis set effects including the role of d orbitals. In the case of X = F, where the interaction is strong, the improvement of the sp basis set (STO-3G to 3-21G) represents a substantial improvement in the description of the interaction. When d orbitals are added (3-21G to 3-21G+), the improvement of the description of the "strength of interaction" is again appreciable. However, in the case of X = CH_3 where the "strength of interaction" is relatively small, and inherently more difficult to describe, we find that the change in the sp basis set (STO-3G to 3-21G) hardly makes any improvement in the description at all, while the addition of d orbitals (3-21G to 3-21G+) makes a considerably larger jump in the description of the interaction. This implies that for the case where the S···O nonbonded interaction is strong, the d orbitals do not play a crucial role in describing the interaction as they do in the case where the S···O interaction is relatively weak (X = CH_3) and therefore more difficult to describe.

However, at this level of calculation one cannot fully exclude the possibility of certain artefacts concerning the role of d orbitals. One has to emphasize that in all the present calculations five d functions were used, that is the totally symmetric, s-type combination of the six Cartesian d functions was omitted from the basis. This excludes the possibility of a crude artefact, which would have resulted from the considerable participation of a six d set in the description of the s shells.[22-24] However, the d orbitals may still act by improving the deficiencies of the 3-21G basis. Therefore a few calculations were carried out on compound **2a** (X = F) with a 3-21G basis set augmented by an additional set of s and p Gaussian functions using the same exponent as for the d function in the 3-21G+ set. At fixed (3-21G+ optimized) geometry the B(S···O) bond order diminishes with respect to the 3-21G+ value from 0.166 to 0.137.

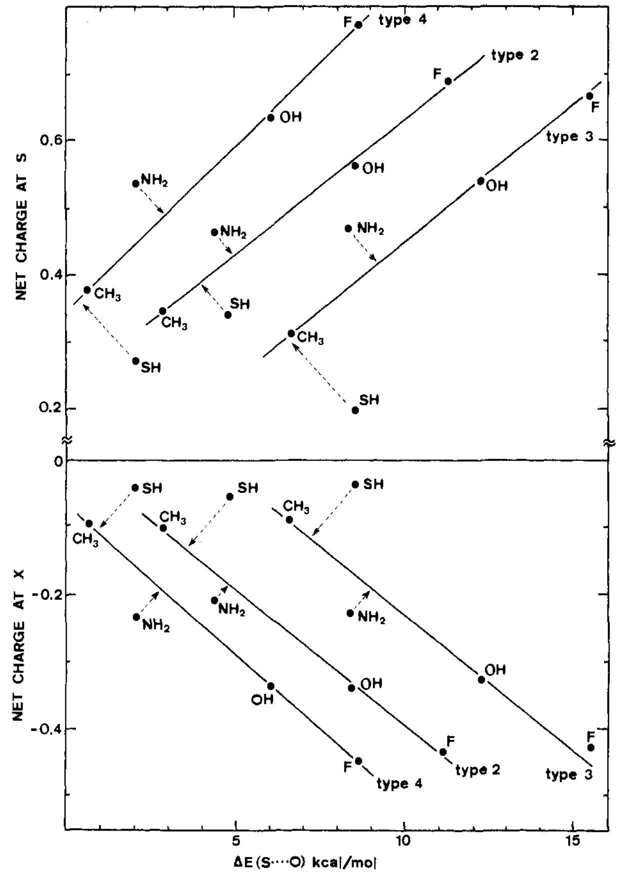

Figure 5. Interdependence of ΔE(S···O) and net charge at S and at X for compounds **2**–**4** computed with the 3-21G+ basis set.

