We are left with the only structure which is ABCB (or the equivalent stacking ABAC), the last one, ABAB, does not correspond to a doubling of the c parameter (Figure 1). The structure can be shown by $Na_xTa_2S_2C$ ($0.85 \leq x \leq 1$).

Finally, the 2H(Ib) structure leads very simply to the ABBA stacking. This structure (Figure 1) is the one exhibited by $Rb_xTa_2S_2C$, $Cs_xTa_2S_2C$, and $Na_xTa_2S_2C$ ($0.15 \leq x \leq 0.80$) and possibly by $K_xTa_2S_2C$.

Due to the poor quality of the powder spectra and the weak intensities of the diffraction lines, no structural calculation has been done. Moreover, the hierarchy of the intensities of the spectra for all our compounds remains unchanged which did not allow us to use possible "sensitive" reflections as has been done in previous work about the M_xTS_2 phases.[5]

Conclusion

Nonstoichiometric $A_xTa_2S_2C$ phases have been obtained. They belong to the class of lamellar chalcogenide intercalation compounds. According to the ionicity diagram, the lithium derivative falls within the octahedral domain, potassium, rubidium, and cesium compounds are found to be in the trigonal prismatic region, whereas sodium is a borderline case with both an octahedral and trigonal prismatic phase.

These phases belong to first-stage compounds (all the van der Waals gaps are statistically occupied). No second-stage phase, in which only each alternate gap would be occupied, has been observed; this can be related to the thickness of the Ta_2S_2C slabs separating the A^+ positive layers (screen effect).

Registry No. Ta_2S_2C, 12539-81-0; $LiTa_2S_2C$, 61490-84-4; $NaTa_2S_2C$, 61490-85-5; KTa_2S_2C, 61490-83-3; $RbTa_2S_2C$, 61490-86-6; $CsTa_2S_2C$, 61490-82-2; $Na_{0.75}Ta_2S_2C$, 61490-88-8; $K_{0.50}Ta_2S_2C$, 61490-87-7; $Rb_{0.75}Ta_2S_2C$, 61490-89-9.

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(11) As used in the previous paper, the parenthetical Ia and Ib mean that the compounds belong to the I stage phase class (each van der Waal's gap statistically occupied), whereas a stands for an octahedral and b for a trigonal prismatic coordination for the alkali metal; 3R and 2H mean respectively a rhombohedral cell with three Ta_2S_2C slabs and a hexagonal cell with two Ta_2S_2C slabs.

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Photoelectron Spectra and Molecular Properties. 59.[1] Ionization Energies of Disulfur Dihalides and Isomerization Surfaces XSSX $\rightleftarrows$ SSX_2

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Photoelectron spectra of disulfur dihalides XSSX (X = Cl, Br) are reported and assigned in comparison to those of HSSH and the F_2S_2 isomers. CNDO energy surfaces for the isomerization XSSX $\rightleftarrows$ X_2SS (X = F, Cl, H) yield total energy minima close to those for the known geometries of FSSF, F_2SS, ClSSCl, and HSSH. The most probable reaction path calculated for an intramolecular halogen or hydrogen 1,2 shift involves a three-membered ring. Reflecting the nonexistence of thiothionyl chloride, Cl_2SS, and thiothionyl hydride, H_2SS, only the difluoro isomers are separated by a CNDO total energy barrier high enough to rationalize their achieved isolation.

Disulfur difluoride, FSSF, and thiothionyl difluoride, F_2SS, rank among the more curious isomers of few-atom molecules. First reported[3] independently in 1963 and 1964 by Kuczkowski[4] as well as by Seel and co-workers,[3] they not only resemble each other regarding essential structural parameters[4] but even give rise to almost identical photoelectron spectra[5] (Figure 1).

FSSF is thermally less stable and changes slowly into F_2SS,[3] a unique rearrangement considering all the isosteric compounds currently known to exist exclusively in either the ABBA or the A_2BC structure as, e.g., ClSSCl or F_2SO. Extending previous studies,[6] we wish to report photoelectron (PE) spectra of ClSSCl and BrSSBr,[2,7] an attempt to generate the unstable ISSI in the gas phase, and CNDO total energy surfaces[2] for the F_2S_2, Cl_2S_2, and H_2S_2 systems.

