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Geminal Conjugation in Disulfides

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ABSTRACT

Some aspects of the spatial and electronic structure of disulfides XSSX (X = H, Alk, Ph, Hal) are considered. It is shown that the growth of the geminal n_S–σ^*_{SX} *conjugation efficiency leads to a shortening of the SS bond that is more than three times as large as the simultaneous SX bond lengthening. The positive effective charge on the sulfur atom also increases as a result of this conjugation. These effects increase with the growth of −I and +M abilities of the substituents X. The* SK_α *line shifts and the HOMO bonding degree* (Δn_S) *have been measured by the X-ray fluorescence spectroscopy method for dialkyl disulfides (Alk = Me, Et, Pr, i-Pr, Bu, i-Bu, t-Bu,* C_5H_{11}, C_8H_{17}, $H_2NCH_2CH_2$, $CH_2CH{=}CH_2$, CH_2Ph*) and* S_8. *With the help of* Δn_S *values that are proportional to the* n_S–σ^*_{SC} *conjugation efficiency, the sequence of the enhancement of the geminal conjugation efficiency has been established for the disulfides investigated. In the framework of the* n_S–σ^*_{SS} *geminal conjugations, the shortening of the SS bonds in* S_8 *is explained. © 1996 John Wiley & Sons, Inc.*

INTRODUCTION

A broad spectrum of disulfide reactivity [1–6] indicates the necessity for studying the peculiarities of their electron and spatial structure with an aim to establish "structure–property" correlations. This can allow us to explain and predict some peculiarities of the reactivities of the disulfides investigated.

The spatial structures of disulfides X_2S_2 (*X* = H, Alk, Hal, Ph) were investigated by infrared (IR) [7–10], Raman (R) [9–12], and microwave (MW) [13–19] spectroscopy and also by electron diffraction (ED) [14,20–33] and X-ray diffraction (XD) [34–37]. Previously [7,15] these disulfides have been assumed to exist in two forms, *XSSX* (*A*) and X_2SS (*B*). Now it is established that all these disulfides, except for the case in which *X* = *F*, can be described by structure (*A*) and exist in the gauche form, which means that the dihedral *XSSX* angle (τ) is approximately equal to 90°. Disulfur difluoride is the only disulfide that has been detected in both (*A*) and (*B*) forms [8,16,17,26]. Experimental data on *SS* and *SX* bond lengths, and valent *XSS* and dihedral *XSSX* angles for disulfides *XSSX* are given in Table 1.

Let us compare the *SS* bond length (l_{SS}) in *XSSX* disulfides with that for a number of allotropes of elemental sulfur and the l_{SS} value for the pure single *SS* bond presented in Table 2. If it is assumed that the most plausible value of the sulfur atom covalent radius (r_{cov}) is equal to 1.04 Å, a conclusion should be drawn that the *SS* bond has an increased bond order not only in S_2, but also in S_6, S_8, and disulfides 1–15.

In the work of Riga *et al.* [50], the interdependence between experimental l_{SS} and l_{SC} values for the series of organic straight-chain and cyclic, saturated and unsaturated, disulfides was considered. The authors believe that the interdependence shown in Figure 1 testifies l_{SS} values to be out of line with l_{SC} values. If one wants to correlate these bond lengths for

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Dedicated to the great chemist Professor Shigeru Oae on the occasion of his 75th birthday.

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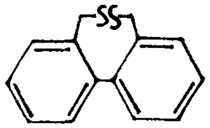
TABLE 1 Experimental Geometry Data for Disulfides

