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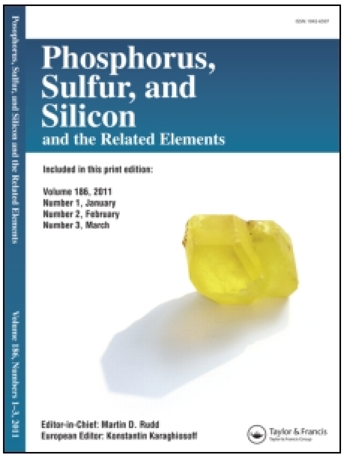

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THE STRUCTURE OF 3,4-DIAZA-1,6,6aλ^4-TRITHIAPENTALENES-A COMBINED EXPERIMENTAL AND THEORETICAL STUDY

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(Received 20 December, 1997)

The X-ray structure of 2,5-bis(piperidyl)-3,4-diaza-1,6,6aλ^4-trithiapentalene (**1**, R = piperidyl) is reported and compared with the equilibrium geometries calculated for the diamino-substituted compound by density functional theory (B3LYP exchange-correlation functional). The molecular geometry and electronic structure of the 3,4-diaza-1,6,6aλ^4-trithiapentalene parent compound (**1**, R = H) has been examined in more detail in conjunction with the nitrogen-free 1,6,6aλ^4-trithiapentalene (**2**, R = H). Whereas Hartree-Fock-calculations predict **1** and **2** as valence isomers in equilibrium, DFT(B3LYP) as well as *ab initio* MP2 calculations result in a single minimum structures of C_{2v}-symmetry. Substitution of methine groups by aza nitrogen in the 3- and 4-positions and introduction of amino groups in the 2- and 5-positions of 1,6,6aλ^4-trithiapentalene (**2**, R = H) stabilize the heterocyclic compound by formation of a polymethine-type substructure. According to DFT calculations the C_{2v}-symmetry is retained in passing from **1** (R = H) to the amino-substituted compound (**1**, R = NH_2). The nucleus-independent chemical shifts (NICS) of the five-membered rings of 3,4-diaza-1,6,6aλ^4-trithiapentalene and of its nitrogen-free congener exhibit aromatic bond delocalization.

Keywords: 1,6,6aλ^4- trithiapentalene; 3,4-diaza-1,6,6aλ^4-trithiapentalene; X-ray structure; NMR chemical shift; aromaticity; *ab initio* quantum chemistry; density functional theory; topological analysis; natural population analysis; natural resonance theory; homodesmic reaction

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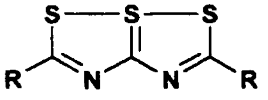
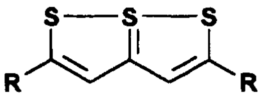
INTRODUCTION

3,4-diaza-1,6,6aλ^4-trithiapentalenes (**1**) are heteroanalogues of the extensively studied 1,6,6aλ^4-trithiapentalenes (7λ^4-[1,2]dithiolo[1,5-b][1,2]dithioles) (**2**).[1] Whereas the parent compound of the series **1** (R = H) is not yet known, various derivatives of **1** have been reported.[2–5] The compounds of the series **1** are distinguished from **2** by two aza nitrogen atoms in place of methine groups. The aza nitrogen atoms offer potential binding sites for electrophilic species. The complex formation behavior of such compounds was investigated by liquid-liquid extraction studies of the metal salt – picric acid – water / ligand – chloroform system. Different extractabilities for transition metal ions in dependence on the nature of the substituent R were observed.[5b] Incorporation of **1** into macrocyclic structures enables the compounds to trap selectively $\mathrm{Ag^{I}}$ and $\mathrm{Hg^{II}}$. [5c]

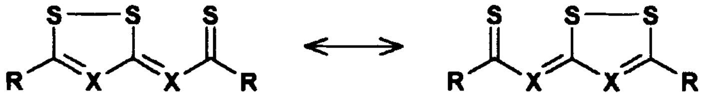


1



2

To the best of our knowledge, 3,4-diaza-1,6,6aλ^4-trithiapentalenes (**1**) have not yet been investigated theoretically by first-principles quantum theoretical methods. The nitrogen-free parent structure 1,6,6aλ^4-trithiapentalene (**2**, R = H) and some derivatives were, however, studied by different semiempirical and nonempirical theoretical models. These calculations were performed to reveal the unique structural features of **2** and to find structure-property relationships.[1] An early interpretation of the structure of **2** involves the no-bond / single-bond resonance of the structures **3a** and **3b**.[6] Later, **3a** and **3b** were no longer considered as resonance structures but as valence isomers. The equilibrium between the isomers was assumed to simulate a time averaged molecular symmetry. In the latter case the symmetric molecule is the saddle point between two minimum structures on the energy hypersurface rather than a single energy minimum structure. This molecular structure, however, has been refuted by experimental results in favor of a single structure **2** of higher symmetry.[1]



