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$\lambda^4\sigma^2$-Sulfur Heterocycles. An *ab Initio* and Density Functional Study

Jürgen Fabian*

Institut für Organische Chemie, Technische Universität Dresden, D-01062 Dresden, Germany

B. Andes Hess, Jr.*

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235

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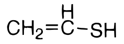
In order to better understand the structure and properties of 2λ-thioallyl (alternatively named 2-thiapropanediyl or thioformaldehyde *S*-methide) and the heterocyclic derivatives 3,4-dimethylenethiophene, naphtho[1,8-*c,d*]thiopyran, thieno[3,4-*c*]thiophene, and thieno[3,4-*f*]benzo[*c*]thionaphthene *ab initio* quantum chemical and density functional theory were utilized. The general conclusions drawn from the distinctly different approaches are the same. The low d-orbital occupation is not compatible with any hypervalency of sulfur including d-valence orbitals. Rather, the structures may be understood as ylidic ones with Coulombic CS-bond contraction, and as indicated by low singlet/triplet (S_0/T_1) splitting energies, the structures are more or less diradicaloid as well. The molecular geometries calculated at the MP2 and DFT/Becke3LYP level of theory are very similar with CS bond lengths between 1.64 and 1.70 Å for the nonclassical structures. The ionization energies are relatively low. For the sake of comparison the quinoid structures benzo[*c*]thiophene, acenaphtheno[5,6-*cd*]thiopyran and naphtho[1,8-*c,d*;5,4-*c′d′*]dithiopyran were included in the study. They proved to be borderline cases between compounds of nonclassical and classical structure. According to the calculated molecular geometry and the charge distribution acenaphtheno[5,6-*cd*]thiopyran has a nonclassical structure.

Introduction and Background

Organic compounds are better understood and are more easily calculated at the *ab initio* level of theory if they are of classical structure. However much can still be learned from calculations performed for compounds possessing nonclassical structures. Among the latter type of interest are compounds which contain tetravalent sulfur. One of the simplest compounds which contains sulfur with a classical structure (with dicoordinated sulfur) is ethenethiol (**1**) for which a simple Lewis−Kekulé can be drawn. However, if sulfur is placed between the two carbon atoms, the formula representation is less trivial with the resulting structure of the nonclassical type. For convenience, the structural formula **2** may be used.

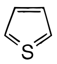


$CH_2{=}\overset{H}{C}{-}SH$

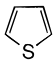
1

$H_2C{=}S{=}CH_2$

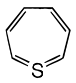
2



3a



3b



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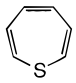

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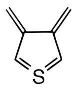

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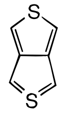

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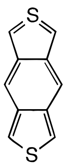

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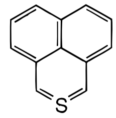

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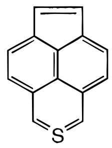
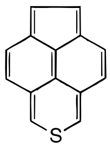
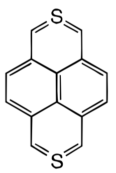


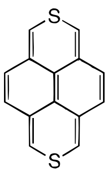
9a



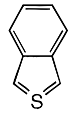
9b



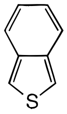
10a



10b



11a



11b

Two σ-types of valence contribute to a tetra(quadro)-valent sulfur atom ($\lambda^4\sigma^2$). The λ-symbol indicates a nonstandard bond of number 4 in **2** whereas the standard number for sulfur is 2 (e.g. in **1**).[1] Formulas with hypervalent sulfur (or any alternative formula discussed below) are not required if the terminal carbon atoms of **2** are bridged by one or two double bonds giving thiophene (**3a**) and thiepin (**4b**), respectively. However, the nature of the bonds remains when the C═S═C fragment is symmetrically bonded to the butadiene fragment at the two and three positions. The resulting molecule is 2,3-dimethylenethiophene (more correctly 2,3-dimethylenethiophene-1-S^{IV}) (**5**) in which the C═S═C fragment is preserved by topological reasons. The heterocycles thieno[3,4-*c*]thiophene (**6**) and thieno[3,4-*f*]benz[*c*]thiophene (**7**) are formally derived from **5**. However, due to the presence of two equivalent sulfur atoms the structure of these heterocycles are less nonclassical, since in each of the two possible resonance structures one of the sulfurs

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(1) (a) Treatment of Variable Valence in Organic Nomenclature (Lambda Convention). *Pure Appl. Chem.* **1984**, *56*, 769. (b) McNaught, A. B. *Adv. Heterocycl. Chem.* **1976**, *20*, 218.

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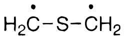
is divalent and one is tetravalent. Another compound with a strongly localized C=S=C structure is naphtho[1,8-*c*,*d*]thiopyran (**8**). The nature of the CS bond should change in passing from **8** to acenaphtheno[5,6-*cd*]thiopyran (**9**) and naphtho[1,8-*c*,*d*;5,4-*c′d′*]dithiopyran (**10**) which may be written by the quinoid formulas **9b** and **10b**, respectively. The prototype of quinoid structures is benzo[*c*]thiophene (**11**) which is iso-π-electronic with thieno[3,4-*c*]thiophene (**6**). As shown by the formulas **11a** and **11b** this molecule possesses a classical quinoid resonance structure **11b** as well as a nonclassical resonance structure **11a** which possesses the aromatic benzene ring.

The formulas of the nonclassical structures have been written with C=S=C for convenience and simplicity. The hypervalency in such structures is generally understood by a model of valency including d-orbitals of sulfur resulting in its octet expansion. However, according to theoretical studies on more highly coordinated sulfur compounds this model is not justified.[2] Spin-coupled valence bond theory, on the other hand, suggests that there is no reason for refuting higher valencies for certain topologies even if d-orbitals are unoccupied. According to this theory all electrons can take part in bonding and the octet rule is superseded by the democracy principle.[3]

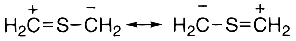
In any case, there are alternative formula representations that may shed light on other features of the nonclassical structure. By replacing the double bonds in **2** with single bonds gives **2a** and **2b**. The nonpolar structure **2a** is a diradical, but has to be understood, in that case, as a singlet molecule with diradicaloid properties. If the formula reflects to some degree reality, the singlet/triplet splitting should be relatively low, i.e. lower than about 25 kcal/mol.[4] The resonance structures of **2b** emphasize the spin pairing not explicitly shown in **2a**. Finally, the charge separation depicted by the two resonance contributors of **2c** indicates an ylidic (betainic) structure. Ylidic formulas now prevail in the description of acyclic structures, while hypervalent ones are often preferred for heterocyclic ones. The ylidic formula suggests polar bonds including some double bond character, while the hypervalent or diradicaloid formulas define more extreme bond characteristics and a lower bond polarity.