Experimental Section

Disulfur Dihalides. Purified[8] ClSSCl in ether solution was allowed to react with stoichiometric amounts of gaseous dry HBr (generated by slowly dropping bromine into tetraline) to yield either ClSSBr or BrSSBr.[9] After distillation under reduced pressure (ClSSBr, bp 37 °C (0.1 mm); BrSSBr, bp 48 °C (0.1 mm)) traces neither of HBr nor of HCl were revealed by the PE spectra.

In analogy to the synthesis of SSO[10] from Cl_2SO and Ag_2S, preparation and characterization of unstable[11] ISSI were attempted by passing ClSSCl over KI in a heated tube connected to the PE spectrometer (see Figure 2). However, no direct evidence for the generation of ISSI could be obtained with ClSSCl pressures ranging from 0.05 to 1 Torr: below 85 °C the PE spectrum of pure ClSSCl was recorded, between 85 and 110 °C increasing amounts of iodine began to show up, and above 110 °C no more ClSSCl could be detected while outside the oven zone a yellow deposit of elemental sulfur formed.

Photoelectron Spectra. The helium I spectra were recorded using Perkin-Elmer PS 16 instruments with 127° electrostatic deflection analyzers and calibrated by Xe and Ar $^2P_{3/2}$ ionizations. A resolution of ~30 meV was achieved.

Calculations. The CNDO/2 calculations for the XSSX and X_2SS systems with X = F, Cl, H were performed at the Hochschul-Rechenzentrum Frankfurt and included $3d_S$ orbitals in the basis set. The results have been checked and improved by subsequent Koopmans corrections based on a second-order perturbation treatment.[12,13] The Koopmans correlation diagram (Figure 3) containing more than 40 PE spectroscopically assigned ionizations of 13 different sulfur compounds supports the assumed reliability of semiempirical calculations for chemically related molecules, yielding the linear regression[2]

$$-\mathscr{E}_J^{\mathrm{CNDO}} = 0.335 + 0.931(\mathrm{IE}_n^{\mathrm{v}}) \qquad (1)$$

with the standard deviation SE = 0.431.[2]

For the isomerization surface calculations, the CNDO/2 version used has been coupled to a coordinate program[2] developed to au-

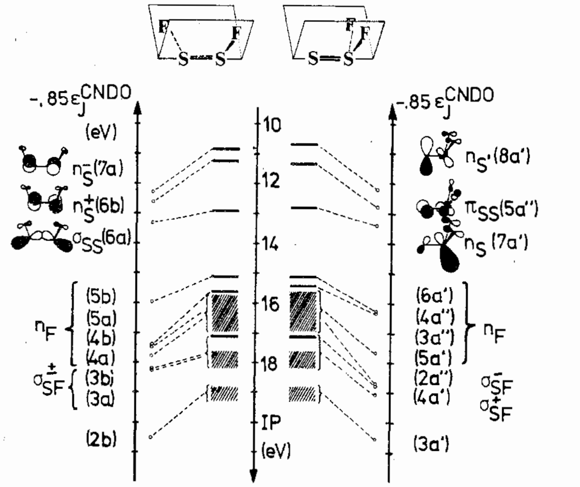

Figure 1. Isomers FSSF and F_2SS: microwave structures,[4] ionization potentials IP_n (eV),[5] and correlation with CNDO/2 eigenvalues $-0.85\mathcal{E}_J^{CNDO}$ (eV).[2]

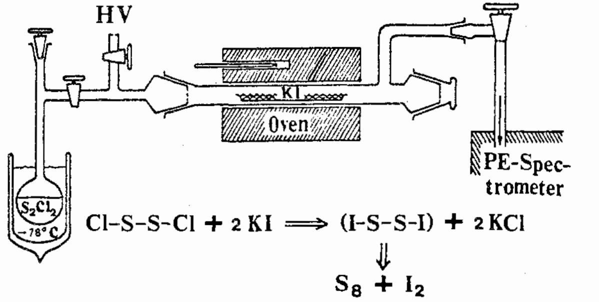

Figure 2. Apparatus used in the attempted preparation of ISSI.