3a X = CH, N **3b**

The most convenient and widely used formulas of the compounds under study are **1** and **2** with the three-atom sulfur bridge. These formulas reflect the correct symmetry. The molecular geometry of **2** was confirmed in structural studies including those of the unsubstituted compound **2** (R = H).[7,8] The formulas **1** and **2** are however be misleading in suggesting hypervalency of the central sulfur by octet expansion. As is well known, the model of d-orbital participation of sulfur is not substantiated for compounds containing higher-coordinated sulfur atoms.[9] Thus the λ^4-nomenclature generally used with formulas **1** and **2** and, concomitantly, with the corresponding chemical names does not reflect the very nature of the bonding and the real valency of the central sulfur atom.

Ab initio calculations of 1,6,6aλ^4-trithiapentalene (**2**) with stipulated geometries in the early seventies provided the first information about its electronic structure.[10] It was not until the early ninetieth that beyond Hartree-Fock calculations of **2** were performed by Cimiraglia and Hofmann using second-order Møller-Plesset perturbation theory (MP2).[11] However, the size of the molecule prohibited geometry optimization at that time. At the restricted Hartree-Fock (RHF) level of theory, geometry optimization resulted in a wrong non-symmetrical ground state of **2** corresponding to the C_s-symmetric α-(1,2-dithiole-3-ylidene) thiocarbonyl structures **3a** / **3b** (X = CH). Single-point MP2/6–31G* calculations, however, indicated the energetically favored C_{2v}-symmetric molecule **2**. The molecular symmetry is obviously determined by electron correlation.[11] Full MP2 geometry optimizations performed with the 6–31G* basis set, as well as geometry optimization with the more extended basis set 6–311G** (including frequency calculations by Spanget-Larsen et al.),[12] confirmed Cimiraglia's and Hofmann's conclusion. If consideration of the electron correlation is necessary to obtain the correct molecular symmetry, the density functional theory (DFT) may be an alternative in calculating **1** and **2**. DFT takes electron correlation inherently into account and is also less expensive than MP2.

The intent of this paper is to calculate structures and properties of 3,4-diaza-1,6,6aλ^4-trithiapentalenes (**1**) both by density functional theory and conventional *ab initio* quantum theory. The results will be compared by those of **2** (R = H). In conjunction with the X-ray study of 2,5-bis(piperidyl)-3,4-diaza-1,6,6aλ^4-trithiapentalene (**1**, R=piperidyl), particular attention will be paid to the diamino derivatives of **1** (R = NH_2, NMe_2, anilino).

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COMPUTATIONAL

DFT and *ab initio* quantum chemical calculations were carried out using the GAUSSIAN-94 series of programs.[13] The functional used throughout this study consists of a non-local hybrid RHF/DFT exchange functional as defined by Becke's three-parameter-equation in conjunction with the non-local Lee-Yang-Parr correlation functional (B3LYP for short).[14] This composite functional is one of the HF/GGA approaches.[15] In numerous calculations it has provided results competitive with those of high-level *ab initio* quantum chemistry.[16] All molecular geometries were optimized using the B3LYP functional using the $6\text{–}31G^*$ (= 6–31G(d)) standard basis set. The ground state optimum structures were confirmed by the second derivatives. All characteristic values of the Hessian matrix are positive. Second-order Møller-Plesset (frozen core) *ab initio* calculations[17] were performed using the same basis set mentioned above. In addition, the most extended Gaussian basis set 6–311+G(3df,3dp) that is triple-zeta in the valence and contains higher angular moment functions at all atoms as well as a set of diffuse functions (+) has been employed.

The calculation of chemical shifts is based on Ditchfields "gauge including atomic orbital" procedure[18], abbreviated GIAO-SCF. The calculation of the ^{13}C and ^{1}H chemical shifts has made good progress in the last few years.[19] In addition, magnetic properties have provided useful information about aromatic bond delocalization for years.[20] A useful criterion has been more recently introduced by Schleyer et al.[21] As a probe of the magnetic "ring current" effect the negative magnetic shielding is calculated at the center of the ring (nucleus-independent chemical shifts, NICS).