$H_2\dot{C}-S-\dot{C}H_2$

2a


$H_2\overset{+}{C}-S-\overset{-}{C}H_2 \longleftrightarrow H_2\overset{-}{C}-S-\overset{+}{C}H_2$

2b


$H_2\overset{+}{C}=S-\overset{-}{C}H_2 \longleftrightarrow H_2\overset{-}{C}-S=\overset{+}{C}H_2$

2c

Some of the compounds studied here have been synthesized and some of their derivatives are stable compounds. The parent compound **2** is formed from chloromethyl trimethylsilyl sulfide by 1,3-elimination and was trapped by cycloaddition with activated alkenes and alkynes.[6] The majority of the acyclic thiocarbonyl S-ylides have been observed in pericyclic reactions, such as the formation of thiiranes by electrocyclic ring closure or formation of tetrahydrothiophenes by [3 + 2]cycloaddition with ethenes. The early studies of thiocarbonyl S-ylides by Kellogg et al.[6] were later scrutinized by Huisgen, Mloston, and co-workers.[7] Kellogg[6a] considered these compounds as fundamental examples of compounds with "tetravalent sulfur" derived from **2**. Huisgen, however, classified thiocarbonyl S-ylides as "1,3-dipoles", which are distinguished by cycloaddition reactions with various dipolarophiles.[8] Adamantanethione *S*-methide and two other derivatives of **2** have been studied recently by Maier and co-workers using the matrix isolation technique.[9]

Heterocyclic S-ylides have been known since the 1960s. Cava[10] and co-workers first found evidence for the formation of substituted thieno[3,4-*c*]thiophenes (**6**). The colored tetraphenyl derivative was the first and for many years the sole stable heterocycle of this series.[10d,11] The properties of this compound have been studied in detail.[12] On the other hand, the parent compound and alkyl-substituted derivatives have only been trapped by cycloaddition reactions.[10a,b] More stable compounds have been prepared which contain alkylthio and acceptor groups.[10f,13] Potts and McKeough also prepared the perphenyl-substituted thieno[3,4-*f*]benzo[*c*]thiophene (**7**).[11] The deeply colored naphtho[1,8-*cd*]thiopyrans[14] and acenaphtheno[5,6-*cd*]thiopyrans[15] derived from **8** and **9** were studied by Schlessinger and co-workers. The very long wavelength and intense absorptions observed for **8** and **9** are of interest in connection with near infrared absorbing organic chromophores.[16] The parent compound

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and alkyl-substituted derivatives are very reactive species that easily undergo cycloaddition with dipolarophiles. The stable, but also reactive, quinoid benzo[*c*]thiophene was first synthesized by Mayer and co-workers.[17] Appropriately substituted heterocycles enabled polymeric structures to be produced.[18] The potential formation of conducting polymers has been examined for polymers derived from **6** and **11**.[19] Photoylides have been reviewed in ref 20. Heterocyclic S-ylides were generated in photochemical reactions or are observed by photocoloration reactions.[20,21] Berson and co-workers generated 3,4-dimethylenethiophene (**5**) by photolysis[21a] and gave detailed information about its spectral properties in low temperature matrices[21b] and its chemical reactivity in cycloaddition.[21c] This compound is unequivocally a singlet molecule. The appropriate linking of two molecules resulted in a tetraradical.[21e]

Nonclassical compounds such as thieno[3,4-*c*]thiophene (**6**) and naphtho[1,8-*cd*]thiopyran (**8**) have been previously calculated by semiempirical π-approximations using the PPP-method.[12b,22] Early predictions about molecular geometries and electronic distributions obtained by PPP calculations[22a] in the π-approximation and by MNDO calculations[19gi,23] in the all valence electron approximation showed that nonclassical compounds are clearly distinguished from classical ones. The band structure of polymers derived from **6** and **11** has also been calculated at the MNDO-level.[19g] PPP- and CNDO/S calculations were utilized to interpret the spectral properties of tetraphenyl-**6**.[12b,d] In connection with the study of the violation of the Hund's rule,[21d,24a] Lahti and co-workers extensively studied the singlet/triplet splitting in 3,4-dimethylenethiophene (**5**) with semiempirical INDO/SDCI and MNDO/UHF methods.[24b,c] According to these calculations, **5** is more stable in the singlet ground state than in the triplet state. Heterocycles such as **6**, **11**, and some heterocyclic photoylides were calculated at the RHF levels of *ab initio* theory.[25ab] Post-Hartree–Fock *ab initio* and density functional theory calculations were done for **2**[25c,d] and for **6** and heteroanalogs.[25e,f]

Computational Details

Calculations were carried out with the programs GAUSSIAN-92[26] and GAUSSIAN-94.[27] For the sake of comparability, we employed the standard basis set 6-31G* in all calculations. Using conventional *ab initio* quantum chemistry methods, correlation energy was included by Möller–Plesset perturbation theory up to the second order based on the Hartree–Fock single determinant wave function.[28] If not stated otherwise, all innermost occupied and outermost virtual orbitals were considered. Calculations by density functional theory (DFT) are based on the generalized gradient approximation (GGA).[29] This approximation appears at present to be the most promising DFT procedure for applications in organic chemistry. The performance of this approximation has been assessed in several recent papers.[30] A useful HF-DFT hybrid functional has been advocated by Becke[31a] and consists of the nonlocal exchange functional defined by Becke's three-parameter equation. In the version implemented in the above mentioned GAUSSIAN codes[31b] it can be combined with the nonlocal Lee–Yang–Parr correlation functional[31c] (Becke3LYP, also denoted as B3LYP). Recent comparative studies with the Becke3LYP functional involve molecular structure[30f] and electron density.[30g] This functional was employed throughout the study. In general, geometries were optimized completely. Stationary points, minima and saddle points, were characterized by the number of negative eigenvalues of the Hessian matrix (zero for minima and one for saddle points, respectively).

