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On the Nature of Hypervalent S–O Bonds in Sulfuranes[*]

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Sulfuranes with pseudo-trigonal-bipyramidal geometry are hallmarked
by two apical hypervalent S–O bonds. According to Musher's classification,
the quasi-linear arrangement of the atoms involved can be interpreted ap-
proximately in terms of an s-p basis, assuming four-electron-three-center
bonds. However, substantial differences between the electronegativities of
the apical groups give rise to rather unsymmetric three-center bonds. In
spirosulfuranes, the unsymmetric polarization of the O–S–O bonds is ter-
minated at around an interatomic distance of 2.26 Å, balanced by an S–O
single bond with a length of 1.63 Å. These asymmetric O–S–O bonds are
formed in sulfonium salts with spirosulfurane geometry. Further asymmetry
of the O–S···O grouping can be generated only for two-electron-three-center
bonds formed by S(II) atoms.

After a few guidelines on the basic forms of sulfuranes, starting with
SF_4, a short review of the analogous azasulfuranes and their sulfonium salts
is presented, demonstrating how the N lone pair participates in the forma-
tion of S(IV)–N multiple bonds which, in turn, terminate the hypervalent
bonds. These three centers possess only three electrons and form a transi-
tional state with long S···O single-bond/no-bond resonance interactions
(2.13–2.80 Å) between four-electron-three-center (*i.e.* hypervalent) bonds and
two-electron-three-center bonds. The unsymmetric sulfuranes (or sulfonium
cations) are best described by six-electron-five-center bond models. S–O bonds
retaining a bond number of at least $n = 1/4$ can still be regarded as hyper-
valent. Further polarization ($n < 0.2$) of these bonds balanced by covalent
bonds ($n > 0.8$) results in three-electron-three-center systems with no hy-
pervalent character.

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INTRODUCTION

In 1973, crystal structure determination[1] of the first stable diaryldiacyloxyspirosulfuranes (**1**) with two, almost collinear, apical S–O bonds substantiated Musher's theory[2] concerning the hypervalent bonding formed by three atomic centers (O–S(IV)–O) with the participation of four electrons. These S(IV)–O bonds (1.83 Å) are significantly longer than the S–O single bond (1.70 Å).[3] The smaller bond order ($B - 1/2$) explains the longer axial bonds in the hypervalent compounds, as compared with the conventional two-electron-two-center equatorial bonds.[4] The latter corresponds to a bond order of unity. The essential criterion for the stability of hypervalent bonds is that the heteroatom should be sufficiently electropositive to donate electrons to the bond, and that the ligand is sufficiently electronegative to attract electrons to the bond. Further structure determinations[5-7] have shown that an increase in the group electronegativity of one substituent leads to the strengthening of the hypervalent bond formed with the other one (*e.g.* replacement of one of the $(CH_3)_2C <$ moieties in **6** by $(CF_3)_2C <$, resulting in **6a**, transforms the O–S–O bonding from the relatively symmetric 1.814(2) + 1.787(2) Å pair into the unsymmetric 1.713(2) + 1.955(2) Å pair). It follows that hypervalent bonds are easily deformable (and highly polarizable), which in turn accounts for the »long bridge« between the covalent bonds (varying in the range 1.4 – 1.7 Å) and the S(II)$\cdots$O close contacts, first reported[8] in 1961.

The link between these »two-electron-three-center« bonds[9] and their hypervalent »four-electron-three-center« analogs was established by X-ray analysis of 1-[2'-(N-methylcarbamoyl)phenyl]-3H-2,1-benzoxathiol-1-ium (**8**) chloride.[10,11] The parameters of the three-center bonds (S–O = 1.635(2) Å, S$\cdots$O = 2.260(2) Å and O–S$\cdots$O = 179.4(1)° agree with those of 3-benzoylimino-4-methylperhydro-1,2,4-oxathiazine (**7**)[12] (S–O – 1.685(3) Å, S$\cdots$O = 2.245(3) Å, O–S$\cdots$O = 173.2(3)°) and the unsymmetric sulfurane **5**[5] (S–O = 1.662(2) Å, S$\cdots$O = 2.248(2) Å, O–S$\cdots$O = 170.5(1)°). Further, more than twenty crystal structure analyses of tetracoordinate S(IV) compounds with symmetrically and unsymmetrically enlarged heterorings, including N–S–O or N–S$^+\cdots$O= bridges, have revealed[11,13,14] that the S–O distances are distributed evenly in the range 1.63–2.80 Å. Notwithstanding, within this wide range, Musher's hypervalent bonds exist almost exclusively in those sulfuranes which contain symmetric X–S(IV)–X three-center bridges[15] (*e.g.* an N–S–N bridge in spirodiazasulfurane – **1a**[16]). This is why it is so »difficult to assess the effect of the changes in the bond order values on the actual geometry of the hypervalent sulfur compounds«.[4]