The interpretation of topological features of the charge densities ρ(r) and their derivatives make use of the atoms-in-molecules theory of Bader et al.[22] For this purpose the bond critical points are determined first. These are points of minimum electron density along the bond, but of maximum density in the direction normal to the bond. The set of paths define a zero flux surface separating a pair of atoms and divide a molecule into atomic regions. Numerical integration of the charge density within the atomic region provides the electronic population of the atoms. Consideration of the nuclear charge finally provides the atomic charge of the atom. Based on the topological electron density method Cioslowski and Mixon defined localized orbitals and AOM (atomic overlap matrix) derived covalent bond orders.[23] The localized orbitals are distinguished by the ionicity.

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The natural population analysis (NPA) of Weinhold et al.[24] opens an alternative access to atomic charges. The NPA calculation is less expensive than the AIM calculation. The NPA analysis is based on occupancies of natural atomic and natural bond orbitals (NBO). This method also enables π-electron population to be extracted. Because of their different definition AIM and NPA atomic charges more or less differ in magnitude.[25] Although charges are not observable they significantly contribute to the chemist's conceptual understanding. Based on the natural bond orbitals the electron density is analysed with respect to Lewis structures by natural resonance theory (NRT).

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RESULTS AND DISCUSSION

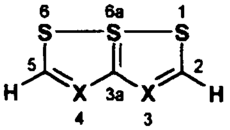
The parent structure

Calculated within the RHF approach, the C_{2v}-symmetric **1** (R = H) is a transition structure with one imaginary frequency of 365 cm^{-1} (first-order saddle point). This structure is about 8.2 kcal/mol higher in energy than the C_s-symmetric minimum energy structure. This result is reminiscent to the barrier of nitrogen-free **2** (R = H) in Ref. 11 with a barrier height of 10.7 kcal/mol calculated at the same level of theory.[11] Thus RHF calculations of **1** show the same deficiency reported for **2**. Failure of the RHF method in the case of **2** is independent of the basis set.[12,26]

In contrast to the results of RHF calculations, DFT(B3LYP) as well as MP2 calculations of 3,4-diaza-1,6,6aλ^4-trithiapentalene (**1**, R = H) predict C_{2v}-symmetry. The calculated geometric data of **1** and **2** are collected in Table I along with experimental data of **2**. The experimental data are well reproduced. The central CS bonds are longer than the outer CS bonds whereas the opposite is suggested by the chemical formulas. In all cases the SS bonds are exceedingly long (more than 2.35 Å) compared to the SS bonds of monocyclic conjugated disulfides (about 2.1 Å). The SSS subunit of **1** and **2** is approximately in a straight line with a bond angle of about 175°. The structure of **1** (R = H) appears closely related to **2** (R = H) if the comparison is limited to sulfur bridge. Compared with **2** the SS bonds in **1**(R = H) are only sligthly contracted. Replacement of CC by CN leads to short CN bond lengths. The calculated CN bond lengths of **1** are 1.313 and

1.341 Å, respectively (B3LYP/6–31G*). The CN average bond lengths of pyridines amounts to 1.337 Å.[27]

TABLE I Selected theoretical and experimental bond lengths in Å and bond angles in deg.



compound		*DFT*		*ab initio*	*Exp.*	
		B3LYP 6–31G(d)	*B3LYP 6–311+G(3df, 3pd)*	*MP2(frozen) 6–31G(d)*	*X-ray[a])*	*ED[b])*
X = N	$S_1 - S_{6a}$	2.385	2.355	2.336		
	$C_{3a} - S_{6a}$	1.809	1.789	1.779		
	$C_2 - S_1$	1.699	1.686	1.681		
	$C_2 - X_3$	1.313	1.307	1.320		
	$C_{3a} - X_3$	1.341	1.337	1.347		
	$S_1C_2C_3$	124.4	123.8	123.9		
	$C_2C_3C_{3a}$	118.4	118.4	117.0		
	$C_3C_{3a}S_{6a}$	120.6	120.6	121.2		
	$C_{3a}S_{6a}S_1$	87.1	87.3	87.6		
	$S_{6a}S_1C_2$	89.4	90.0	90.3		
	$S_1S_{6a}S_6$	174.2	174.6	175.2		
X = CH	$S_1 - S_{6a}$	2.423	2.386	2.368	2.363	2.328
	$C_{3a} - S_{6a}$	1.758	1.743	1.739	1.748	1.708
	$C_2 - S_1$	1.699	1.686	1.686	1.684	1.698
	$C_2 - X_3$	1.373	1.366	1.374	1.354	1.364
	$C_{3a} - X_3$	1.415	1.414	1.413	1.409	1.422
	$S_1C_2C_3$	120.5	119.9	119.6	120.1	118.7
	$C_2C_3C_{3a}$	120.6	120.4	119.9	120.3	119.4
	$C_3C_{3a}S_{6a}$	118.9	118.9	119.0	118.5	119.2
	$C_{3a}S_{6a}S_1$	88.9	89.0	89.3	89.1	90.1
	$S_{6a}S_1C_2$	91.1	91.8	92.2	92.0	92.6
	$S_1S_{6a}S_6$	177.9	178.0	170.6		