In order to examine the electron distribution and the nature of bonding two very different methods were

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Table 1. Theoretical CS Bond Lengths (R_{CS} in angstroms) and Results of the Atom-In-Molecule (AIM) Calculations and Natural-Population-Analyses (NPA) of Thioformaldehyde *S*-Methide (2): AOM-Based Covalent Bond Orders of CS (p_{CS}) and Atomic Charges at Sulfur and Carbon (q_S, q_C) (total energies in Hartrees)

	AIM					NPA		
theoretical model[a]	R_{CS}	q_{CS}	q_S	q_C	q_C[b]	q_S	q_C[b]	total energy
DFT/6-31G	1.705	1.52	+0.46	−0.39	−0.23	+0.60	−0.30	−476.64293
DFT/6-31G*	1.642	1.95	+0.54	−0.43	−0.27	+0.72	−0.36	−476.71159
DFT/6-311G**	1.639	1.93	+0.48	−0.36	−0.23	+0.70	−0.35	−476.76665
DFT/6-31+G**	1.645	1.93	+0.54	−0.37	−0.27	+0.72	−0.36	−476.72712
MP2/6-31G*	1.644	1.84	+0.61	−0.51	−0.31	+0.69	−0.35	−475.87401
QCISD/6-31G*	1.642	1.81	+0.60	−0.48	−0.30	+0.71	−0.36	−475.88425
CCD/6-31G*	1.636					+0.73	−0.37	−475.87712
MP4SDTQ/6-31G*[c]	1.658	–	–	–	–	–	–	−475.90323

[a] Frozen core for QCISD, CCD, and MP4SDTQ. [b] With hydrogen charges summed up into the charges of carbon atoms. [c] Post HF density of MP4SDTQ not available in Gaussian-94.

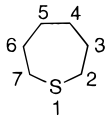
used: the Natural Orbital Analysis (NPA) of Weinhold, Reed, and co-workers[32] and the Atoms-in Molecules (AIM) method of Bader.[33] In Bader's theory of topology the electronic structure is described in a uniform and unbiased way. Atomic regions and bond critical points between the bonded atomic regions are located first. The critical points are points of minimum electron density along the bond, but of maximum density in the direction normal to the bond. The ellipticity of the bond critical point is a measure of the ratio of the rate of intensity decrease in the two directions perpendicular to the bond path. The set of paths defines a zero flux surface separating a pair of atoms. The surfaces divide a molecule into atomic regions. Numerical integration of the charge density within the atomic region gives the population of the atoms. Consideration of the local nuclear charge finally provides the charge of the (nonspherical) atom. This topological electron density method enabled Cioslowski and Mixon to define the AOM (atomic overlap matrix)-derived covalent bond orders and AOM-localized orbitals.[2c,34] The localized orbitals may exhibit ionicity.

The Weinhold−Reed Natural Population Analysis (NPA) is easily applicable and inexpensive, in contrast to the aforementioned method. Serious deficiencies of the Mulliken population analysis[35] are removed in this approach. NPA is a method of calculating atomic and orbital charges based on occupancies of orthonormal natural atomic orbitals on each center. The calculation requires a sequence of transformations of the wavefunctions. The AIM as well as the NPA method are implemented in the Gaussian program.

Results and Discussion

Molecular Structure. Calculated carbon−carbon and carbon−sulfur bond lengths are listed in Tables 1−3. The geometrical parameters derived by DFT calculations are similar to those of the MP2 calculations. The absolute mean deviations of the CS and CC bond lengths amount to 0.03 and 0.02 Å, respectively. The CS bonds are systematically longer in the DFT calculations provided the same basis set is used. If classical structures such as thiophene (**3b**) and thiepin (**4b**) are considered, DFT shows a stronger CC bond length alternation than MP2. Comparing the theoretical values with experimental values of **3b** (CS: 1.716 Å, CC: 1.369 and 1.426 Å, respectively, average values of ED and MW measurements[36]), the results of the MP2 calculations are only better with respect to the CS bond lengths. Thus, both DFT and MP2 methods are adequately useful for predictions of the molecular geometries. The computational time is much lower for DFT.

Table 2. Selected Geometric Parameter (bond lengths *R* in angstroms, angles in deg) of Thiepin (4) with C_{2v} and C_2 Symmetry at the MP2(full)/6-31G* and Becke3LYP/6-31G* Level of Theory



	4 (C_s)		**4** (C_2)		**4** (C_{2v})	
	MP2	DFT	MP2	DFT	MP2[a]	DFT[b]
			Bond Lengths			
S1−C2	1.768	1.788	1.676	1.662	1.656	1.650
C2−C3	1.351	1.345	1.451	1.462	1.465	1.471
C3−C4	1.446	1.455	1.345	1.340	1.346	1.341
C4−C5	1.363	1.356	1.486	1.496	1.497	1.506
			Bond Angles			
C2−S−C5	96.6	99.5	111.8	113.7	116.4	116.8
			Dihedrals			
C3−C4−C5−C6	0.0	0.0	65.1	49.5	0.0	0.0

[a] One imaginary frequency 163*i* cm^{-1}. [b] One imaginary frequency 131*i* cm^{-1}.

In thioformaldehyde *S*-methide (bis(methylene)sulfurane[37]) (**2**) the CS-bond is predicted to be extremely short (1.64 Å) by both the MP2 and DFT methods with the same basis set (6-31G*) (cf. Table 1). Neither extension of the basis set from 6-31G* to 6-311G** nor change of the correlation method in going from MP2 to QCISD or CCD brings about any noticeable changes in geometry. A slightly increased CS bond length of about 1.66 Å is calculated at the MP4SDTQ level. Even this bond length is much shorter than that found or predicted for any sulfidic structure. The CS bond in ethenethiol (**1**), which is isomeric to **2**, is calculated at 1.75 Å (exp 1.77 Å[36]). The calculated CS bond length of 1.66 Å of **2** is also short with respect to that of thiophene (**3b**, exp 1.72 Å[36]) and that of thiepin (**4b**) experimentally studied as the 2,7-di-*tert*-butyl derivative (1.80 Å[38a]).

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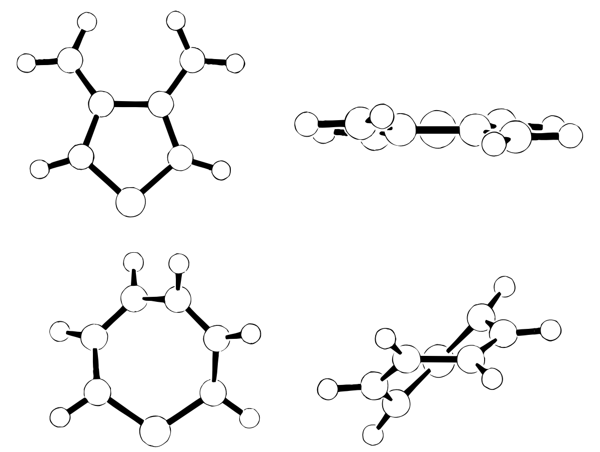
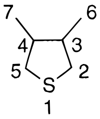


Figure 1. Structures of the isomeric compounds 3,4-dimethylenethiophene (**5**) (upper part) and thiepin (**4a**) (lower part) viewed on two planes perpendicular to each other (both structures are of C_2 symmetry).