Disulfide	1_{SS}(Å)		1_{SX}(Å)	<*SSX*(°)	<*XSSX*(°)	*Reference, method*
HSSH (1)	2.0610(3)[a]		1.3421(5)	97.51(5)	90.76(6)	[7],[b] IR
	2.055(1)		1.327(7)	91.3(5)	90.60(5)	[13], MW
	2.058		1.345	98.1	90.8	[14], MW, ED
	2.05(2)		1.33	95	—	[20], ED
	2.055(1)		1.352(15)	91.8(5)	91.62(5)	[21], ED
FSSF (2)	1.888(10)		1.635(10)	108.3(5)	87.9(15)	[16], MW
	1.890(2)		1.635(2)	108.3(2)	87.7(4)	[26],[b] ED
ClSSCl (3)	1.9504(12)		2.0552(7)	107.66(5)	85.2(1)	[18],[b] MW
	1.937(6)		2.057	107.92(1)	84.9(2)	[19], MW
	2.05(3)		1.99(3)	103(2)	97.1	[28], ED
	1.97(3)		2.07(3)	105(3)	84(11)	[29], ED
	1.931(5)		2.057(2)	108.2(3)	84.8(13)	[30], ED
BrSSBr (4)	1.98(4)		2.24(2)	107(3)	82(12)	[29], ED
	1.96[b]		2.22[b]			corrected data [18,29]
MeSSMe (5)	2.038		1.810[c]	102.8	84.7	[15], MW
	2.04(3)		1.78(3)	107(3)	90	[20], ED
	2.022(3)		1.806(2)	104.1(3)	83.9(9)	[22], ED
	2.029(3)		1.816(3)	103.2(2)	85(4)	[23],[b] ED
MeSSEt (6)	2.031(3)		1.817(4)	103.2(3)	84(7)	[23], ED
F_3CSSCF_3 (7)	2.053(19)		1.829(17)	105(3)	90	[24], ED
	2.030 (5)		1.835(5)	101.6(6)	104(4)	[25],[b] ED
		SH	1.34	98		
F_3CSSH (8)	2.038(5)				91	[31], IR
		SC	1.806(6)	101.2(6)		
		SF	1.611(3)	105.7(8)		
F_3CSSF (9)	1.970(3)				91(3)	[31], IR
		SC	1.829(6)	102.0(6)		
		SCl	2.038(7)	105.2(6)		
F_3CSSCl (10)	1.980(8)				87(2)	[32], ED
		SC	1.805(8)	101.6(14)		
		SBr	2.221(8)	105.5(6)		
F_3CSSBr (11)	1.993(5)				86(4)	[32], ED
		SC	1.817(9)	101.7(9)		
FC(O)SSC(O)F (12)	2.028(4)		1.767(4)	100.5(3)	82.2(19)	[33], ED
PhSSPh (13)	2.030(5)		1.790(12)	106.2(6)	96(1)	[34],[b] XD
	2.023(1)		1.789(3)	105.8(9)		[35], XD
BzSSBz (14)	2.020(5)		1.84(1)	102.9(15)	92.1	[36], XD
 (15)	2.035(1)		1.835(3)	103.82	54.32	[37], XD

[a] Here and below, the numbers in parentheses on the right-hand side are the errors in the last significant digit.
[b] Most plausible data.
[c] By *SX* bond in diorganyl disulfides is meant the SC_{α} bond.

considerably more diverse disulfides, he must transform the bond lengths to their differences from single ones ($l°$)[†], i.e.,

$$\Delta l_{AB} = l_{AB}^{\text{expt}} - l^{\circ}_{AB} \tag{1}$$

The l°_{SX}, Δl_{SX} and Δl_{SS} values for disulfides 1–15 are presented in Table 3. From Table 3 and Figure 2, one can see changes of the *SS* and *SX* distances to be the reverse of each other and the shortening of the *SS* bond to be more than 2–4 times as large as the corresponding *SX* bond lengthening.

In the literature reports [13,16,40,52,53], it had been assumed that there is negative hyperconjugation of the sulfur atom lone 3*p* electron pair (n_S) with the σ^* orbital corresponding to antibonding between the neighboring sulfur atom and the substituent *X* (σ^*_{SX}) in disulfides *XSSX* (see Figure 3). In the literature, this conjugation is known also as the geminal

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[†] The length of the single *AB* bond (l°_{AB}) can be defined by the equation of Shomaker and Stevenson [48,51] with Pauling's values of r_{cov} and electronegativities (*EN*): $l^{\circ}_{AB} = r_{\text{cov}}(A) + r_{\text{cov}}(B) - 0.09|\Delta EN_{AB}|$ or in the case of disulfides *XSSX* l°_{SX} values can be defined as the experimental ones for sulfides *XSX* [4].

TABLE 2 Lengths of the *SS* Bond

Compound	l_{SS}(Å)
S_2	1.90 [20], 1.887 [38, 39], 1.89 [40, 41]
S_6	2.057 [39, 42], 2.07 [43]
S_8	2.037(5) [38], 2.060 [39], 2.04 [40], 2.059(2) [42], 2.046(3)[a] [44], 2.050(3)[b] [44]
Single *SS* bond	2.08 [20, 45, 46], 2.098 [47], 2.046 [48], 2.05 [49]

[a] At 298 K.
[b] At 100 K.