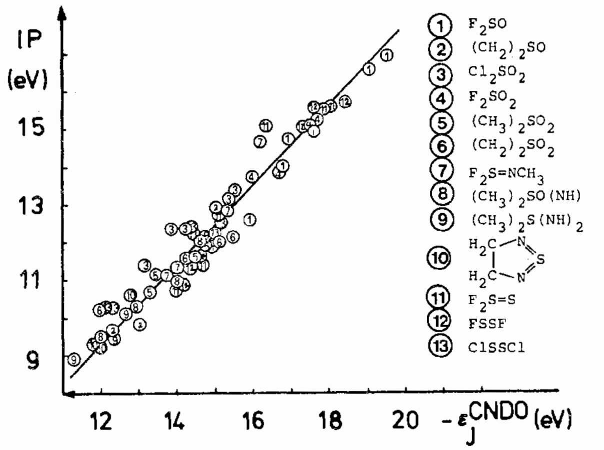

Figure 3. Correlation of PE spectroscopic ionization energies IE_n (eV) vs. CNDO/2 orbital energies $-\mathcal{E}_J^{SCF}$ with Koopmans corrections[12,13] for representative sulfur compounds.

tomatically move one atom stepwise along the *z* coordinate of a given system, thereby crossing 12 *xy* sectional planes with 144 screening points each. For all 1728 configurations the CNDO total energies are subsequently calculated and printed out in matrices for varying coordinates. Alternatively, a plot program[14] can be attached.

The ab initio calculations for HSSH, FSSF, and ClSSCl were carried out at the Computer Center of the University of Basle (UNIVAC 1108) and made use of the standard 4-31G basis set of the Gaussian 70 program system; no d-type functions have been included.

The EHMO (SPDF) calculations for disulfur dibromide BrSSBr included $3s_S/3p_S$ and $4s_{Br}/4p_{Br}$ orbitals in the basis set; the program used also contained a one-electron spin–orbit interaction operator to simulate effects of second-order spin–orbit coupling.[15]

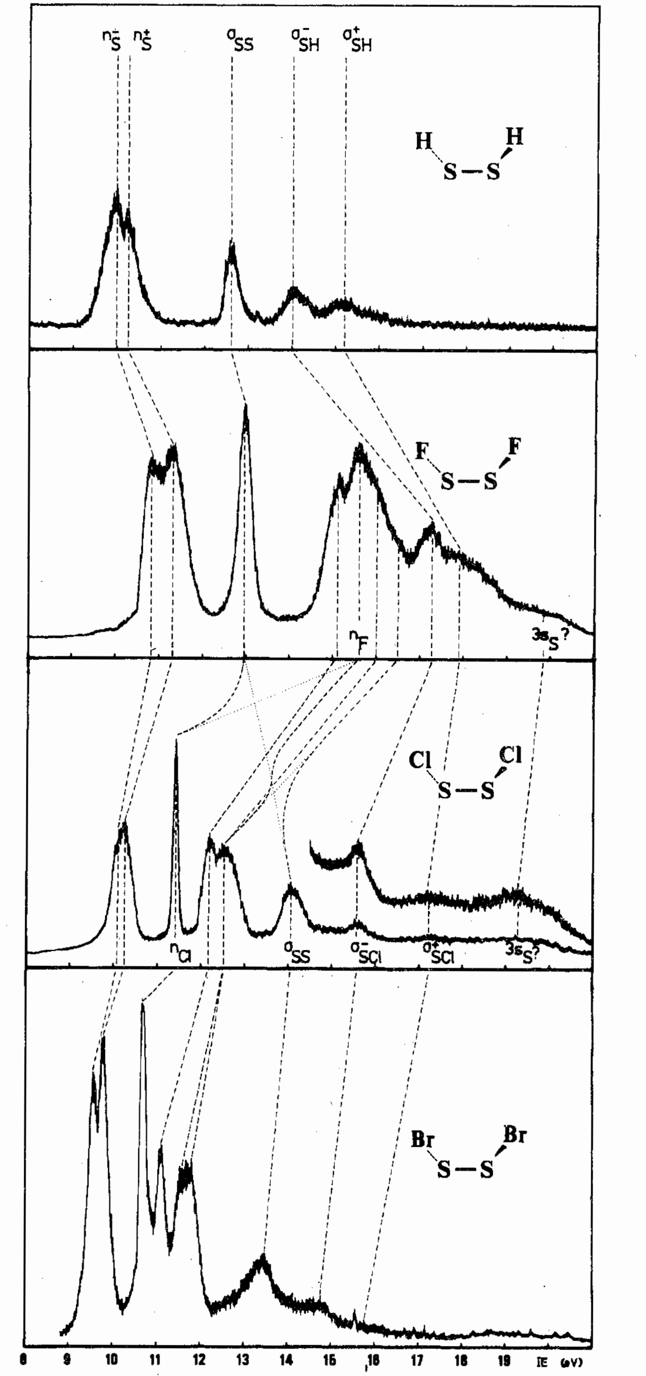

Figure 4. Comparison of XSSX He I PE spectra.