Table 3. Selected Geometric Parameters (bond lengths *R* in angstroms, angles in deg) of 3,4-Dimethylenethiophene (5) with C_{2v} and C_2 Symmetry at the MP2(full) and Becke3LYP Level of Theory



	5 (C_{2v})			**5** (C_2)
	MP2^a	DFT^a	DFT^b	MP2^{a,c}
	Bond Lengths			
S1−C2	1.684	1.676	1.674	1.686
C2−C3	1.432	1.439	1.439	1.433
C3−C4	1.496	1.509	1.509	1.494
C3−C6	1.366	1.361	1.357	1.365
	Bond Angles			
C2−S1−C5	95.8	96.4	96.5	95.9
	Dihedrals			
C2−C3−C4−C5	0.0	0.0	0.0	8.2

^{a} 6-31G*. ^{b} 6-311G**. ^{c} One imaginary frequency 58.8i cm^{-1}.

Astonishingly, a second thiepin optimum structure was located on the MP2/6-31G* and B3LYP/6-31G* energy surfaces with a CSC fragment strongly related to that of the parent structure **2** (cf. Table 2). The nature of these stationary points is unequivocally confirmed by frequency analysis. Whereas the global minimum of thiepin (**4b**) is of a chair structure (C_s-symmetry), as described in ref 38, the additional local minimum was found to have C_2-symmetry (see Figure 1). It corresponds to $\lambda^4\sigma^2$-thiepin (thiepin-1-S^{IV}) (**4a**).

The calculated CS bonds of **4a** are about 1.68 Å and consequently contracted by about 0.11 Å relative to **4b** (cf. Table 2). In agreement with the formulas **4a** and **4b** the bond alternation is the reverse. However, thiepin **4a** is much higher in energy than **4b** (MP2: 39.7 kcal/mol; DFT: 42.4 kcal/mol). In view of the high energy of **4a**, the planar thiepin (C_{2v} symmetry) was calculated as well. This structure is also a stationary point on the energy surface but proved to be a saddle point of first order. It is of higher energy relative to both minimum structures. According to the calculated internal reaction coordinate (IRC), the saddle point is related only to **4b** and represents the transition structure of inversion of **4b**. The barrier is about 46 kcal/mol. With respect to bond length characteristics, the transition structure resembles more **4a** than **4b**.

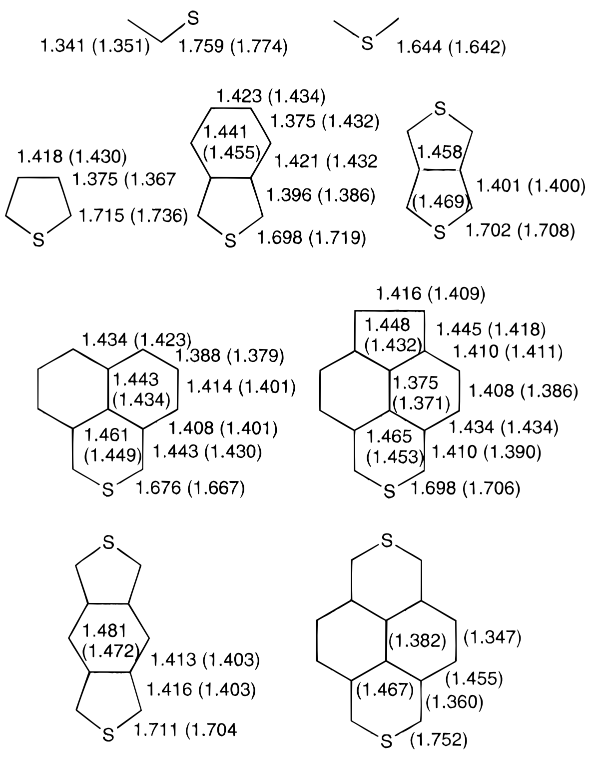


Figure 2. CC- and CS-bond lengths of planar ylidic and nonylidic compounds. All values reported are in angstroms. The first value is MP2(full)/6-31G*, the second value is DFT/6-31G* (in parenthesis). MP2(fz)/3-21G(*) rather than MP2(full)/6-31G* geometries are given for **7** and **9**. Data of **4** and **5** are in the Tables 2 and 3. The geometric data of **1** are those of syn ethenethiol.

3,4-Dimethylenethiophene (**5**) is a typical representative of a nonclassical structure. The bond lengths shown in Table 3 show again a relatively short CS bond length of about 1.68 Å obtained by MP2 and DFT calculations, while the carbon fragment resembles a gauche butadiene structure. The MP2 calculation gave a slightly nonplanar geometry (C_2-symmetry, cf. Figure 1) linked by a transition structure of C_{2v} symmetry. However, the barrier of inversion is extremely low (about 0.01 kcal/mol) and was not detectable with DFT calculations. The barrier may be due to the steric hindrance of the exocyclic hydrogen atoms. Single point calculations at the MP4SDTQ/6-31G* and QCISD(T)/6-31G* level at the above mentioned stationary points of **5** of C_{2v} and C_2 symmetry resulted in the conclusion that the planar structure is preferred at this higher level of theory. It should be mentioned, however, that two related ring structures show clearly a broken symmetry that is not removed at higher levels of theory.[39]

The heterocycles **6** and **7** are more thiophene-like, but the CS bond remains shorter than in thiophene (cf. Figure 2). The presence of the two thiophene rings indicates a shift from nonclassical toward classical structures. The MP2 and DFT bond lengths are surprisingly close to those of tetraphenyl-**6** as determined by X-ray diffraction study (1.706; 1.407 and 1.452 Å). Remarkably, thieno[3,4-*c*]thiophene (**6**) displays bond

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(38) (a) Yamamoto, K.; Yamazaki, S.; Murata, I.; Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N. *Tetrahedron Lett.* **1982**, 3195. (b) Murata, I. *Phosphor, Sulfur, Silicon* **1988**, *43*, 243. (c) Reinhoudt, D. N. *Rec. Trav. Chim. Pays-Bas* **1982**, *101*, 277.

(39) For example, 3-methylenethiet and 1,3-dithiet, about the latter compound cf. Janssen, R. A. J. *J. Phys. Chem.* **1993**, *97*, 6393.