TABLE 3 Deviations of Experimental Lengths of the *SS* and *SX* Bonds in Disulfides from the Single Ones (in Å)

Disulfide	$-\Delta l_{SS}$[a]		l_{SX}[b]	Δl_{SX}	$\Sigma\sigma_I(X)$	$\Sigma\sigma_R^\circ(X)$
1	0.019		1.3356	0.006	0.00	0.00
2	0.190		1.5921	0.043	1.08	−0.88
3	0.130		2.006	0.049	0.94	−0.50
4	0.12		(2.18)	0.04	0.88	−0.38
5	0.051		1.805	0.011	−0.02	−0.32
6	0.049		1.804	0.013	−0.02	−0.30
7	0.050		1.819	0.016	0.80	0.22
		SH	(1.34)	0.00		
8					0.40	0.11
		SC	(1.80)	0.006		
		SF	(1.56)	0.051		
9	0.110				0.94	−0.33
		SC	(1.80)	0.029		
		SCl	(2.00)	0.038		
10	0.100				0.87	−0.14
		SC	(1.80)	0.005		
		SBr	(2.18)	0.041		
11	0.087				0.84	−0.08
		SC	(1.80)	0.017		
12	0.052		(1.77)	0.00	0.6	0.2
13	0.050		1.771	0.019	0.24	−0.22
14	0.060		(1.81)	0.03	0.06	−0.26
15	0.045		(1.81)	0.025	—	—

[a] $\Delta l_{SS} = l_{SS}^{expt} - l_{SS}^\circ = l_{SS}^{expt} - 2.08$.
[b] The values calculated by the Shomaker and Stevenson equation are given in parentheses.

and anomeric or gauche effect [54,55]. Its efficiency is defined as described in reference [56],

$$\beta \sim S_{ij}^2/\Delta E_{ij} \qquad (2)$$

where ΔE_{ij} is the difference between energies of *i* and *j* orbitals conjugated, S_{ij} being their overlapping integral. The influence of this geminal conjugation on disulfides can be illustrated by the resonance structures

$$X\text{–}\overset{\curvearrowright}{S}\text{–}S\overset{\curvearrowright}{\text{–}}X \leftrightarrow X\text{–}S^+{=}SX^- \leftrightarrow X^-S{=}S^+\text{–}X$$
$$\rightarrow X^{-\delta}\text{---}S^{+\delta} = S^{+\delta}\text{---}X^{-\delta} \qquad (3)$$

Hence, n_S–σ^* conjugation must lead to *SS* bond stabilization and *SX* bond destabilization, and also to a decrease in the sulfur atom total electron density (Q_S).

The first ionization potential (IP_1) of disulfides corresponds to the n_S–σ^* HOMO and must increase as the result of the geminal conjugation. In disulfides, there is the competitive n_S–n_S conjugation which leads to the appearance of bonding $n_S + n_S$ and antibonding $n_S - n_S$ occupied levels and to IP_1 decreasing. It should be noted that the $n_S - n_S$ interaction does not lead to sufficient integral redistribution of the electron density and changes of bond lengths and leads only to the n_S level splitting (ΔIP_{12}). The ΔIP_{12} value is the usual parameter of the n_S −

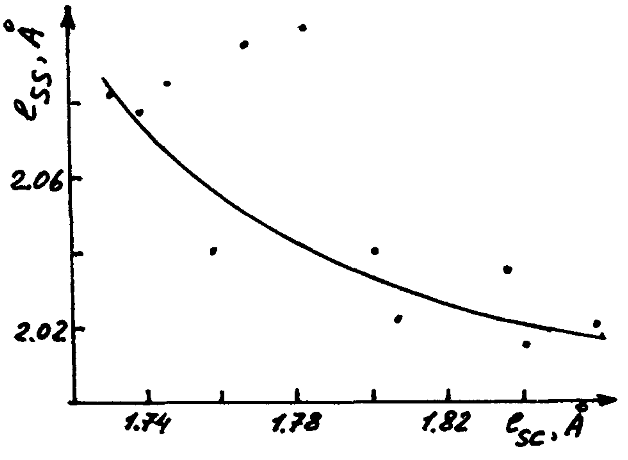

FIGURE 1 Comparison of *SC* bond length with the *SS* bond length in organic disulfides, taken from reference [50].