[a]) Ref. 7 [b]) Ref. 8.

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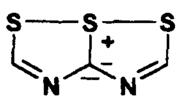
A closer examination of the data in Table I reveals the strength and weakness of the DFT geometry. While the overall structural features are satisfactorily predicted at the DFT(B3LYP) level the CS and SS bonds are calculated systematically longer than the corresponding MP2 bonds. In consideration of the experimental geometric parameter of **2**(R = H), MP2 results are closer to the experimental structures. The weakness of DFT in overestimating the bond lengths of second and higher row elements is known from calculations of various small molecules[28] and heterocyclic compounds. The DFT CS and SS bonds of monoheterocyclic sulfur compounds such as 1,2-dithiete, 1,2-dithiin and 1,2-dithiol-3-thione are longer by 0.02 and 0.03 Å, respectively, than the corresponding MP2 bond lengths. The error seems not to be confined to the B3LYP functional. Spanget-Larsen et al. mentioned the same type of deviation in DFT calculations using Becke's gradient-corrected exchange functional combined with Perdew's and Wang's correlation functional (BPW91).[12] Bonds will be calculated shorter if the standard basis set 6–31G(d) is replaced by the more extended basis set 6–31+G(3df,3pd). The calculated bond lengths are now actually more close to MP2 bond lengths but the calculated bond lengths are still too large. The absolute mean deviation between the theoretical and experimental CS and SS bond lengths (relative to X-ray diffraction data) decreases in passing from DFT with the standard basis set (0.03 Å) through DFT with the extended basis set (0.01 Å) to MP2 (0.005 Å). The good performance of MP2 in connection with the standard basis set is considered as a fortunate choice in treating the electron correlation and the basis set. Any unbalanced change of the two counteracting effects will deteriorate the close agreement between calculated and experimental geometric parameters.[29]

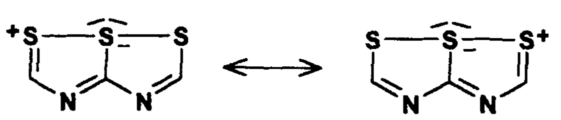
In contrast to the results of the analysis of sulfurane SH_4, the parent structure of the tetravalent sulfur of **1** and **2**, by natural resonance theory (NRT) hypervalent resonance structures (corresponding to the formulas **1** and **2**) are not dominant in the electronic structure of these compounds. Rather, there are essential contributions by **3a** and **3b** in the order of about 30 %. Additional Lewis structures with contributions of the same order of magnitude are structures that differ from **3a** and **3b** by pushing an electron pair to the thiocarbonyl sulfur or to the aza nitrogen. Consequently the calculated covalent valency of the central sulfur is about 2.2 rather than 4. Therefore, the sulfur is not tetravalent.

While the above given interpretation of the sulfur bonds was given in terms of resonance structures, Gleiter and Hoffmann described the SSS bond of **2** alternatively by a linear electron-rich three-center bond that could be stabilized as part of a cyclic 10π-electronic system.[30] This model was supported in a RHF based study of the deformation density.[31] The orbital population analysis of relaxed MP2 density and of the Kohn-Sham-orbital DFT densities carried out in this study is fully in accordance with the 10π-electronic system. Since each of the outer sulfur atoms contribute two electrons and the carbon (or nitrogen) atoms one electron, the remaining central sulfur will participate with one electron only. Consequently, the effective core charges of the main atoms are +1 for all atoms except those of the outer sulfur atoms (+2).