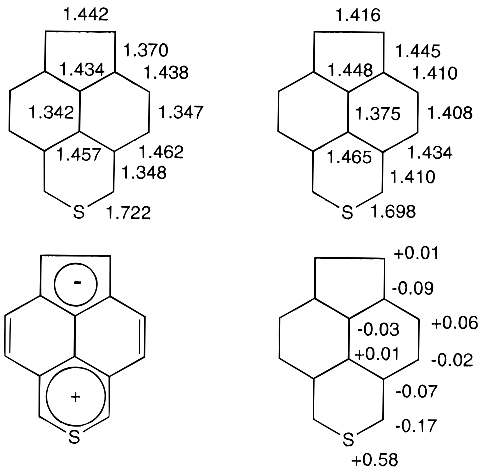

Figure 3. Upper part: Selected bond lengths in angstroms of acenaphtheno[5,6-*cd*]thiopyran (**9**) calculated by RHF/6-31G* (on the left) and MP2/3-21G(*) calculations (on the right). Lower part: Hypothetical resonance contributor of acenaphtheno[5,6-*cd*]thiopyran (**9**) and calculated DFT/6-31G* charge distribution (charges of adjacent hydrogen summed up).

lengths similar to the quinoid benzo[*c*]thiophene (**11**). These compounds clearly represent borderline cases. However, the relatively short CS bond lengths in the CSC fragment of about 1.67 Å of naphtho[1,8-*cd*]thiopyran (**8**) indicate a typical nonclassical structure. The naphthalenoid residue is linked by long CC bonds to the CSC group. According to the MP2 and DFT calculations on **9**, there is little structural change in going from the nonclassical **8** to the quinoid **9**. This was not expected. Whereas the RHF geometry of **9** shows a pronounced quinoid bond alternation according to **9b**, consideration of electron correlation by MP2 and by DFT favors a more delocalized structure on the carbon skeleton more similar to **9a** (cf. Figure 3).

This example reveals again that DFT provides considerably better results than RHF and is useful as an alternative to MP2 in predicting the geometries of conjugated systems. A quinoid structure, however, was found for **10** by DFT (cf. Figure 2). The CS bonds in **10** are now longer than in thiophene, and the two CSC groups are linked to naphthalene by essential CC-double bonds.

Electron Distribution. The parent structure **2** is again taken as an example to compare results of the analysis of electron densities and wavefunctions obtained by DFT and by conventional *ab initio* correlation methods employing different Gaussian basis sets. The results are shown in Table 1. Cioslowski's AOM-derived covalent bond orders of the CS bond of **2** are remarkably large and more or less independent of the theoretical model used. CS bond orders derived by DFT (about 1.94) are slightly larger than those of *ab initio* calculations (about 1.82). Large bond orders are concomitant with short CS bond lengths calculated at the same level of theory. These results may suggest that **2** has ylene character corresponding to formula **2**. The nature of the localized natural orbitals and the Bader atomic charges provide additional information about the electronic structure of **2**. According to the AOM-based localization procedure the four CH bonds and two of the CS bonds are described by localized bonds. The allyl-type three-center four-electron bond accommodates the remaining valence electrons. Since all the aforementioned localized bonds are of very low ionicity, the calculated Bader charges are mainly due to the allylic π-electron system. The charge of about +0.5 at the sulfur atom and the counter charges at the terminal groups thus indicate a partial ylidic character. This charge distribution corresponds, in principle, to that depicted by charge-separated resonance forms such as **2c**. However, the charge separation is less than expected. NPA charges are larger than the AIM charges (Table 1). The NPA charge at sulfur is +0.72 compared with +0.53 calculated by the topological theory (DFT/6-31G*). The population analysis allows one to extract π-charges from the total charges assuming effective core charges of 2 for sulfur and 1 for carbon. In agreement with conclusions drawn from the AIM calculations, the π-charge at sulfur (+0.66) is nearly the same as the total atomic charges (+0.72).

The DFT calculation of **2** with the 6-31G basis set without polarization functions at sulfur and carbon results in a different molecular and electronic structure than obtained with 6-31G* and by more extended basis sets (cf. Table 1). The CS bond lengths are exceedingly large while the covalent bond orders are low. This effect is well known. It does not provide an argument for any participation of d-type valence orbitals. The inspection of the electron population shows that the sulfur d-orbital occupancy is very low. Similar results are reported in the literature for many sulfur organic compounds including those of compounds with higher coordinated sulfur atoms.[2] The d-functions play primarily a polarization role although they are necessary to properly describe the molecular geometry and the energetics. The surprisingly short CS bond of **2** is not caused by octet expansion involving d-valence orbitals.

The comparison of the results of the AIM theory and of AOM-derived parameters revealed the unique nature of the electronic structure of **2** and suggest either a sulfurane or S-ylide structure. This nonclassical sulfidic structure is sharply distinguished from classical sulfidic ones, such as ethenethiol and thiophene. The latter ones display distinctly longer CS bonds (more than 1.71 Å), lower covalent bond orders (lower than 1.30), and lower charge separations (cf. Table 2). By contrast, the covalent CS bond order of **2** (1.95) is nearly as large as that of thioformaldehyde (2.11). In addition, the ellipticity of the sulfidic CS bonds reflects the varying double bond character. The ellipticity of the bond in **2** amounts to 0.42 and decreases to less than 0.25 for the aforementioned classical compounds. The unexpected low ellipticity of the CS bond of thioformaldehyde, however, is exceptional and has been discussed in terms of the ionic components of the thiocarbonyl bond.[40]

Although the allyl anion (propenide), which is iso-π-electronic to **2**, differs in the molecular charge from **2**, the comparison of their bond orders is informative. Its CC bond order of 1.68 is considerably lower than that of **2** (cf. Table 2). Sulfur dioxide (SO_2) is another compound taken for comparison in which the terminal methylene groups of **2** are replaced by oxygen. The DFT calculation confirms previous *ab initio* quantum chemical results,[2c] implying that the SO bonds are strongly ionic with large negative charges at the oxygen atoms. On the other hand, the electron charge shift is opposite if the sulfur in **2** is replaced by oxygen. The resulting formaldehyde *O*-methide is the parent structure of the carbonyl ylides. The ylidic charge distribution of the heteroanolog of this compound is completely hidden beneath the total charge distribution with a charge distribution opposite to the

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(40) Bachrach, S. M.; Salzner, U. J. *Mol. Struct. (THEOCHEM)* **1995**, *337*, 201.