The optimized S···O bond lengths (R (Å)) and the corresponding B(S···O) bond orders obtained with this basis set containing 17 sp functions on sulfur (5s4p) were compared with the 3-21G (4s3p) and 3-21G+ (4s3p1d) results:

basis on S	R (Å)	B(S···O)
13 AO (4s3p) (3-21G basis)	2.5809	0.106
17 AO (5s4p)	2.6062	0.101
18 AO (4s3p1d) (3-21G+ basis)	2.3961	0.166

These data clearly indicate that while the addition of a set of five d orbitals to the 3-21G basis set definitely improves the description of the interaction both in terms of R and B(S···O), the inclusion of the supplemental four sp orbitals actually ruins the description achieved at the 3-21G level. Clearly the d orbitals represent more than just five extra functions in the basis set. A further test was made to eliminate other possible basis errors. An additional d orbital was added to the oxygen atom (the one interacting with S), but all changes were insignificant, indicating that at the 3-

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(23) Hopkinson, A.; Lin, M.; Poirier, R.; Csizmadia, I. G. *C. R. Acad. Sci. Paris* **1981**, *293*, 937–939.
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Table V. Net Mulliken Atomic Charges for the X—S···O Moiety of Compounds **2–5** in CT and TT Conformations at the 3-21G and 3-21G+ Level

compd			X		S		O	
type	X		3-21G	3-21G+	3-21G	3-21G+	3-21G	3-21G+
2	F	CT	−0.4688	−0.4383	0.8002	0.6901	−0.5585	−0.5858
		TT	−0.4344	−0.3988	0.7331	0.6258	−0.5228	−0.5283
	OH	CT	−0.3563	−0.3370	0.6654	0.5702	−0.5538	−0.5749
		TT	−0.3146	−0.2956	0.5874	0.5000	−0.5332	−0.5380
	NH_2	CT	−0.2836	−0.2063	0.6015	0.4578	−0.5469	−0.5456
		TT	−0.2466	−0.2372	0.5315	0.5050	−0.5406	−0.5589
	CH_3	CT	−0.1343	−0.1034	0.4674	0.3483	−0.5350	−0.5472
		TT	−0.0847	−0.0576	0.3799	0.2725	−0.5407	−0.5431
	SH	CT	−0.0755	−0.0526	0.3235	0.3451	−0.5353	−0.5474
		TT	+0.0149	+0.0186	0.2053	0.1497	−0.5294	−0.5337
3	F	CT	−0.4641	−0.4308	0.7396	0.6670	−0.5415	−0.5738
		TT	−0.4308	−0.3918	0.6389	0.5824	−0.4807	−0.4890
	OH	CT	−0.3509	−0.3290	0.6013	0.5442	−0.5361	−0.5629
		TT	−0.3099	−0.2870	0.4921	0.4535	−0.4920	−0.5003
	NH_2	CT	−0.2783	−0.2278	0.5377	0.4731	−0.5296	−0.5462
		TT	−0.2391	−0.1946	0.4432	0.4098	−0.5003	−0.5082
	CH_3	CT	−0.1248	−0.0920	0.4038	0.3141	−0.5177	−0.5340
		TT	−0.0747	−0.0442	0.2995	0.2247	−0.5007	−0.5057
	SH	CT	−0.0570	−0.0362	0.2428	0.2041	−0.5161	−0.5332
		TT	+0.0268	+0.0343	0.1023	0.0914	−0.4876	−0.4950
4	F	CT	−0.4682	−0.4486	0.8405	0.7804	−0.3663	−0.4261
		TT	−0.4436	−0.4057	0.7836	0.6701	−0.3243	−0.3325
	OH	CT	−0.3552	−0.3417	0.7030	0.6358	−0.3605	−0.3998
		TT	−0.3267	−0.3041	0.6461	0.5509	−0.3361	−0.3442
	NH_2	CT	−0.2813	−0.2363	0.6315	0.5386	−0.3510	−0.3685
		TT	−0.2587	−0.2134	0.5909	0.5030	−0.3435	−0.3511
	CH_3	CT	−0.1253	−0.0985	0.4884	0.3764	−0.3367	−0.3536
		TT	−0.0998	−0.0713	0.4440	0.3304	−0.3421	−0.3467
	SH	CT	−0.0641	−0.0469	0.3475	0.2775	−0.3374	−0.3554
		TT	−0.0122	−0.0021	0.2800	0.2129	−0.3287	−0.3357
5	F		−0.4633	−0.4311	0.8571	0.7410	−0.4048	−0.4197
	OH		−0.3489	−0.3299	0.7223	0.6232	−0.3994	−0.4118
	NH_2		−0.2771	−0.2291	0.6578	0.5529	−0.3928	−0.3998
	CH_3		−0.1179	−0.0915	0.5139	0.3921	−0.3815	−0.3895
	SH		−0.0489	−0.1992	0.3656	0.2869	−0.3833	−0.3903