For all molecules investigated, structures have been reported, i.e., HSSH,[16] FSSF,[4] ClSSCl,[17] BrSSBr,[18] and F_2SS,[4,19] on which the calculations are based.

XSSX Photoelectron Spectra (PES) and Assignments

The PE spectra of ClSSCl[2,20] and of BrSSBr[2,20] are compared with those of HSSH[2,21] and FSSF[5] in Figure 4, and the vertical ionization energies are correlated with calculated eigenvalues in Table I assuming validity of Koopmans theorem.[2,22]

With few exceptions, assignment of the PES ionizations to characteristic molecular orbitals is partly obscured by strong mixing of the latter under C_2 symmetry. Therefore, two interrelated approaches were chosen: the chemical comparison along the series of known XSSX molecules (Figure 4) and the correlation with ab initio or EHMO–SO (spin–orbit) calculations (Table I).

Table I. Correlation of XSSX Vertical Ionization Energies, IE_n (eV), with Calculated Eigenvalues, $-\mathcal{E}_J$ (eV), of Molecular Orbitals Ψ_J, Characterized by Their Main Contribution and Their Irreducible Representation

HSSH			FSSF			ClSSCl			BrSSBr		
IE_n	$-\mathcal{E}_J^{4-31G}$	"Ψ_J"	IE_n	$-\mathcal{E}_J^{4-31G}$	"Ψ_J"	IE_n	$-\mathcal{E}_J^{4-31G}$	"Ψ_J"	IE_n	$-\mathcal{E}_J^{EHMO}$	"Ψ_J"
10.01	10.54	n_S^-(9a)	10.84	11.93	n_S^-(13a)	(10.1)[a]	11.02	n_S^-(17a)	9.60	10.72	n_S^-($13e_{1/2}$)
10.28	10.64	n_S^+(8b)	11.25	12.39	n_S^+(12b)	(10.3)	11.30	n_S^+(16b)	9.85	10.74	n_S^+($12e_{1/2}$)
12.62	12.83	σ_{SS}(8a)	12.94	13.86	σ_{SS}(12a)	11.43	12.32	(16a)	10.79	11.28	($11e_{1/2}$)
14.02	15.07	σ_{SH}^-(7b)	15.11	16.91	(11b)	12.20	13.59	(15b)	11.21	11.50	($10e_{1/2}$)
15.2	15.88	σ_{SH}^+(7a)	15.6	18.55	(11a)	12.52	14.05	n_{Cl}(15a)	11.6	12.81	n_{Br}($9e_{1/2}$)
	24.35	$3s_S$(6b)	(16.0)	18.73	n_F(10b)	(12.6)	14.13	(14b)	11.8	12.87	($8e_{1/2}$)
			(16.5)	19.3	(10a)	14.07	15.88	σ_{SS}(14a)	(13.1)	14.54	σ_{SBr}^-($7e_{1/2}$)
			17.26	19.35	σ_{SF}^-(9b)	15.65	16.05	σ_{SCl}^-(13b)	13.49	14.65	σ_{SBr}^+($6e_{1/2}$)
			(18.0)	19.90	σ_{SF}^+(9a)	(17.02)	16.72	σ_{SCl}^+(13a)	14.6	14.93	σ_{SS}($5e_{1/2}$)
			(20.0)	24.55	$3s_S^-$(8b)	(19.3)	23.29	$3s_S^-$(12b)	(15.5?)	16.63	s($4e_{1/2}$)
										19.89	s($3e_{1/2}$)

[a] Values in parentheses are ill-defined maxima.