Table 4. Theoretical CS Bond Lengths (*R* in angstroms) and Results of the Atom-In-Molecule (AIM) Calculations of the Nonclassical Thioformaldehyde *S*-Methide (2) and of Some Related Compounds: AOM-Based Covalent Bond Orders (*p*), Ionicities (*I* in %), and Elipticities ϵ of the Bonds and AIM Atomic Charges (*q*) Calculated at the DFT/Becke3LYP/6-31G* Level of Theory (total energies in Hartrees)

compound	R_{CS} R_{XY}	p_{CS} p_{XY}	I_{CS} I_{XY}	ϵ_{CS} ϵ_{XY}	q_C q_X	q_S q_Y	total energy
thioformaldehyde *S*-methide **2**	1.642	1.95	0.7 (C → S)	0.42	−0.43	+0.54	−476.71159
syn ethenethiol (**1**)	1.774	1.23	3.6 (C → S)	0.09	−0.18	+0.04	−476.77675
thiophene (**3**)	1.736	1.28	1.1 (C → S)	0.22	−0.23	+0.20	−553.00260
thioformaldehyde	1.618	2.12	37.1 (S → C) 9.7 (C → S)	0.04	−0.58	+0.42	−473.46237
allyl anion (X = C,Y = C)[a]	1.398	1.70	4.0 (C → C)	0.31	−0.35	−0.04	−117.28105
sulfur dioxide (X = S,Y = O)	1.464	1.64	63.3 (S → O)	0.15	−1.15	+2.30	−548.58739
formaldehyde *O*-methide (X = O,Y = C)	1.304	1.19	66.3 (C → O)	0.60	+0.43	−1.14	−153.71234
naphtho[1,8-*cd*]thiopyran	1.667	1.51	1.5 (C → S)	0.32	−0.31	+0.45	−860.24542

[a] Basis set 6-31+G* rather than 6-31G*.

ylidic one (cf. Table 2). If the π-charges are extracted from the total charges, the charge distribution becomes ylidic with charges of +0.47 at oxygen and −0.24 at the carbon atoms. The corresponding π-charges of **2** are +0.66 and −0.33. An enhancement of the π-charge separation relative to **2** is found for SO_2 (+1.04 for S, −0.52 for C). Other structures related to **2** are the corresponding N- and P-ylides. Bis(methylene)phosphorane has also been described as strongly ylidic.[41] Table 4 contains AIM results of a typical nonclassical heterocycle derived from **2** (naphtho[1,8-*cd*]thiopyran (**8**)). The covalent bond order of 1.51 of **8** is considerably lower than that of **2** (1.95) but markedly higher than that of thiophene (1.28). Also the charge separation in **8** is close to that in **2**.

In order to examine the change of the electronic structure over the whole series of heterocyclic compounds considered in this study NPA charges were calculated at the DFT/Becke3LYP/6-31G* level of theory. The atomic charges at sulfur (q_S) result in the following order:

4b < **10** < **3b** < **11** < **6** < **7** < **9** < **5** < **8** < **2**
(q_S): +0.25 +0.41 +0.45 +0.52 +0.57 +0.58 +0.58 +0.66 +0.70 +0.72

According to this analysis sulfur is a better electron donor in nonclassical heterocyclic compounds. 3,4-Dimethylene thiophene (**5**) and naphtho[1,8-*cd*]thiopyran (**9**) appear strongly related to the parent structure **2**. These compounds differ greatly in their electronic structure from classical compounds such as thiepin (**4b**) and thiophene (**3b**) which exhibit charges at sulfur about half as large as **2**. As already shown and rationalized for the parent structure **2** the π-charges of the sulfur-containing heterocycles are close to the above mentioned total charges. The π-charges range from +0.27 for **10** (the first planar structure on the left) and +0.36 for **3b** up to +0.60 for **8** and +0.69 for **2**. Atomic charges calculated by the Mulliken population analysis (MPA) are not presented in this paper. Since the calculations were restricted to the 6-31G* basis set, MPA provides essentially the same result as NPA with nearly the same sequence of charges. As well known,[42] the Mulliken charges differ from the Weinhold−Reed NPA charges in their magnitude. The Mulliken charges in the series studied are about one-third lower than NPA charges. The charge is not physically observable and cannot be defined uniquely. In contrast to the charges obtained by population analyses, AIM charges, such as presented in Tables 1 and 2, are the result of an "observable-based" interpretation of the electronic wavefunctions.[2c]

According to charge distribution and molecular geometry acenaphtheno[5,6-*cd*]thiopyran (**9**) is an exceptional case. The structure of **9** is closely related to the nonclassical structure **8** expressed by formula **9a**, although the structural change in passing from **8** and to **9** should provide the quinoid structure **9b** which is closer to classical structures. The earlier mentioned idea that **9** may contain the aromatic thiopyrylium and cyclopentadienide substructure is, however, not consistent with the calculated charges of the corresponding fragments. As shown in Figure 3, the positive charge at sulfur is mostly compensated for by the other atomic charges in the six-membered ring giving a total charge +0.12, whereas the charge of the five-membered ring amounts to −0.19 only.

Formula Representation. On first sight, the results about the molecular and electronic structure outlined above may appear inconsistent. According to the calculated bond lengths and the AOM-based covalent bond orders the CS bond nonclassical structures exhibit double bond character providing arguments in favor of the sulfurane (2λ-thioallyl) structure given by formula **2**. In principle this is the ylene structure. According to Pople and co-workers, the short bond lengths, as found for various of 1,3-dipoles, favor a hypervalent bond description of these compounds.[43] In view of the MO calculations, however, the convenient hypervalent $\lambda^4\sigma^2$ formulation cannot be substantiated. The sulfur d-orbitals participate to a minor extent. Although larger occupancies of d-orbitals are found in nonclassical structures than in classical ones, the d-functions act rather as polarization functions.

On the other hand, there is a considerable charge separation in **2** and in related compounds. This corresponds to the formulas **2c** rather than to formula **2**. According to the topological analysis the electron migration is lower than expected for the pure ylidic structure. Some ylidic bond character also is encountered in the series of nonclassical heterocycles considered. It is tempting to rationalize the contracted bonds in such ylidic structures by electrostatic interaction. The oppositely charged atoms in ylidic structures should undergo an attractive Coulombic interaction that is largest in the parent structure. The relatively long and polarizable C−S bond may respond sensitively to this attractive force, resulting in relatively short bonds. This bond contraction seems not to be confined to ylidic compounds.

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[41] (a) Regitz, M.; Scherer, O. J. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; George Thieme Verlag: Stuttgart, 1990; p 22. (b) Schoeller, W. W.; Niemann, J. *J. Am. Chem. Soc.* **1986**, *108*, 22, and further references therein.

[42] Wiberg, K. B.; Rablen, P. R. *J. Comput. Chem.* **1993**, *14*, 1504.

[43] Kahn, S. D.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1871.