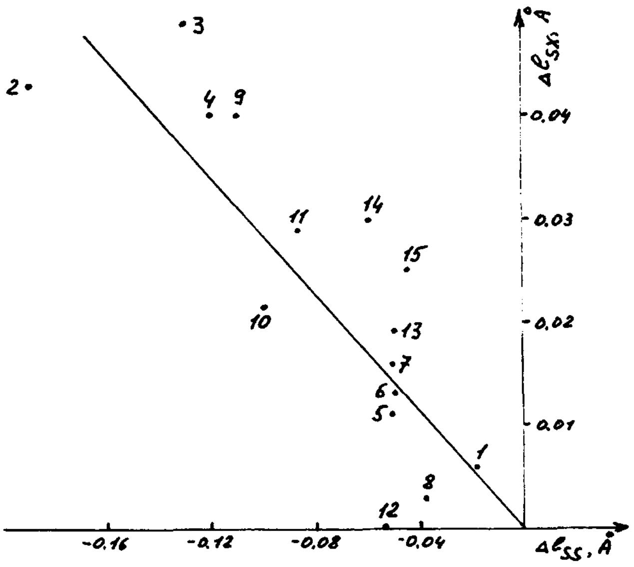

FIGURE 2 Relationship between *SS* bond shortening and *SX* bond lengthening in disulfides. The mean of Δl_{SX} values is used for asymmetrical disulfides. Numbering of points corresponds to that of the compounds.

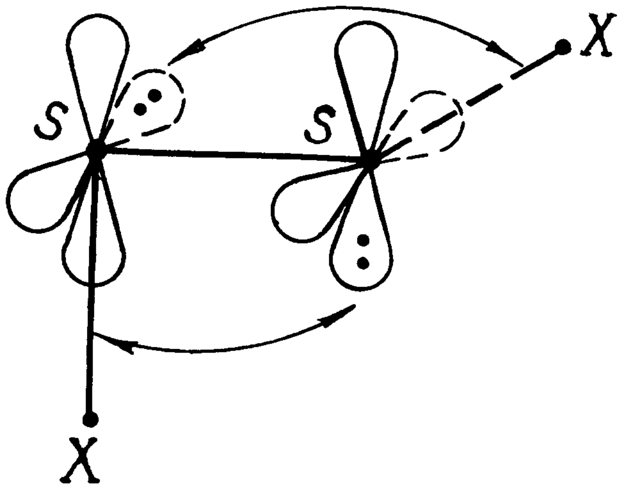

FIGURE 3 Scheme of the geminal n_S–σ^*_{SX} conjugation in disulfides *XSSX*.

n_S interaction efficiency which increases with the growth of the τ value deviation from 90° [50,57]

$$\Delta IP_{12}, eV = 0.13 + 1.78 \cos \tau \qquad (4)$$

METHODS

Fluorescent SK_α and SK_β spectra were obtained by use of the X-ray spectrometer "Stearate." The spectra were excited by AgL radiation (X-ray tube operated at 0.4 Å and 6–10 kV) and analyzed by a quartz crystal (plane of rhombohedron, bend radius 500 mm). Samples of solids and viscous liquids were prepared by rubbing them on a checkered nickel plate. Samples of volatile liquids were prepared by evaporating the investigated compounds at 10^{-5} torr on an iridium or nickel plate maintained at 77 K. During the exposure time (about 30 seconds for one K_α spectrum and about 10 minutes for one K_α spectrum), the samples were maintained at liquid nitrogen temperature.

The SK_α spectra were repeated 16–20 times and the SK_β spectra 3–5 times and the results averaged by the technique described in reference [58].

RESULTS AND DISCUSSION

In organic disulfides, the n_S–σ^* conjugation efficiency can be studied by X-ray fluorescence spectroscopy. This method offers possibilities to define both the effective charge on the sulfur atom (q_S), which is proportional to the SK_α line shift (ΔSK_α) [58,59], and the HOMO bonding degree with the help of SK_β spectra and internal standard technique [60,61]. The SK_α and SK_β spectra of Alk_2S_2, Alk = Me (5), Et (16), Pr (17), Bu (18), C_5H_{11} (19), C_8H_{17} (20), $H_2NCH_2CH_2$ (21)[†], *i*-Pr (22), *i*-Bu (23), *t*-Bu (24), $CH_2CH{=}CH_2$ (25), CH_2Ph (14), and S_8 (26) have been investigated. The SK_β spectra obtained are presented in Figure 4.