Table II. Ionization Energies of Lone Pairs n_X and σ_{HX} Bonds of Hydrogen Halides

	IE, eV		
	HF	HCl	HBr
n_X	16.05	12.80	11.70/12.00
σ_{HX}	19.9	16.4	15.5

For HSSH, numerous calculations at various levels are reported in the literature.[23,24] The STO 4-31G results correlate satisfactorily with the vertical ionization potentials observed (Table I) and thus further support the generally accepted orbital sequence. Therefore, the unambigous assignment of the HSSH PE spectrum constitutes a favorable starting point for the spectroscopic comparison of XSSX molecules (Figure 4).

Switching over to the FSSF PE spectrum, one expects[25,26] four additional n_F lone pair ionizations in the 16–17-eV region as well as quite a high-energy shift of the σ_{SF} assigned PE bands. This leads to the tentative connection lines inserted in Figure 4 and is in accord with the ab initio calculations, which, however, indicate considerable mixing of symmetry-equivalent n_F and σ_{SF} orbitals. Therefore, it seems not too surprising that the center of gravity of ionizations with predominant n_F character (Table I: $\overline{IE(n_F)}$ = 15.8 eV; F atom $IE(n_F)$ = 17.4 eV[25]) is even slightly lowered relative to that of HF[27] (see Table II).

Also for the other disulfur dihalides, the hydrogen halide values allow reasonable guesses where to expect n_X and σ_{SX} ionizations.

For ClSSCl, the ab initio results show strong interactions especially between σ_{SS}(a) and n_{Cl}(a) orbitals as described by the avoided crossing of the (a)-type connection lines in Table I. Accordingly, the highest σ_{SS} contribution is found in the orbital denoted σ_{SS}(14a), whereas the third PE band corresponds to an orbital with predominant n_{Cl} character, in full agreement with its reported He I/He II intensity decrease.[7] Along the XSSX series, the valence part composition of the third highest occupied orbital $\sum c_S^2$:$\sum c_X^2$ changes from almost 1:0 for X = H and 3:1 for X = F to more than 2:1 for X = Cl.

The BrSSBr PE spectrum (Figure 4) displays a band pattern similar to that of ClSSCl but shifted to lower ionization energies. The mean value of the lone pair assigned ionizations $\overline{IE(n_{Br})}$ = 11.35 eV is again lowered relative to HBr (Table II). According to the EHMO–SO calculation,[15] which includes spin–orbit coupling, strong orbital mixing especially between n_S/n_{Br} and σ_{SS}/σ_{SBr} takes place: within the C_2' spinor group[15] all orbitals belong to the same irreducible representation $e_{1/2}$ (Table I).

Comparison of the XSSX PE spectra (Figure 4) reveals movement and split of the first two bands, which have been assigned to ionizations predominantly from the sulfur lone pairs, n_S. Their center of gravity $\overline{IE(n_S)}$ increases with increasing calculated charge q_S at the sulfur atoms (see Table III).

Table III. Correlation of XSSX Lone-Pair Ionization Energies and Calculated Charges q_S

	X in XSSX			
	Br	H	Cl	F
$\overline{IE(n_S)}$, eV	9.73	10.15	10.2	11.05
q_S	0.05+	0.12+	0.14+	0.51+

Table IV. Split of the First Two XSSX PE Bands vs. the Dihedral Angle ω

	X in XSSX			
	H	F	Cl	Br
$\Delta IE_{1,2}$, eV	0.27	0.41	0.2	0.25
ω,[4,16–18] deg	90.6	87.9	84.8	83.5

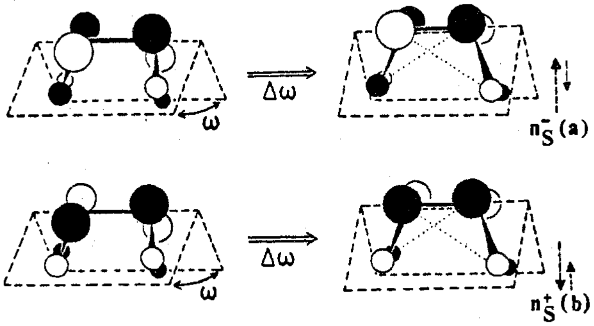

Figure 5. Conjugation and spiroconjugation in XSSX derivatives depending on the dihedral angle ω.

More difficult to rationalize is the difference $\Delta IE_{1,2}$, i.e., the split of the lone-pair combinations n_S^-/n_S^+, which obviously depends not only on the dihedral angle ω (see Table IV).