A SURVEY OF SULFURANE FORMS
AND STRUCTURES

Let us now review the structures of representative sulfuranes and analogous sulfonium salts reported in the literature. Preliminary structural data will also be presented on several other members of the spirosulfurane family, which have been synthesized by the team of Professor I. Kapovits (Budapest) and analyzed (by means of X-ray diffraction) in our laboratory in the past few years. We will mainly look into the reasons for and the magnitude of the polarization of S–>O bonds embedded in various three-center systems.

First, the bonding of a new sulfurane (**10**) with four C–S bonds[17] is presented. In the pseudo-trigonal-pyramidal geometry of the bis(2,2'-biphenylylene)sulfurane molecule (hereinafter {SC₄}R,R'), sitting on a twofold axis of the monoclinic space group $C2/c$,

1 2 3 4

1a 2a 2b 5

6 6a 6b 7

8 9 10 11

12 13 14

8a 9a 9b 15

16a 16b 17 18
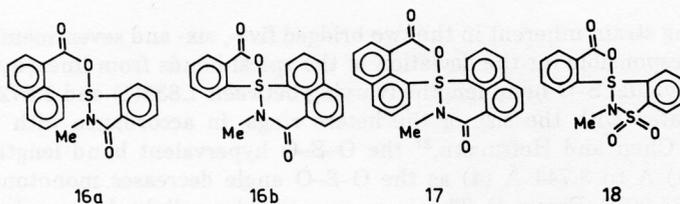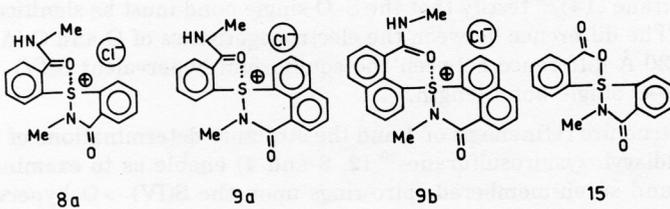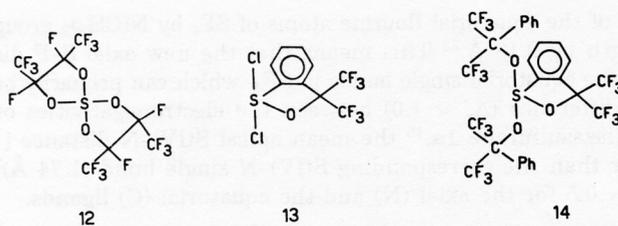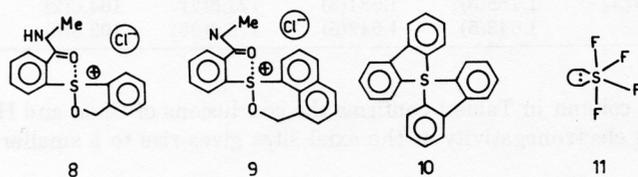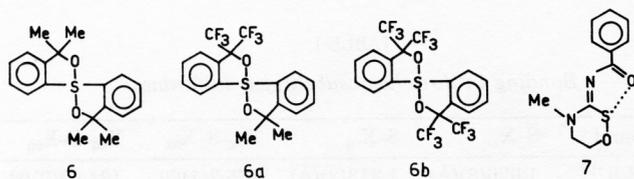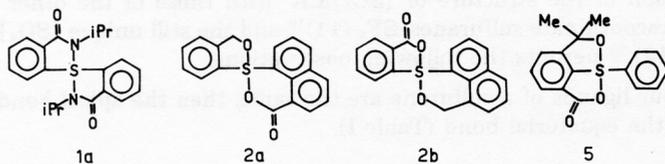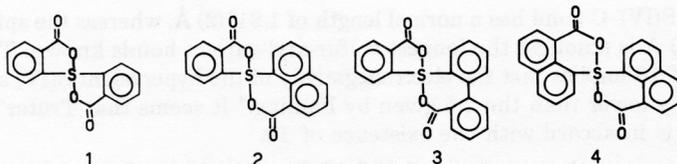
the equatorial S(IV)–C bond has a normal length of 1.813(2) Å, whereas the apical S(IV)–C bond (1.926(2) Å is amongst the longest sulfur-aryl-carbon bonds known. The successful synthesis of **10** implies that the electronegativity of the hypervalent S(IV) atom should be substantially lower than the 2.5 given by Pauling.[3] It seems that Truter's empirical value[18] of 1.0 is in accord with the existence of **10**.