The appearance of some positive q_S in Alk_2S_2 as a result of n_S–σ^*_{SC} conjugation must lead to deviation from the additivity rule:

$$\Delta SK_\alpha(Alk_2S_2) > \Delta SK_\alpha^{add}(Alk_2S_2) \qquad (5)$$

$$\Delta SK_\alpha^{add}(Alk_2S_2) = 0.5\Delta SK_\alpha(Alk_2S) \qquad (6)$$

The measured ΔSK_α values for the dialkyl disulfides investigated, and for the corresponding dialkyl sulfides, and deviations from the additive scheme (6) are presented in Table 4. These data show that the maximal deviations from the additivity rule are observed for disulfides 5, 16 and somewhat smaller deviations for 14, 17, 22. The deviations observed for

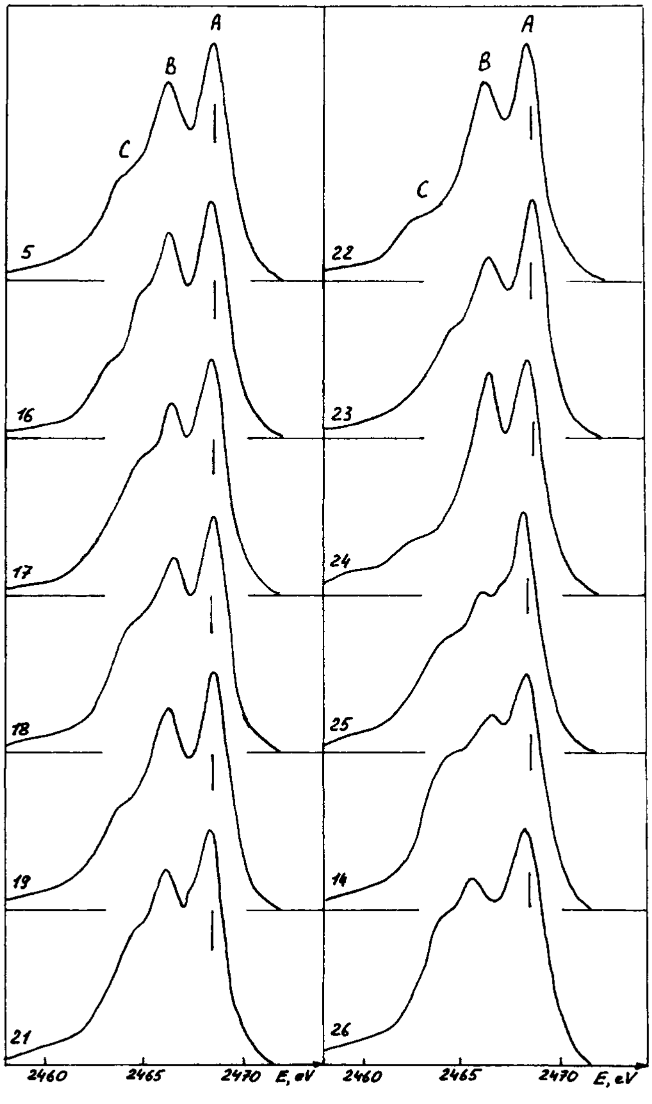

FIGURE 4 SK_β fluorescent spectra of dialkyl disulfides and S_8. Vertical lines correspond to the energy of $Hn_S \rightarrow 1s_S$ transition. Numbering of spectra corresponds to that of the compounds.

[†] This means the dihydrochloride $H_2NCH_2CH_2SSCH_2CH_2NH_2 \cdot 2HCl$.

TABLE 4 X-ray Spectral Parameters of the Electron Structure of Disulfides Alk_2S_2 and S_8