A qualitative model (Figure 5) would predict that the split n_S^-/n_S^+ should increase with (i) decreasing dihedral angle ω, (ii) different "through-bond" interactions between each of the n_S^-(a) and n_S^+(b) combinations and other orbitals of (a) or (b) symmetry, and (iii) decreasing spiroconjugation $n_S \pm n_X$. Considering all possible interactions and their interplay, even a reversal of the sequence n_S^+/n_S^- may occur.[2,21,23,27–29]

For HSSH with almost perpendicular lone pairs a split of 0.27 eV is observed; i.e., relative to the n_S ionization of H_2S at 10.43 eV[31] the PE bands assigned n_S^-(a) and n_S^+(b) are shifted by 0.42 eV and by only 0.14 eV, respectively. This can be explained in terms of second-order perturbation $\delta\mathcal{E}_J \propto \beta_{nm}^2/(\alpha_n - \alpha_m)$[32] with the next (a)-type ionization σ_{SS}(a) being only 2.61 eV away, while the next (b)-type band assigned

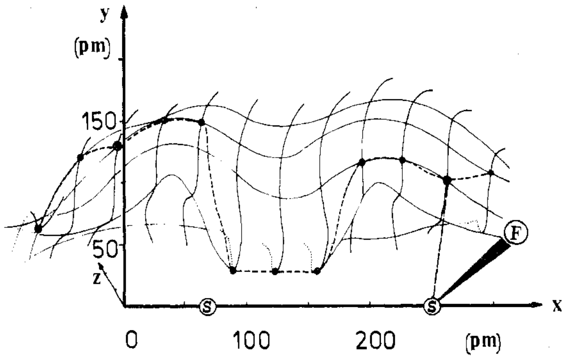

Figure 6. Coordinate hypersurface for the FSSF ⇄ SSF_2 isomerization; the dashed line connects the minima $E_{\text{total}}^{\text{CNDO}}$.

σ_{SH}^-(b) follows at a 3.72-eV distance (Table I).

In the halogen derivatives, the dihedral angle ω decreases (Table IV), and assuming $\Delta IE_{1,2} \propto \cos \omega$,[29] for BrSSBr with $\omega = 83.5°$ a 0.1-eV split increase is estimated. The strongest split, however, is found for FSSF, exhibiting the largest energy difference (Table I: $\Delta IE_{3,4} = 3.05$ eV) between the next two following orbitals $\sigma_{SS}(a)/n_F(b)$ and with negligible counteracting spiroconjugation (Figure 5) because of the gap >5 eV between n_S and n_F ionizations. In ClSSCl the first two PE bands strongly overlap, and both n_{Cl}(a) at 11.43 eV and n_{Cl}(b) at 12.20 eV are close enough in energy to also permit counteracting spiroconjugation (Figure 5). As pointed out before, BrSSBr is a special case because due to spin-orbit coupling all orbitals belong to the same symmetry species $e_{1/2}$ in C_2' spinor group notation.

CNDO Total Energy Surfaces for Isomerizations XSSX ⇄ SSX_2

The orbital sequences for XSSX molecules as predicted by the ab initio calculations (Table I) and supported by PE spectroscopic comparison along the series (Figure 4) can be reproduced by the semiempirical CNDO procedure. In addition, the known thermodynamical properties of the F_2S_2 isomers[3] are reflected by the CNDO total energies.[5] Therefore it has been attempted to approximate isomerizations XSSX ⇄ SSX_2 by CNDO reaction surfaces under the following assumptions: (i) intramolecular 1,2 shift of X, (ii) movement of X along a fixed SSX fragment with subsequent variations around the detected energy minima, and (iii) neglect of multiconfigurational interactions (see Concluding Remarks).

For FSSF ⇄ SSF_2, the movement of one F atom along the SS axis crossing 12 bisectional planes of 144 screening points each (cf. Experimental Section) is displayed in Figure 6: according to the 12 CNDO total energy minima connected by a dashed line, the pathway winds around the S atom, crosses an almost planar three-membered ring, and turns up again to reach the F position in SSF_2. The hypersurface $E_{\text{total}}^{\text{CNDO}} = f(x, z)$ and a cut along the potential energy valley are shown in Figure 7.