21G+ level intramolecular basis set superposition effects are negligible.

It is to be noted that quite recently Morokuma et al. analyzed the role of d orbitals in the S···N interaction found in ammonioalkylsulfuranes.[25] Here the d orbitals on sulfur seem to be indispensable for the description of the interaction. Mayer et al. analyzed the bond orders for a couple of model compounds closely related to our molecules of type **3** with X = OH and CH_3.[26,27] These calculations were done at fixed experimental geometries and used STO-3G and STO-3G* basis sets. The d-orbital effects found in this work are certainly exaggerated, but the qualitative conclusions seem to be correct in the light of the present more detailed analysis.

There is one more point to discuss when we are considering the role of d orbitals in the description of S···O interaction. In the nearly linear —(X—)S···O═ structure that looks like a "premature" >(X—)S—O— hypervalent part in a sulfurane one may wonder to what degree the "bonding" between the "nonbonded" S···O moiety is due to ionic and to what degree it is due to covalent interaction. The computed Mayer type bond order between sulfur and oxygen, B(S···O), indicated that the covalency is increased when d orbital was included in the basis set. In other words, the d orbitals were essential in the description of the covalent component of the "bonding" between the "nonbonded" S···O atoms. By the same token we may wonder whether the inclusion of d orbital decreases the ionic character of the "bonding" between the "nonbonded" S···O atoms. For this reason we computed the net atomic charges using Mulliken's population analysis without the inclusion of d orbitals (3-21G basis) and with the inclusion of d orbitals (3-21G+ basis). The net charges for the three atoms in the X—S···O unit are summarized in Table V. The results do indicate a decrease in ionic character when going from 3-21G to 3-21G+. In general the S becomes less positive and the O slightly more negative. The net charge at X also reflects the fact that the more electronegative X the greater the interaction. This is clearly illustrated in Figure 5, which is similar to the previous plots. The major difference in this case is that the NH_2 and SH points do not coincide as they did in the ΔE vs. B(S···O) and ΔR(S···O) plots. This illustrates the importance of the two factors, that is, electronegativity (NH_2) and polarizability (SH) (note in this case that the atoms are homonuclear (S—S)), where compounds with X = NH_2 and SH show similar S···O interaction (similar ΔE's). Both basis set and conformation of the NH_2 group may affect the Mulliken net charge and thus account for the observed discrepancy in the case of NH_2.

Conclusion

In addition to the experimentally determined parameters that include (i) the excessive population of the CT conformation, (ii) the S···O distance (shorter than the sum of van der Waals radii), (iii) the near linearity of the X—S···O fragment, and (iv) the lengthening of the Y═O bond (with respect to some ideal value), we have established three, theoretically defined, computable parameters for the quantitative characterization of the "strength of S···O interaction". These theoretical parameters were the following: (i) the S···O shrinkage from the TT to the CT conformation as measured by ΔR(S···O); (ii) the difference between the energies of the TT and CT conformation as measured by ΔE(S···O); and (iii) the S···O bond order index in the CT confor-

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mation, B(S···O), computed by the definition of Mayer.