Disulfide		ΔSK_α, eV · 1000, with respect to S_8						
N	Alk	Alk_2S	Alk_2S_2	$\Delta SK_\alpha(Alk_2S_2)-0.5\Delta Sk_\alpha(Alk_2S)$	$Hn_S(K_8)$ (eV)	E_A (eV)	Δn_S (eV)	$\delta(\Delta H)$ [66], calc-expt (kcal/mol)
5	Me	−63(6)	10(6)	42(7)	2468.43(4)	2468.27(3)	0.16(5)	−0.68(23)
16	Et	−61(9)	8(8)	38(9)	2468.41(5)	2468.26(2)	0.15(5)	−0.75(25)
17	Pr	−47(6)	−6(7)	18(8)	2468.34(4)	2468.26(5)	0.08(6)	−0.73(25)
18	Bu	−47(6)	−20(9)	4(9)	2468.26(5)	2468.31(2)	−0.05(5)	−0.84(62)
19	C_5H_{11}	—	−6(8)	—	2468.34(5)	2468.42(5)	−0.08(7)	—
20	C_8H_{17}	−38(10)	−9(6)	10(8)	2468.32(4)	2468.4(1)	−0.1(1)	—
21	$H_2NCH_2CH_2$	—	−17(9)	—	2468.27(5)	2468.22(5)	0.05(7)	—
22	*i*-Pr	−66(6)	−15(6)	18(7)	2468.29(4)	2468.10(3)	0.19(5)	—
23	*i*-Bu	—	−10(9)	—	2468.31(5)	2468.31(4)	0.00(6)	—
24	*t*-Bu	—	−7(9)	—	2468.41(5)	2468.15(4)	0.26(6)	0.50(58)
25	$CH_2CH=CH_2$	−49(7)	−17(10)	8(11)	2468.27(6)	2468.03(6)	0.24(8)	—
14	CH_2Ph	−61(10)	−5(9)	25(11)	2468.34(5)	2468.16(4)	0.18(6)	—
26	S_8	—	—	—	2468.39(4)	2468.1(1)	0.3(1)	—

the rest of the dialkyl disulfides are within the limits of experimental error. Nevertheless, from the data presented in Table 4, one can see that Q_S values in dialkyl disulfides are slightly lower than those expected from Equation 6.

This shows the importance of substituent resonance effects in the formation of the sulfur atom effective charge for these compounds. In fact, in previous work [61], we have established that, in disulfides, the Q_S value decreases sufficiently with the growth of π-donor abilities of substituents at the sulfur atom (unlike dialkyl sulfides). This is in agreement with the existence of the linear correlation between Δl_{SS} values in disulfides 1–14 and the sums of σ_I and σ_R° constants of substituents X (taken from reference [62])

$$-\Delta l_{SS},\ \text{Å} = 0.068(4)\Sigma\sigma_I = 0.099(6)\Sigma\sigma_R^\circ + 0.022$$

$$r = 0.991, s = 0.006, n = 14 \tag{7}$$

where r is the correlation coefficient, s is the standard error of estimation, and n is the number of points. In reality, as mentioned previously, the growth of the geminal n_S–σ_{SX}^* conjugation efficiency should lead to shortening of the SS bond (that is the growth of the $-\Delta l_{SS}$ value) and to positive q_S increasing. Hence, it seems natural that the two values ($-\Delta l_{SS}$ and q_S) increase with the substituent π-donor ability, i.e., with the growth of the sulfur atom ability to donate its lone electron pair to the σ_{SX}^* level (or with the ΔE_{ij} value decreasing in Equation 2).

Let us consider the SK_β fluorescent spectra of dialkyl disulfides presented in Figure 4. An intense short-wave peak A corresponds to the transition from the HOMO† n_S–σ_{SC}^* into the K vacancy of the sulfur atom, and the rest of the maxima correspond to transitions from σ levels of SS and SC bonds. In previous reports [60,61] we had introduced into the SK_β spectra of S(II) compounds the internal standard that is the energy of the transition from a hypothetical n_S level (Hn_S) to the $1s_S$ hole to analyze effectively the short-wave structure of the SK_β spectra. This energy ($Hn_S(K_\beta)$) is determined by the effective charge of the sulfur atom, which is proportional to the SK_α line shift. Hypothetical levels are introduced using the hypothetical orbitals (HO) concept proposed by Jolly [63] (he refers to it as the LOIP concept) and developed by us [60,61,64,65]. The HOs are molecular orbitals (MOs) of model fragments disturbed by the coulombic effect of substituents. We can obtain the $Hn_S \rightarrow 1s_S$ transition energy with the help of measured ΔSK_α values and the correlation found in reference [61] between the energy of the $n_S \rightarrow 1s_S$ transition in the SK_β spectra of sulfides (containing a practically "pure" n_S level) and ΔSK_α values:

$$Hn_S(K_\beta), eV = 5.6(3)\Delta SK_\alpha(\text{eV}) + 2468.37(1)$$

$$r = 0.973, s = 0.06, n = 25 \tag{8}$$

The HOMO bonding degree (Δn_S) is defined as

$$\Delta n_S = Hn_S(K_\beta) - E_A \tag{9}$$

The Δn_S value may serve as the parameter of the n_S–σ^* conjugation efficiency.† The HOMO bonding degree, that is, the positive Δn_S value, increases with this conjugation. From these data, presented in Table 4, it follows that the n_S–σ_{SC}^* conjugation efficiency increases in the sequence

$$C_8H_{17} \sim C_5H_{11} \leq Bu \leq i - Bu \leq H_2NCH_2$$
$$\leq Pr < Et \sim Me \leq CH_2Ph \sim i$$
$$- Pr \leq CH_2CH = CH_2 \leq t - Bu \tag{10}$$