A comparison of the structure of {SC$_4$}R,R' with those of the other two homo-substituted tetracoordinate sulfuranes, SF$_4$ (**11**)[19] and the still unique {SO$_4$}Q,Q' tetraoxysulfurane (**12**),[20] permits the following observations:

a) If the four ligands of a sulfurane are the same, then the apical bond is *ca.* 0.11 Å longer than the equatorial bond (Table I).

TABLE I

Bonding in three homosubstituted sulfuranes

Compound	S–X$_{ax}$	S–X$_{eq}$	X$_{ax}$–S–X$_{ax}$	X$_{eq}$–S–X$_{eq}$
{SC$_4$}R,R'[17]	1.926(2)(Å)	1.813(2)(Å)	175.2(1)(°)	121.52(9)(°)
{SO$_4$}Q,Q'[20]	1.755(3)	1.631(3)	171.5(2)	104.6(2)
SF$_4$[19]	1.643(5)	1.542(5)	176.8(25)	103.8(6)

b) The fourth column in Table I confirms the conclusions of Chen and Hoffmann,[21] *i.e.* an increase in electronegativity at the axial sites gives rise to a smaller equatorial angle.

c) Replacement of the equatorial flourine atoms of SF$_4$ by N(CH$_3$)$_2$ groups increases the axial bond length by 0.13 Å.[22] This means that the new axial S–F distances are 0.23 Å longer than the equatorial single bonds in SF$_4$, which can primarily be attributed to the substantial difference (Δ_e = 1.0) between the electronegativities of F and N. Similarly, in spirodiazasulfurane **1a**,[16] the mean apical S(IV)–N distance [1.898(4) Å] is *ca.* 0.16 Å longer than the corresponding S(IV)–N single bond (1.74 Å)[23] which is attributable to Δ_e = 0.5 for the axial (N) and the equatorial (C) ligands.

d) The structure determinations of [SO$_4$]Q,Q',[20] a dichlorosulfurane (**13**)[24] and a trialkoxysulfurane (**14**),[25] testify that the S–O single bond must be significantly shorter than 1.70 Å. The difference between the electronegativities of O and C (Δ_e = 1.0) suggests a *ca.* 0.20 Å difference between the equilibrium hypervalent S(IV)–>O distance and the S(IV)–O single bond length.

A novel structure refinement of **1** and the structure determinations of three closely related diaryldiacyloxyspirosulfuranes[26] (**2, 3** and **4**) enable us to examine the effects of five-, six- and seven-membered spiro-rings upon the S(IV)–>O hypervalent bonds (Table II).

a) The ring strain inherent in the two bridged five-, six- and seven-membered rings seems to be responsible for the deviation of the apical bonds from linearity. However, while the individual S–O bond lengths (varying between 1.838(1) and 1.872(3) Å) cannot be correlated with the size of the hetero rings, in accordance with the second prediction of Chen and Hoffmann,[21] the O–S–O hypervalent bond length increases from 3.648 (**1**) Å to 3.744 Å (**4**) as the O–S–O angle decreases monotonously from 177.7(4)° to 174.9(2)° (Figure 1). This is accompanied by a slight decrease in the length