The calculations predict thiothionyl fluoride SSF_2 to be only slightly more stable than the difluorodisulfane isomer FSSF ($\Delta E_{\text{total}}^{\text{CNDO}} \approx 0.1$ eV); but—under the assumptions specified above—the barrier to the three-membered ring transition state should amount to about 1–2 eV. During an intramolecular isomerization the characteristic orbitals of FSSF (Table I) would transform into those of SSF_2 as indicated in Figure 1: $n_S^-(7a) \rightarrow n_{S(SF_2)}(8a'')$, $n_S^+(6b) \rightarrow \pi_{SS}(5a'')$, and $\sigma_{SS}(6a) \rightarrow n_{(S)S(F_2)}(7a')$. Finally, additional bond lengths as well as angle variations around the minima yield structural data close to the experimental ones (see Table V).

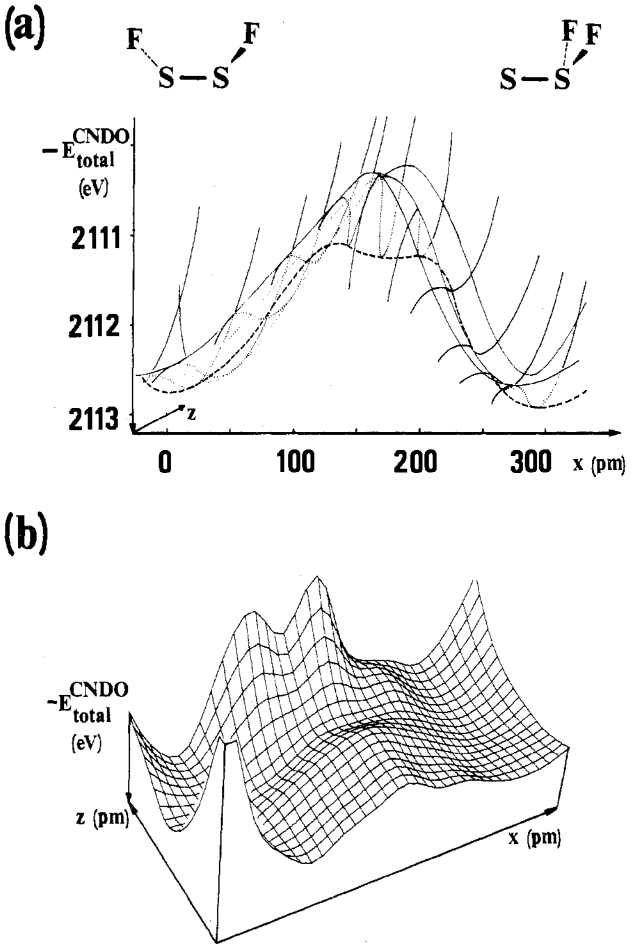

Figure 7. Total energy hypersurface for FSSF ⇄ SSF_2 isomerization (a)[14] and cut along the potential vally (b).

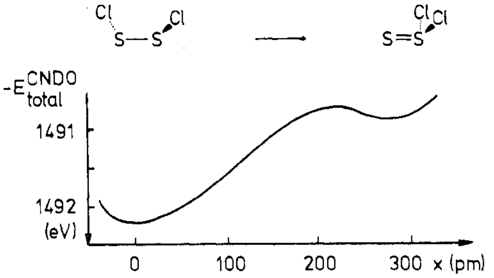

Figure 8. CNDO total energy minima along the "reaction coordinate" of the moving Cl atom during an assumed intramolecular isomerization ClSSCl ⇄ Cl_2SS.

Table V. Experimental and Calculated Geometries and Dipole Moments for the F_2S_2 Isomers

		d_{SF}, pm	SSF, deg	ω or FSF, deg	μ, D
FSSF	calcd	163	110	89	1.72
	exptl[3,4]	163.5	108.3	87.9	1.45[32]
F_2SS	calcd	160	109	93	(4.45)[a]
	exptl[4,19]	159.8	107.5	92.5	1.03

[a] Inexplicable deviation; various calculations always yielded values of μ > 4 D.