As far as the structural changes in the X—S—A=B—Y(Z)=O system were concerned we have established the following pattern: (i) Substitution in X enhances the "strength of the S···O interaction in the following order: F > OH > NH_2 ≃ SH > CH_3. (ii) Changes at position B influence the "strength of interaction" in the order HC(sp^2) < N(sp^2). It is quite likely that changes at position A will respond analogously. (iii) Changes at the O=Y—Z moiety influence the "strength of interaction" in the order OCH > ONO. The position of the nitroso group (O$\ddot{\mathrm{N}}$/) in that order is hard to establish since rotation about the B-Y bond changes a 1,5 S···O interaction to a 1,4 S···N interaction or visa versa.

We have shown that, in addition to electrostatic forces, changes in the Mayer bond index (covalent interactions) are associated with formation of short S···O close contacts. The proper description of these covalent interactions, as measured by the Mayer bond order index, cannot be achieved without the inclusion of sulfur d orbitals.

Finally, the strongest S···O interactions may be regarded as "premature" hypervalent bonds similar to those found in certain nonsymmetric dioxysulfurane derivatives.

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Supplementary Material Available: Tables including the optimized geometries at STO-3G, 3-21G, and 3-21G+ levels and total energies and structures **2**–**5** (15 pages). Ordering information is given on any current masthead page.

The Ethyl Dication ($CH_3CH_2^{\cdot 2+}$): Classical (Open) or Nonclassical (Bridged)?

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Abstract: Ab initio molecular orbital theory using basis sets up to 6-311G** and with electron correlation incorporated at the fourth-order Møller–Plesset level has been used to examine the ethyl radical (**1**), cation (**2**), and dication (**3**). Previously demonstrated preferences for an open (or classical) structure (**1a**) for the ethyl radical and for a bridged (or nonclassical) structure (**2c**) for the ethyl cation have been confirmed. This trend is reversed, however, in the ethyl dication, which returns to a preference for an open structure (**3a**). The ethyl dication is characterized by a short C–C bond (1.433 Å), quite long β C–H bonds (1.121, 1.202 Å), and facile interconversion between staggered (**3a**) and eclipsed (**3b**) conformations. It lies in a moderately deep potential well, being separated from highly exothermic fragmentation to $CH_2^{\cdot +}$ + CH_3^+ and to $C_2H_4^{\cdot +}$ + H^+ by barriers of more than 100 kJ mol^{-1}. The calculated difference (0.5 eV) between vertical and adiabatic ionization energies of the ethyl radical agrees well with a value (0.41 eV) derived from recent experimental data. Our calculated ionization energy for the process $C_2H_5^+ \rightarrow C_2H_5^{\cdot 2+}$ (19.7 eV) is reasonably close to a recent experimental value (19.1 eV).

The ethyl cation has been the subject of considerable recent attention as a prototype for the comparison of classical (open) and nonclassical (bridged) species.[1] There is now substantial theoretical[2] and experimental[3] evidence that the preferred structure of the ethyl cation is bridged rather than open. This contrasts with the situation for the ethyl radical, which has a preferred open structure.[4] Indeed, the experimental observation of a significant difference between vertical and adiabatic ionization energies for the ethyl radical has been taken as evidence for the qualitative difference in structure between the radical (open) and cation (bridged).[3] We present here theoretical evidence that removal of an additional electron, leading to the ethyl dication, reverses the change produced by the initial ionization, returning to a preference for an open isomer. The implications regarding vertical and adiabatic ionization processes that yield the ethyl dication are discussed.

Method and Results

Standard ab initio molecular orbital calculations were carried out with modified versions[5,6] of the Gaussian 80[7] and Gaussian 82[8] series of programs. Optimized geometries were obtained with the 6-31G* basis set[9] at both Hartree–Fock (HF) and second-order Møller–Plesset (MP2)[10] levels of theory using gradient techniques.[11] Unless otherwise noted, it is the latter values which are quoted in the text. Improved relative energies were obtained through calculations with the 6-311G** basis set[12] and with

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