4a

sulfonium ylid resonance structure



4b

pentamethinium thiolat resonance structures

Whereas the sulfonium ylide resonance structure **4a** may appear as the most attractive model of the 10π-electronic system (cf. Ref. la), the calculation actually indicates a surplus of electrons at the central sulfur atom and a shortage of electrons in the remaining backbone, in particular at the outer sulfur atoms (Fig. 1). Structure **4b** may appear strange because of the electron decet at the central sulfur. A general argument in favor of a structure like that was given by Geratt et al. in terms of the general valence bond theory. According to him valencies must not governed by the octet rule but rather by the "free democracy principle" accepting a higher flexibility of the valency.[32] A more transparent picture of the bonding may be given by Cioslowski's localized orbitals. According to this analysis, two lone pairs are actually placed at the central sulfur but the two SS bonds display a high "ionicity" (43.2 %). That means that charge is shifted in the σ-system from the central sulfur, which is negatively charged in the π-system, to the outer sulfur atoms, positively charged in the π-system. Consequently, the net charges at the three sulfur atoms are calculated to be low. The π-electron distribution of **4b** is reminescent of the pentamethinium thiolate substructure. Polymethine structures are delocalized chain structures that occur in cyanine dyes and other series of dye molecules. They may also appear as substructures in cyclic compounds.[33]

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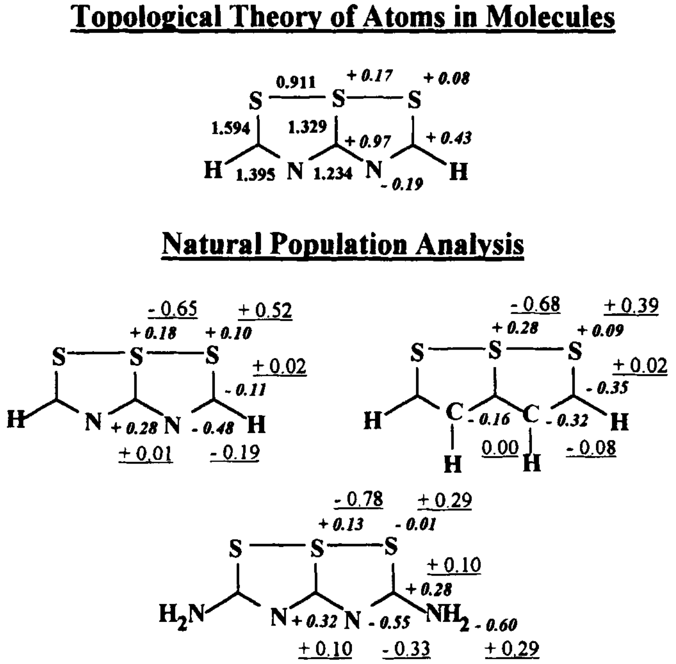

FIGURE 1 AOM derived covalent bond orders on the left (on top only) and charges on the right calculated by two different theoretical models (total atomic charges in italics, π-charges underlined, B3LYP/6–31G*)

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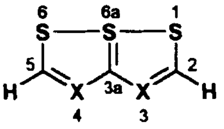
Magnetic properties are characteristic molecular entities. ^{13}C- and ^{1}H-NMR chemical shifts and NICS values were calculated by GIAO-SCF. Calculated and experimental values of **1** and **2** are listed in Table II. The calculated ^{13}C chemical shifts of **2** vary in the same order as experimentally observed. The absolute shift values are more overestimated than expected, in particular for carbon atoms bound to sulfur. In the case of aromatic hydrocarbons the error amounts to about 5 ppm only. The numerical agreement between theory and experiment is better for the ^{1}H NMR chemical shift of **2**. The chemical shift of **1** are predicted at lower fields than for **2**. The deshielding of ring protons suggest a strong ring current. According to NICS values of about – 8 ppm **1** and **2** display aromatic bond delocalization. The heterocycles **1** and **2** (R = H) are iso-π-electronic with naphthalene (NICS – 9.9 ppm [21c]). According to the broad experience of Schleyer et al. NICS values less than about – 2 ppm are observed for aromatic ring systems and more than + 2 ppm for antiaromatic ones.[21c] Cyclic compounds with NICS values in the range of - 2 and + 2 ppm are non-aromatic (cycloolefinic).