Analogous calculations for the S_2Cl_2 system yield a different reaction surface: the cut along the valley of $E_{\text{total}}^{\text{CNDO}}$ minima (Figure 8) suggests that ClSSCl is the only stable isomer and that the energy barrier for the $Cl_2SS \rightarrow$ ClSSCl conversion should be rather small ($\Delta E_{\text{total}}^{\text{CNDO}} \approx 0.15$ eV).

The CNDO hypersurface ClSSCl ⇄ Cl_2SS is supported by experimental observations: so far only ClSSCl has been detected,[32] and additional calculations around the corresponding potential trough predict a molecular structure close

Table VI. Experimental and/or Calculated Geometries and Dipole Moments for the Cl_2S_2 Isomers

		d_{SCl}, pm	SSCl, deg	ω or ClSCl, deg	μ, D
ClSCl	calcd	201	111	85	1.48
	exptl[17]	205.7	108.2	84.8	1.6[33]
Cl_2SS (calcd)		201	108	93	2.89

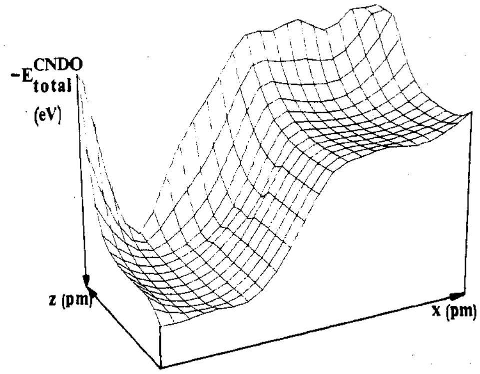

Figure 9. CNDO total energy hypersurface[14] for the HSSH ⇄ SSH_2 isomerization (without $3d_S$ orbitals).

to the one determined for the gas phase.[17] (See Table VI.)

The concluding example deals with the HSSH ⇄ H_2SS isomerization, i.e., with molecules small enough to incorporate some additional variations into the calculations. Thus the SS bond length has been changed by 0.5-pm steps between 200 and 206 pm, and/or the HSSH dihedral and HSH angles, respectively, have been opened stepwise by 1° from 97 to 106°. Furthermore, two series of calculations without and with inclusion of $3d_S$ orbitals were carried out. The total energy minimum hypersurface resulting from CNDO calculations without $3d_S$ enlargement of the basis set is displayed in Figure 9.

Analogous to the case of the S_2Cl_2 system, the CNDO calculations predict only the experimentally observed C_2 isomer to be stable (E_{total}^{CNDO}: HSSH, −635.43 eV; SSH_2, −631.56 eV; barrier −631.57 eV). The enlarged basis with $3d_S$ orbitals leads expectedly to more negative CNDO total energies, but the difference between the two isomers is reduced to an unrealistic 0.8 eV, and a (probably artificial) barrier of 0.9 eV results.

Concluding Remarks

Summarizing facts and speculations, small molecules like the S_2X_2 series are an advantageous starting point to rationalize experimental data for larger and more complex derivatives S_2R_2, e.g., the differences of the first two ionization energies in terms of n_S^-/n_S^+ splitting and additional n_S/σ_{SS} mixing. The FSSF ⇄ SSF_2 isomerization,[3] with both isomers structurally[4,19] and PE spectroscopically[5] characterized, constitutes a unique and stimulating example for reaction surface calculations. Considering the crudeness of both the semiempirical CNDO procedure employed and the underlying assumptions, the results—although in reasonable agreement with the experimental observations—are recommended for reexamination by a more sophisticated treatment. This applies especially to the pathway of the moving atom, because multiconfigurational interactions have been neglected completely. On the other hand, low-cost computations, adjusted by PE spectroscopic correlation, as the ones reported may help to get a first insight into simple reactions, e.g., whether two species of a system are at all connected by a potential valley.

Acknowledgment. We thank Professor F. Seel[1] (University of Saarbrücken), who drew our attention to the S_2F_2 system.[5] S. Wolfe and B. Schlegel (Queens University, Kingston, Canada) kindly provided the plot program.[14] This work has been supported by the Fonds der Chemischen Industrie, Max-Buchner-Stiftung (stipend to B.S.), and Land Hessen.

Registry No. HSSH, 13465-07-1; FSSF, 13709-35-8; ClSSCl, 10025-67-9; BrSSBr, 13172-31-1; F_2SS, 16860-99-4; Cl_2SS, 60646-38-0.

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