Table 5. Singlet/Triplet Splitting Energies $\Delta E(S_0/T_1)$ in kcal/mol and Ionization Energies $\Delta E(S_0/D_1)$ in eV. Stabilization Energies ΔE in kcal/mol According to Eqs 1 and 2 (DFT/Becke3LYP/6-31G*)

compound	$\Delta E(S_0/T_1)$	$\Delta E(S_0/D_1)$	ΔE (eq 1)	ΔE (eq 2)	compound	$\Delta E(S_0/T_1)$	$\Delta E(S_0/D_1)$	ΔE (eq 1)	ΔE (eq 2)
2[a]	20.6[b]	7.4[c]	63	–	**7**	10.6	6.0	–	–
3	72.7	8.5	0	67	**8**	5.8	5.8	29	37
5	−3.1[d]	6.2	43	21	**11**[e]	43.5	7.2	16	48
6	22.4	6.7	29	32					

[a] The molecular structure of **2** was restrained to planarity upon excitation and ionization; $\Delta E(S_0/T_1)$ and $\Delta E(S_0/D_1)$ of the isomeric ethenethiol **1** are 75.2 kcal/mol and 8.6 eV, respectively. [b] MP2(full)/6-31G* gives 24.5 kcal/mol, and QCISD/6-31G* 17.3 kcal/mol. [c] MP2 (full)/6-31G* gives 7.1 eV; and QCISD 6.9 eV. [d] MP2 (full)/6-31G* gives 7.4 eV. [e] $\Delta E(S_0/T_1)$of benzo[*c*]thiophene (**11**) is 26.4 kcal/mol lower and the ionization energy 0.5 eV lower than the corresponding energies calculated for classical benzo[*b*]thiophene isomer (the experimental ionization energies differ by 0.45 eV in that case).

Table 6. Total Energies of the Calculated Heterocycles in Hartrees at Different Levels of Theory: Singlet States (S) and Some Lowest Energy Doublet (D) States of Radical Cations and Triplet States (T) Derived Therefrom. Symmetries are given in Parentheses

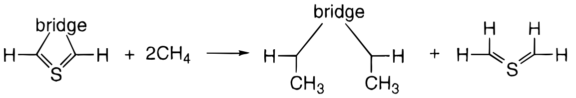
compound (symm)[a]	multipl	theoretical model[b]	basis set	total energy	compound (symm)[a]	multipl	theoretical model[b]	basis set	total energy
				ab inito					
3b (C_{2v})	S	MP2(full)	6-31G*	−551.95597	**7** (C_{2v})	S	MP2(fz)	3-21G(*)	−1172.44362
4a (C_2)	S	MP2(full)	6-31G*	−629.00837	**7** (C_{2v})	D	MP2(fz) SP	3-21G(*)	−1172.22633
4a (C_{2v}) TS	S	MP2(full)	6-31G*	−628.99852	**7** (C_{2v})	T	MP2(fz) SP	3-21G(*)	−1172.39451
4b (C_s)	S	MP2(full)	6-31G*	−629.07172	**8** (C_{2v})	S	MP2(fz)	3-21G(*)	−853.30749
5 (C_2)	S	MP2(full)	6-31G*	−629.02744	**8** (C_{2v})	D	MP2(fz)	3-21G(*)	−853.12150
5 (C_{2v}) TS	S	MP2(full)	6-31G*	−629.02736	**8** (C_{2v})	T	MP2(fz)	3-21G(*)	−853.28668
5 (C_{2v})	D	MP2(full)	6-31G*	−628.80204	**9** (C_{2v})	S	RHF	6-31G*	−932.27525
5 (C_{2v})	T	MP2(full)	6-31G*	−629.01550	**9** (C_{2v})	D	MP2(fz)	3-21G(*)	−928.79697
6 (C_{2v})	S	MP2(full)	6-31G*	−1025.57014	**11** (C_{2v})	S	MP2(full)	6-31G*	−705.12228
				DFT					
3a (C_{2v})	S	DFT/B3LYP	6-31G*	−553.00260	**6** (C_{2v})	T	DFT/B3LYP	6-31G*	−1027.32829
4a (C_2)	S	DFT/B3LYP	6-31G*	−630.30831	**7** (C_{2v})	S	DFT/B3LYP	6-31G*	−1181.00265
4b (C_s)	S	DFT/B3LYP	6-31G*	−630.37587	**7** (C_{2v})	D	DFT/B3LYP	6-31G*	−1180.78111
4 (C_{2v}) TS	S	DFT/B3LYP	6-31G*	−630.30419	**7** (C_{2v})	T	DFT/B3LYP	6-31G*	−1180.98568
4 (C_{2v})/1[c]	D	DFT/B3LYP	6-31G*	−630.08668	**8** (C_{2v})	S	DFT/B3LYP	6-31G*	−860.24542
4 (C_{2v})/2[d]	D	DFT/B3LYP	6-31G*	−630.11445	**8** (C_{2v})	D	DFT/B3LYP	6-31G*	−860.03348
4 (C_{2v})	T	DFT/B3LYP	6-31G*	−630.33771	**8** (C_{2v})	T	DFT/B3LYP	6-31G*	−860.23614
5 (C_{2v})	S	DFT/B3LYP	6-31G*	−630.33006	**9** (C_{2v})	S	DFT/B3LYP	6-31G*	−936.46978
5 (C_{2v})	S	DFT/B3LYP	6-311G**	−630.41699	**10** (C_{2v})	S	DFT/B3LYP	6-31G*	−1334.64239
5 (C_{2v})	D	DFT/B3LYP	6-31G*	−630.10062	**11** (C_{2v})	S	DFT/B3LYP	6-31G*	−706.63570
5 (C_{2v})	T	DFT/B3LYP	6-31G*	−630.33503	**11** (C_{2v})	D	DFT/B3LYP	6-31G*	−706.37122
6 (C_{2v})	S	DFT/B3LYP	6-31G*	−1027.36393	**11** (C_{2v})	T	DFT/B3LYP	6-31G*	−706.56638
6 (C_{2v})	D	DFT/B3LYP	6-31G*	−1027.11890					

[a] TS = transition structure. [b] In the case of open shell structures UMP2 and UKS calculations. The *ab initio* energies are those after projection. The spin contamination is low in DFT calculations. SP = single point calculation. [c] CS bond lengths of 1.647 Å. [d] CS bond lengths of 1.737 Å.

Unexpectedly short bonds are also found in zwitterionic heterocycles known as mesoionic compounds.[44]

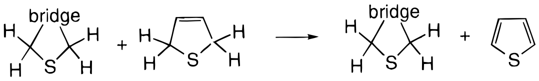
It should be mentioned that spin-coupled GVB calculations reveal an electronic structure of 1,3-dipoles that justify hypervalent formulas for 1,3-dipoles with first row atoms, such as ozone and diazomethane which are mostly considered as an ylidic structures.[3] Formulas with hypervalencies, however, cannot reflect the actual charge distribution. GVB calculations of **2** or related compounds have not been hitherto performed.

Stabilization, Excitation, and Ionization Energies. In order to estimate the relative stabilities, "isodesmic reactions" have to be defined. Isodesmic reactions are transformations in which the number of bonds of each formal type is conserved, and only the relationship among the bonds is altered.[28] Along these lines correlation energy contributions inherent in individual bonds are largely canceled. The following reaction describes the so-called methylation energy. The parent structure **2** is extracted in the first series, and the bond of the residue is saturated by methyl groups. Unfortunately, several conformations of the product may be conceived differing in the spacial arrangement of the methyl groups. However, the differences in energy between conformers is small and does not overshadow the main conclusions.