TABLE II Calculated and experimental chemical shifts[a)]



	1 (X = N)	*2 (X = CH)*	
	calc.	*calc.*	*exp.*[b)]
C_2/C_5	197.87	174.87	161.69
C_3/C_4	-	130.50	128.64
C_{3a}	202.92	191.19	177.45
$H(C_2/C_5)$	10.56	9.23	9.18
$H(C_3/C_4)$		7.80	7.96
NICS[c)]	-7.70	-8.28	-

[a)] ^{13}C and ^1H chemical shifts calculated at the GIAO-SCF/6–311+G(2d,p)/B3LYP/6–31+G(d,p) level, relative to TMS(δ-values in Ref. 39).

[b)] Ref. 1c) and references given therein,

[c)] NICS values calculated at the GIAO-SCF/6–31+G(d)//B3LYP/6–31+G(d,p) level.

1,2-Diamino-3,4-diaza-1,6,6aλ^4-trithiapentalenes

The crystal structure of compound **1** (R = piperidyl) is shown in figure 2. The central ring system provides a nearly planar geometry as typical found in trithiapentalene structures.[1,3,4] The angles between the planar central ring system and the piperidyl groups are insignificantly different and relatively small with 9.9° for the N(13) – C(14) – C(18) plane and 2.8° for the N(7) – C(8) – C(12) plane. As a result the molecule is non-symmetric and there is no mirrow plane including the S(6a) – C(3a) axis as expected by formula **1**(R = piperidyl). This characteristics has also been observed for 3,4-diaza-1,6,6aλ^4-trithiapentalenes (1, R = anilino and phenyl).[3a,d] In

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the case of dimethylamino substituents (1, R = NMe_2) a symmetrical molecule was reported.[4] The bond lenghts for the different compounds are shown in Table III. For **1** (R = anilino) short intramolecular distances (2.48 and 2.84 Å) are found between hydrogen atoms af the aromatic fragment and the nearest sulfur atoms S(1) and S(6a), respectively.[3d] In the case of **1** (R = piperidyl) a more close inspection of the structure revealed unusual short CH...N and CH...S interatomic distances with 2.314 and 2.333 Å and 2.513 and 2.501 Å, respectively (fig. 2). They are shorter than the sum of the corresponding van der Waals radii (H 1.2- 1.45 , N 1.55 and S 1.80 Å).[34] Retrievel of the structural data of a large number of neutron diffraction studies has reveiled especially the occurence of short CH···N and CH···S contacts in crystals.[35] In addition, the CH groups adjacent to nitrogen have been proven to be particularly efficient in H bonding. Also in the case of **1** (R = piperidyl) the CH groups of **1** involved in H bondings are also linked to nitrogen atoms.

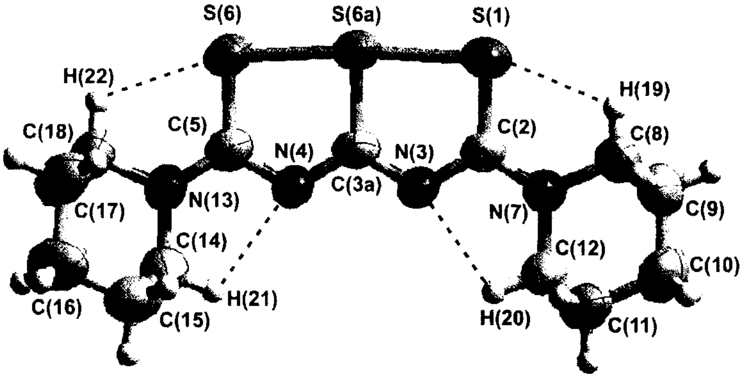
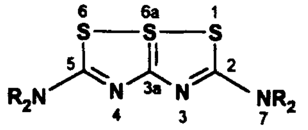


FIGURE 2 X-ray structure and atomic numbering for 2,5-bis(piperidyl)-3,4-diaza-1,6,6aλ^4-trithiapentalene with intramolecular H-bondings of the typ CH···N and CH···S

No appreciable intermolecular interactions are observed between the molecules. The molecular structures of the substituted 3,4-diaza-1,6,6aλ^4-trithiapentalenes (**1**) are closely related to 1,6,6aλ^4-trithiapentalene (**2**) with SS bonds of about 2.35 Å. The exocyclic CN bonds (exp. 1.326/1.336 Å, DFT 1.348 Å, *ab initio* 1.352 Å) are remarkably short compared with the experimental CN bond lengths of aniline (1.400 Å, MW)[36a], 2-aminopyridine (1.403 Å, MW)[36b] and formamide (1.368 Å, ED).[36c] The CN bond lengths are also shortened with respect to the average value of 1.375 Å extracted from the Cambridge Data File with amino groups attached to C_{arom}.[25] Rather CN bond lengths as short as 1.34 Å are found and represent amidinium structures.[27]