TABLE II

Bond distances and the corresponding bond number values (n) *for
11 spirosulfuranes and sulfonium cations*

| Comp.	C–O	O–S	S···O	O–C (Å)	n_{co}	n_{so}	n_{so}	n_{co}
6	1.437(4)	1.787(2)	1.814(2)	1.437(4)	0.98	0.56	0.51	0.98
6b	1.390(9)	1.832(5)	1.819(5)	1.392(9)	1.12	0.48	0.50	1.12
6b*	1.385(9)	1.831(5)	1.816(5)	1.375(10)	1.14	0.48	0.51	1.17
1	1.320(9)	1.842(3)	1.842(3)	1.320(9)	1.37	0.46	0.46	1.37
2	1.334(2)	1.838(1)	1.869(2)	1.333(3)	1.32	0.47	0.42	1.32
3	1.342(5)	1.857(3)	1.862(3)	1.334(5)	1.28	0.44	0.43	1.32
4	1.346(4)	1.872(3)	1.872(3)	1.346(4)	1.27	0.42	0.42	1.27
6a	1.436(5)	1.713(2)	1.955(2)	1.369(5)	0.98	0.72	0.31	1.19
2a	1.437(4)	1.684(3)	2.046(2)	1.297(4)	0.98	0.80	0.23	1.47
2b	1.449(4)	1.688(3)	2.113(2)	1.288(5)	0.95	0.79	0.18	1.51
9	1.468(6)	1.648(4)	2.253(5)	1.260(2)	0.90	0.91	0.11	1.63
8	1.461(3)	1.635(2)	2.260(2)	1.258(2)	0.91	0.95	0.11	1.64
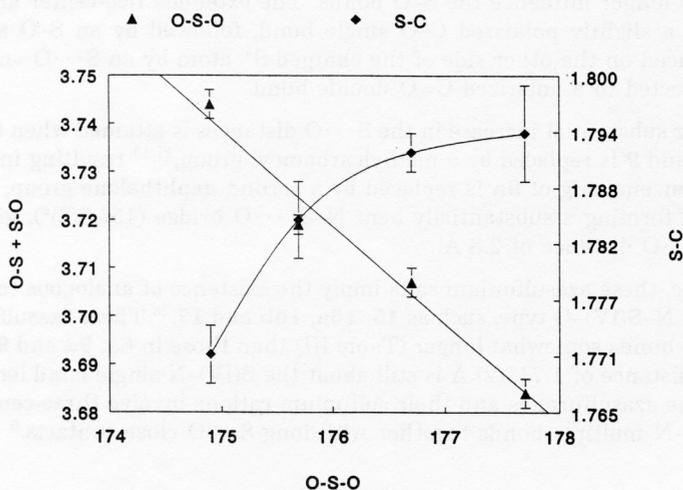
Figure 1. Sums of axial S–O distances (Å) and equatorial covalent C_{aryl}–S bond lengths (Å) in diacyloxysulfuranes **1–4**, plotted against the O–S–O angles (°). A Linear regression analysis resulted in the equation d(O–S + S–O) = –0.021(O–S–O)° + 7.29 for the hypervalent bonds with a high correlation coefficient R = 0.987.

of the equatorial S(IV)–C bond, which gains a stronger π-bond character at the expense of the hypervalent O–S–O three-center.

b) Accordingly, hypervalent bonds exist only in pairs. If one of them turns into a covalent bond, then the other is no more than an S···O close contact.

c) An S–O bond formed within a five-membered ring always induces a somewhat stronger interaction in the adjoining ring than those embedded in six- or seven-membered rings.

An alternative replacement of one of the >C=O groups in **2** by a CH$_2$ moiety results in substantial asymmetry of the new O–S–O bridges.[27] This can be attributed to the greater electronegativity of the >C=O group than that of >CH$_2$. The aforementioned »ring effect« on the strongly polarized hypervalent bonds explains the significant difference in the S$\cdots$O bond lengths (**2a**: 2.046(2) Å vs. **2b**: 2.113(2) Å), while the counterbalancing S–O single bonds are the same (Table II). Similarly, the strain generated in the five-membered ring of **5** fused along the considerably shortened S–C$_{aryl}$ bond (from ca. 1.81 to 1.75 Å) to the common benzene ring accounts for the longest S$\cdots$O distance of 2.25 Å measured in dioxysulfuranes.[5] In **2a**, **2b** and **5**, the observed polarization of one of the hypervalent bonds is accompanied by a substantial shortening of the adjoining »carboxylate« C–O single bond (1.297(4), 1.288(4) and 1.282(2) Å. The corresponding C–O single bond lengths in the alkoxy moieties are 1.437(4), 1.449(4) and 1.489(3) Å, respectively.