[†] As mentioned previously, there is the competitive $n_S - n_S$ conjugation. But $n_S + n_S$ and $n_S - n_S$ levels do not resolve in SK_β spectra because of the small difference between energies (0.2–0.6 eV [57]) and a rather large width of partial lines in the SK_β spectra (≈1.2 eV).

[†] The $n_S - n_S$ interaction can lead only to small integral destabilization of $n_S \pm n_S$ levels.

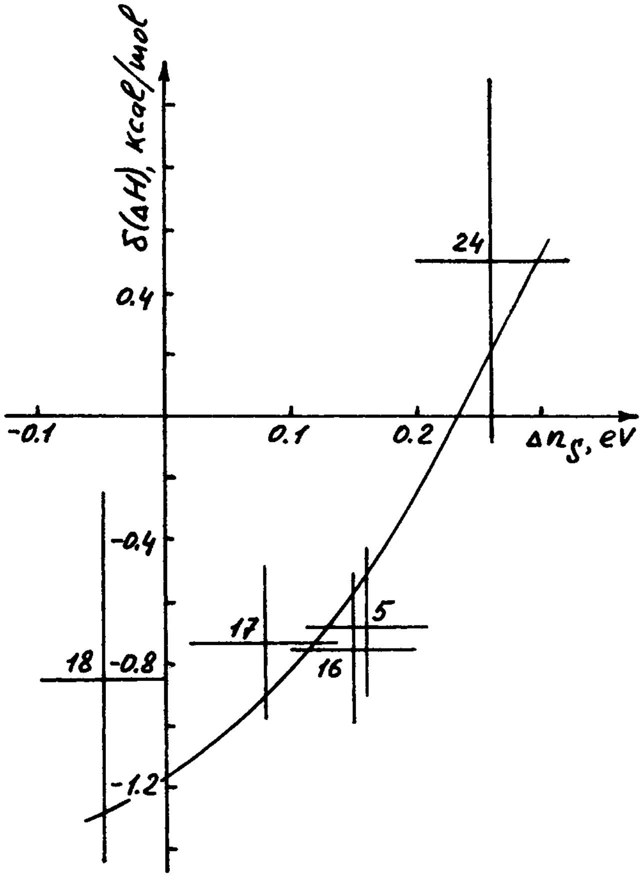

FIGURE 5 Comparison of differences between calculated and experimental heats of formation of dialkyl disulfides (taken from reference [66]) with Δn_S parameter value. Numbering of points corresponds to that of the compounds.

The analysis of this sequence shows that the geminal conjugation efficiency increases with the number of branches at the C_α atom, the shortening of the alkyl straight chain, and the appearance of an sp^2 hybridized C atom bonded with the C_α atom.

In sequence (10), the stability of the SS bond must increase and the stability of the SC bonds must decrease. The validity of sequence (10) is indirectly confirmed by calculations of the heat of formation of disulfides 5, 16, 17, 18, 24 reported in reference [66] by application of Allinger's force field method on the assumption that the heat of the SS bond formation is constant and equal to 8.9 kcal/mol for all of these disulfides. The difference between the calculated and experimental heats of disulfide formation changes, as shown in Figure 5, is in line with the Δn_S values, i.e., the parameter of the SS bond stabilization assumed to be constant in calculations carried out in reference [66].

Our X-ray spectral data obtained for S_8 indicate that there is a strong n_S–σ^*_{SS} conjugation in this compound. From Figure 2, it follows that this conjugation leads to SS bond shortening that is 2–4 times as large as the corresponding SX bond lengthening. Hence, we can draw a conclusion that the SS bond in S_8 has a higher bond order. Therefore, the length of the SS single bond must be larger than 2.05 Å (see Table 2), and the most reliable value of r_{cov} for the sulfur atom is equal to 1.04 Å.

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