(eq 2)

To attain a second estimate about the relative stability, a completely different series was calculated. This reaction consists of an exchange reaction converting the delocalized ylidic heterocycle with 2,5-dihydrothiophene into the dihydro derivative of the heterocycle and thiophene, or vice versa. The relative energies may be slightly effected by changes of the ring strain.



(eq 3)

In the calculations of both isodesmic series the Becke 3LYP/6-31G* model was used. The results are collected in Table 5.

The nonclassical compounds are again clearly discriminated from the classical ones. According to the reaction 1 the stability increases in series 1 in the order **5** < **6** ≈

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(44) Mann, M.; Fabian, J. *J. Phys. Org. Chem.* **1995**, *8*, 536.

8 < **11** < **3**, and according to reaction 2 in the order **5** < **6** < **8** < **11** < **3**.

Consistently, 3,4-dimethylenethiophene (**5**) represents the least stable compound and thiophene (**3**) the most stable one.

The diradical nature of the systems studied has been estimated from calculations of the S_0/T_1 splitting energies. It is calculated by the energy difference method from the lowest energy singlet and triplet states (adiabatic S_0/T_1 splitting. energy). Correspondingly the first adiabatic ionization energies are obtained from the optimized ground and the relaxed mono ionized (cation) states. The calculated data are contained in Table 5.

The S_0/T_1 energy gap for the nonclassical structures is in fact low, and the compounds may be considered as diradicaloid. Within the DFT method, 3,4-dimethylenethiophene (**5**) even appears as a triplet ($\Delta E_{\mathrm{ST}} = -3$ kcal/mol). Since this molecule is actually a singlet molecule, as correctly predicted by *ab initio* correlation methods (cf. footnote of Table 5), this result indicates a weakness of DFT method. Although the energy gap is by far better predicted by DFT than by the RHF level of *ab initio* theory ($\Delta E_{\mathrm{ST}} = -43$ kcal/mol in the latter case), absolute values obtained by DFT should be considered with suspicion. The aim of this study is again to reveal trends rather than absolute values. The S_0/T_1 energy gap decreases in the following sequence: **3b** > **11** > **6** > **7** > **8** > **5**. After 2,3-dimethylenethiophene (**5**), naphtho[1,8-*cd*]thiopyran (**8**) is the most diradicaloid compound.

The ionization energies of nonclassical compounds are considerably lower than those of isomeric classical compounds. The prediction for thiophene (**3b**) of 8.50 eV compared with the experimental value of 8.87 eV measured by PES indicates the error of the theoretical model. Changes in ionization energies are more reliably estimated. The semiclassical benzo[*c*]thiophene is more easily ionized by 0.45 eV[12c] while the calculated difference amounts to 0.5 eV. The ionization energy of thieno[3,4-*c*]thiophene (**6**) is calculated to 6.67 eV. The experimental value of tetraphenyl-**6** is actually low (6.19 eV[14]). The total energies of the calculated singlets, doublets, and triplets are compiled in the Tables 1, 4, and 6.

Conclusions

The less expensive DFT calculations provide a description of the molecular and electronic structures closely similar to those of MP2 calculations. The interpretation of the molecular and electronic structure, however, proved to be complicated. As detailed with the parent structure **2** more than one structural formula has to be invoked to reflect the actual electronic structure. The calculated electronic distribution confirmed the ylidic nature of **2**. This compound is derived from propenide by replacing the central methine group by sulfur. The allylic 3- center 4-electron type bond remains. Both the analysis of the electronic structure by the topological theory Atoms-in-Molecules (AIM) and by the Natural Population Analysis (NPA) revealed a low electron shift in the π-bond system. The calculated total charges of **2** and those of more complex heterocyclic structures closely reflect the π-charges. The calculated π-charges of **2** imply that the charge separation is less than that described by a picture in which the two resonance structures of **2c** are superseded.

A salient structural feature of **2** is the short CS bond. This bond is shorter by at least 0.07 Å than sulfidic CS bonds and only about 0.03 Å shorter than the CS double bond. The unexpected bond length contraction is fully reflected in the large AOM-derived covalent bond orders. The bond order of **2** is approximately 1.95 (DFT) and 1.85 (MP2) and thus increased by 0.7 relative to that of the CS bond of classical compounds. It is also increased by 0.2 relative to the CC bond of the iso-π-electronic allyl structure. Thus the double bond character is larger than expected for the ylidic structure. The short CS bond and the high bond order may favor the 2λ-thioallyl formula **2**. The negligible occupancy of the d-orbitals, however, does not justify any hypervalent structures including d-valence orbitals. In terms of the spin-coupled GVB-theory the hypervalency is not bound to involvement of d-valence orbitals. However, formulas like **2** disregard the characteristic ylidic charge distribution. Therefore the question has been asked whether the Coulombic charge attraction may rationalize the CS bond contraction of ylidic structures.

Formula **2a** directs attention to another feature of the structure of parent compound **2**, the singlet diradical character of the compound. In order to assess the diradicaloid character singlet−triplet (S_0/T_1) splitting energies have been calculated. The singlet−triplet energy gap of **2** amounts to at least 20 kcal/mol which means the diradicaloid character of **2** is not large. Some heterocyclic derivatives of **2** have singlet−triplet energy gaps that are lower than that of the parent compound. 3,4-Dimethylenethiophene (**5**) has the lowest gap in the series considered, amounting to a few kcal/mol when calculated at beyond-Hartree−Fock (MP2) level.

The nonclassical heterocycles show typical features of the parent compound but to a lesser extent. There is a smooth crossover in this series from nonclassical structures to classical ones. Thus the CS bond length decreases from 1.68 to 1.72 Å in passing from naphtho[1,8-*c,d*;5,4-*c′d′*]dithiopyran (**8**) of nonclassical structure to thiophene (**3b**) as a classical structure, while the NPA charges decrease from +0.70 to +0.45. On the other hand, the stabilization energies increase. Quinoid compounds such as benzo[*c*]thiophene (**11**) take an intermediate position and behave semiclassically. Unexpectedly, acenaphtheno[5,6-*cd*]thiopyran (**9**) proved to be more closely related to the nonclassical heterocycles than to the classical ones.

Although the $\lambda^4\sigma^2$-formulas representation is convenient for avoiding the complex description by various resonance contributors and displaying the correct molecular symmetry, the need for the higher valency description does not necessarily follow from the MO-theory. The partial ylidic nature of the electronic structure cannot be disregarded.

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