This complex phenomenon is somewhat more pronounced in the corresponding sulfonium salts **8**[11] and **9**.[13] The bond length sequence along the extended six-electron-five-center system (Table II) is quite similar for **8** and **9**, suggesting that steric factors (a substantial geometric difference is indicated by the O–S–O angles: 179.4(1)° vs. 173.9(3)°) no longer influence the S–O bonds. The extended five-center array is characterized by a slightly polarized C–O single bond, followed by an S–O single bond, counterbalanced on the other side of the charged S$^+$ atom by an S$\cdots$O »no bond« interaction directed to a polarized C=O double bond.

A further substantial increase in the S$\cdots$O distances is attained when the –CH$_2$–O moiety of **8** and **9** is replaced by a methylcarbamoyl group,[11,13] resulting in **8a** and **9a**. When the benzene ring of **9a** is replaced by a second naphthalene group, the twisted wings of **9b**, forming a substantially bent N–S$^+\cdots$O bridge (156.6(2)°), give rise to a very long S$\cdots$O distance of 2.8 Å.

Of course, these azasulfonium salts imply the existence of analogous (neutral) azasulfuranes of N–S(IV)–O type, such as **15**, **16a**, **16b** and **17**.[28] These azasulfuranes contain S(IV)–N bonds somewhat longer (Table III) than those in **8a**, **9a** and **9b**, but even the longest distance of 1.743(2) Å is still about the S(IV)–N single bond length.[23] Consequently, the azasulfuranes and their sulfonium cations involve three-center systems formed by S–N multiple bonds together with long S$\cdots$O close contacts.[6]

TABLE III

Bonding of the six-electron-five-center systems formed in sulfonium salts
*(**8a**–**9b**) of N–S$^+\cdots$O type and azasulfuranes (**15**–**17**) of N–S$\cdots$O type*

Compound	C–N (Å)	N–S (Å)	S$\cdots$O (Å)	O–C (Å)	N–S$\cdots$O (°)
sulfonium salts:					
8a	1.375(3)	1.685(2)	2.373(2)	1.243(2)	178.3(1)
9a	1.396(8)	1.671(5)	2.448(5)	1.229(8)	164.9(4)
9b	1.406(4)	1.664(2)	2.795(2)	1.232(3)	156.6(2)
azasulfuranes:					
15	1.371(3)	1.734(2)	2.132(2)	1.294(5)	178.9(2)
16a	1.367(2)	1.743(2)	2.130(1)	1.291(2)	174.0(1)
16b	1.380(2)	1.710(1)	2.247(1)	1.269)2)	174.2(1)
17	1.383(2)	1.694(1)	2.598(2)	1.250(2)	157.4(1)

DISCUSSION

The above survey reveals that, depending on the apical ligands and the steric effects generated by five-, six- or even seven-membered rings *etc.*, one of the S–O bonds forming hypervalent three-centers in sulfuranes is polarized in a stepwise mode on one side of the sulfur atom, while the other gains a substantial covalent character. The latter starts from the equilibrium 1.81 Å in **6**[5] and **6a**[7] and ends up at about the S(IV)–O single bond length (*ca.* 1.63(1) Å) which, in turn, terminates the polarization of the other bond at a distance of about 2.25 Å.

To estimate the boundaries of O–S–O hypervalent bonds formed under different circumstances (vide supra), each S–O distance is plotted against the other pertaining to the same, but either O–S(IV)–O or O–S(II)···O grouping. Apart from the visible discrepancies shown by sulfoxides[29,30] with an S=O double bond, the scatter plot (Figure 2) shows a correlation between the two distances. Similarly to the hyperboloid curves presented by Bürgi[31] for triatomic linear systems (triiodide anions, the S–S···S grouping in thiathiophthenes and OH···O bonds), this plot depicts the coupled changes in the quasi-collinear O–S–O distances within a wide range of covalent bonds and S···O non-bonding interactions. If it is assumed that the directional hypervalent bonds are longer than single bonds, but somewhat shorter than S···O close contacts, then they are located along the *curvature* of the hyperboloid function. The question is how far such elongated S–>O distances can still be regarded as hypervalent.

The correlation curve (Figure 2) for O–S(IV)–O three centers can be approximated analytically by the form derived by Pauling[32] from a simple intuitive model of chemical bonding:
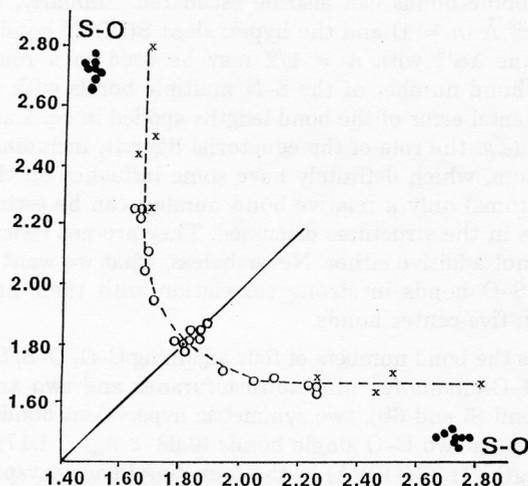

Figure 2. Correlation plot of interatomic distances in linear O–S–O systems. The O–S(IV)–O bonds (open circle) are distinguished from the two-electron-three center O–S(II)···O arrays by **x**. The black spots forming two remote clusters represent O=S(IV)···O bond pairs observed in sulfoxides.

$$d(n) - d(1) = \Delta d = -c \log n \qquad (1)$$

where n is the bond number, practically equal to the bond order (B). To determine c for S–O hypervalent bonds, both d(n) and d(1) should be assigned with care. A search in the Cambridge Structural Database (January 1992 state) for S(IV)[O,O',O''] and S(IV)[O,O',C] moieties led to the selection of 30 entries with $R < 0.08$ for further consideration. A study of the environment and distribution of S(IV)–O single bonds in the 30 trigonal pyramids demonstrated that the nine S(IV)[O,O',C] moieties {Refcodes: BAJREJ, DAFCOC, GELTUM, GESCAI (a&b), SANXTO (a&b), SANXTP and XTBCOC) selected with $R < 0.05$ gave the most reliable mean of 1.62(2) Å for the S(IV)–O single bond length.

The next step was to estimate the equilibrium S(IV)–O hypervalent bond length to which $n = 1/2$ can be assigned in a zero-order approximation. For this, as suggested by spectroscopic studies,[33-35] we assume that the d orbitals or other high-energy atomic orbitals on the central atom are not extensively involved in the apical bonding of this class of compounds. In addition, the oxygens involved in the three-center bonds are not terminal atoms. As we have seen above, they are bound to either C_{sp}^3 (alkoxy) or C_{sp}^2 (acyloxy) carbon atoms, which differ in their group electronegativities. A survey of the structures available demonstrated, that in the symmetric diaryldialkoxyspirosulfuranes **6** and **6b**, the C–O bonds involving oxygen attached to sulfur are the closest to single bonds. Accordingly, in the bond order estimation, the mean of the S–O distances in **6** and **6b** (1.82(2) Å) will be used as the hypervalent bond length for a bond number of 1/2. Introduction of d(1) = 1.62(2) and d($1/2$) = 1.82(2) Å into eq. 1 gives $c = 0.664$.

Mutatis mutandis, through the use of eq. 1, if reliable distances are assumed (1.43(1) and 1.19(1) Å ($c = 0.797$)), the bond number (n) of the accompanying C–O bonds between single and double bonds can also be estimated. Similarly, the S(IV)–N single bond length of 1.74[23] Å ($n = 1$) and the hypervalent S(IV)–N bond length (1.90(1) Å) in spirodiazasulfurane **1a**[16] with $n = 1/2$ may be used in a rough, zero-order approximation of the bond number of the S–N multiple bonds with $c = 0.532$. Bearing in mind the experimental error of the bond lengths applied in eq. 1 and our ignorance of numerous cofactors (*e.g.* the role of the equatorial ligands, including the lone electron pair of the S(IV) atom, which definitely have some influence on the bonding around the central sulfur atoms) only a relative bond number can be estimated for the S–O, S–N and C–O bonds in the structures discussed. They are not strictly commensurable and, consequently, not additive either. Nevertheless, what we want to see is the internal motion of the S–O bonds in strong correlation with their neighbours, forming together six-electron-five-center bonds.

Table II presents the bond numbers of four adjoining C–O, O–S, S–O and C–O bonds along the C–O–S–O–C chains for nine spirosulfuranes and two analogous sulfonium salts. At the upper end (**6** and **6b**), two symmetric hypervalent bonds with a total $n \sim 1$ are sandwiched between two C–O single bonds ($0.98 < n_{co} < 1.17$). The mean of the eight C–O bond lengths (1.334(10) Å) in the four diaryldiacyloxyspirosulfuranes (**1–4**) agrees with the corresponding C–O distance in carboxylic acid esters,[36,37] which suggests that the multiple bond character ($n_{co} = 1.32$) is an intrinsic property of these C–O bonds and independent of the adjacent S–O hypervalent bonds. Thus, the greater group electronegativity of the $>C=O$ group *vs.* those of the $>C(CF_3)_2$ and $>C(CH_3)_2$ moieties accounts for the bond number of $n_{so} = 0.46$ for the symmetric spirosulfurane

1, whereas the lower bond number in **2–4** (n_{min} = 0.42) can be attributed exclusively to the strain differences exerted by the five-, six- and seven-membered heterorings. For example, in **4** the strain exerted by the butterfly-like naphthalene wings results in an O–S–O angle of 185.1(2)°, *i.e.* the hypervalent apical bonds are titled towards the S lone electron pair located in the plane of the equatorial ligands (Figure 3).

In the other five compounds, the hypervalent bonds gradually alter in opposite directions. Therefore, the final state of the strongly unsymmetric O–S–O three-centers can be properly described only by two single bonds ($n > 0.9$) followed by an S···O close contact (n_{so} = 0.1), which is then terminated by a C–O bond having a strong multiple bond character ($n_{co} > 1.6$). Within this continuous rearrangement of the bond character, the central four-electron-three-center O–S–O system turns into a three-electron-three-center state with one electron increasingly localized on one of the C–O bonds, while the other is delocalized on the molecule, around the central S atom. This smooth quantitative process results in a novel sulfurane structure. By the loss of one electron from the unsymmetric sulfurane molecule, a sulfonium cation is formed, in which the >C=O double bond is substantially polarized ($n_{co} < 1.7$). Further S–O bond polarization is permitted only on the two-electron-three center O–S(II)···O groupings (Figure 2). Their S(II) atom is bound covalently to one oxygen and one carbon atom.[12,30,38] The longest S(II)···O close contact[39] of 2.81 Å is balanced by an S(II)–O single bond with a length of 1.68 Å. In principle, the O=S(IV)···O three-centers with very long (2.6–2.8 Å) through-space S···O interactions ought to behave as the closing group of the extremely polarized hypervalent bonds.[29] This is not so. With rigid S=O double bond distances (1.48–1.50 Å), they do not lie on the hyperboloid curve depicted in Figure 2. Nevertheless, it is worth noting, that the S=O double bond in sulfoxides {R,R'S(IV)=O} enjoys priority in the formation of S···O through-space interactions. For example, methyl-2-nitrobenzene-sulfenate ($C_7H_7NO_3S$) has a two-electron-three-center O–S···O bridge with S–O distances of 1.654(2) Å and 2.458(2) Å.[30] In contrast, in the quasi-collinear O–S···O array of the analogous methyl-2-nitrobenzene-sulfinate ($C_7H_7NO_4S$), the S–O single bond is replaced by an additional S=O double bond which results in a substantially increased S···O distance of 2.743(4) Å. Simultaneously, the bond angle is reduced from 176.4(2)° to 171.9(2)°, while the S(IV)–O single bond (1.689(2) Å »ousted« from its position makes an angle of 77.6(2)° with the weakened S···O close contact.

In azasulfuranes[28] and azasulfonium cations, the N lone pair is delocalized on the S-carbamoyl moiety embedded in a five- or six-membered heteroring. The S(IV)–N
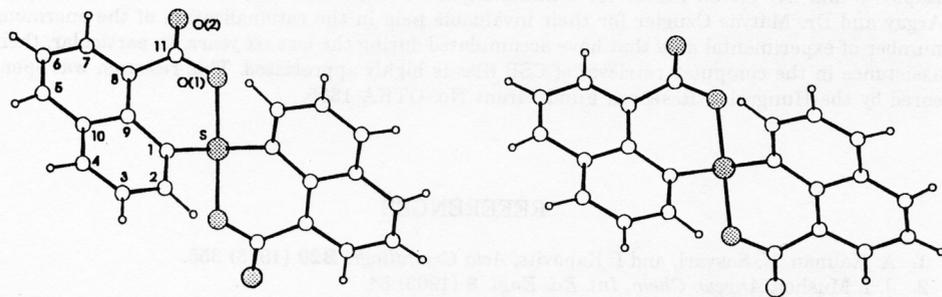

Figure 3. Stereoscopic view of the molecular structure of diaryldiacyloxysulfurane **4**, showing a rather twisted geometry.

multiple bonds in **8–9b** and **15–17**, (Tables II and III) account for the exclusively transitional three-electron-three-center form of azasulfuranes and the analogous sulfonium cations, with $S \cdots O$ distances in the range 2.13–2.80 Å. There is only one azasulfurane (**18**)[27] on the threshold of N–S–O four-electron-three-center hypervalent bonds. This can be attributed to the sulfonyl group replacing the $C=O$ group in **15**. The strong electron-withdrawing effect of the bulky SO_2 group prevents the S(IV)–N bond from gaining a multiple bond character. In the asymmetric unit of **18**, there are two molecules, one of which has an S(IV)–N bond somewhat longer than, whereas the other is practically equal to, the corresponding single bond distance of 1.74 Å (Table IV). The different intermolecular environments of the symmetry-independent molecules presumably account for the small, but visible difference in their bonding. Similarly to the bond number for **2a** ($n_{so} = 0.25$), their elongated S–O bond distances have a mean bond number of 1/4 and there is an accompanying C–O bond with increased multiple bond character (from $n_{co} = 1.32$ to $n_{co} = 1.5$).

TABLE IV

*Bonding of the S(VI)—N—S(IV)—O—C five-center chains found in the symmetry-independent[27] **18** azasulfurane molecules*

	S–N	N–S	S···O	O–C (Å)	N–S···O	S–N–S (°)
19a	1.615(2)	1.786(3)	2.011(2)	1.304(3)	178.4(2)	120.8(2)
19b	1.617(2)	1.746(2)	2.046(2)	1.288(3)	178.1(2)	121.8(2)
mean:	1.616(2)	1.766(3)	2.029(2)	1.296(3)	178.3(2)	121.3(2)

Summary: A comparison of the bonding in **2a**, **2b**, **15** and **18** clearly reveals that spirosulfuranes can be described with a four-electron-three-center model in the range of S–O distances 1.70–2.03 Å ($n_{so} = 3/4$ *vs.* 1/4). From these upper and lower »thresholds«, they rapidly turn into a transitional three-electron-three-center bridge, which coalesces with the bonding of sulfonium cations. Within the second range, on either side ($3/4 < n_{so} < 1/4$), the word hypervalent may be used only with care. Hopefully, a study of charge density distributions in **2a** and **2** (novel X-ray diffraction data collections at low temperature are in progress) will shed more light on this question.

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SAŽETAK

O prirodi hipervalentnih veza u sulfuranima

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Uz opširne literaturne podatke i neobjavljene rezultate prikazana je priroda veze sumpor-kisik u sulfuranima, azasulfuranima i sulfonijevim solima. Sulfurani imaju dvije hipervalentne veze između atoma sumpora i kisika koji se nalaze na vrhovima pseudo-trigonske bipiramide. Hipervalentne veze nastaju između tri atoma centra (O–S(IV)–O), i to participacijom četiri elektrona. Nesimetrični sulfurani imaju različite udaljenosti O–S→O i mogu se opisati modelima veze između šest elektrona i pet središta. Hipervalentne veze postoje jedino u parovima, ako se jedna od njih pretvori u kovalentnu vezu, druga se toliko izduži da nastaje bliski kontakt između atoma sumpora i kisika. Na temelju podataka iz kristalnih struktura i stupnja polarizacije veza S–O raspravlja se o mogućim dodatnim hipervalentnim vezama sumpora i kisika.