TABLE III Calculated and experimental bond lengths of 2,5-diamino-3,4-diaza-1,6,6aλ^4 trithiapentalene in Å



	Experiment			*Theory*		
	piperidyl c)	*anilino* d)	*N(Me)$_2$* e)	*DFT* a) *NH$_2$*	*ab initio* b) *NH$_2$*	*DFT* a) *piperidyl* f)
$S_1 - S_{6a}$	2.328 / 2.346	2.225 / 2.475	2.346	2.405	2.368	2.398
$C_{3a} - S_{6a}$	1.792	1.789	1.856	1.832	1.803	1.822
$C_2 - S_1$	1.713/1.716	1.691/1.731	1.705	1.727	1.704	1.740
$C_2 - N_3$	1.340/1.335	1.344/1.336	1.347	1.328	1.333	1.330
$C_{3a} - N_3$	1.320/1.338	1.325/1.353	1.309	1.329	1.335	1.327
$C_2 - N_7$	1.326/1.336	1.356/1.332	1.332	1.348	1.352	1.354

a) B3LYP/6–31G(d), b) MP2/6–31G*, c) This work, d) Ref. 3, e) Ref. 4, f) DFT optimized on the basis X-ray structure.

For computational simplicity the 2,5-diamino derivative has been calculated first in place of **1** (R = piperidyl). According to DFT(B3LYP) calculations **1** (R = NH_2) is a planar molecule. The structural features of the unsubstituted 3,4-diaza-1,6,6aλ^4-trithiapentalene are essentially retained. Both the short endocyclic and exocyclic CN bonds are calculated in good agreement with the experimental data. Again, the exocyclic bond length of **1**(R = NH_2) with 1.331 Å is in contrast to the considerably longer CN bond lengths of aniline (1.386 Å), 2-aminopyridine (**4**) (1.367 Å) and 2,7-diamino-1,8-aza-naphthalene (**5**) (1.368 Å) calculated at the same level of theory (B3LYP/6–31G*).

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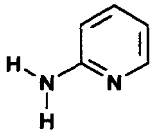
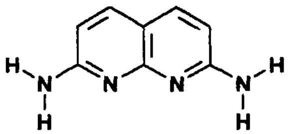
In an attempt to support the formation of hydrogen bondings in the free molecule, **1**(R = piperidyl) was optimized starting from the experimental X-ray structure. No dramatic change on optimization within the B3LYP/6–31G* force field was observed except of the creation of the molecular symmetry. The compound **1** (R = piperidyl) has C_s-symmetry and the amino group is entirely planar. Selected geometrical parameters of this compound are listed in Table III. The calculated atomic distances between the hydrogen atoms and the acceptor atoms of the hydrogen bondings differ only 0.012 Å for CH···S and 0.011 Å for CH···N from the experimental average values.



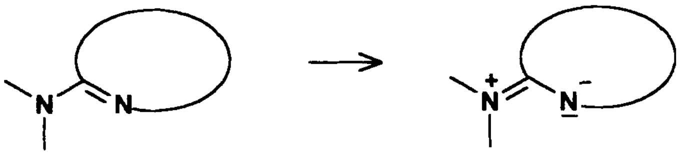
5



6

The question has been raised as to whether the amino groups linked to sp^2 carbon atoms are actually planar. As documented with amides, the answer is dependent upon the theoretical model, because the barrier of pyramidalization may be low. Conclusions from experiment may also be difficult or in error.[37] According to the experiment and to high level *ab initio*[37b,c] and DFT calculations performed in this study, formamide (H_2N-CH=O) is a planar molecule. There is every indication that planarity of 2,5-bis-amino-3,4-diaza-1,6,6aλ^4-trithiapentalene (**1**, R = NH_2) is also correctly predicted at the DFT level of theory. It should be mentioned that pyramidal amino groups are mistakenly calculated both for formamide and **1** (R = NH_2) at the MP2/6–31G* level of theory. Calculations by the Weinhold NBO theory were performed to rationalize the strong interaction within the amidine substructures natural bond orbitals (NBOs) and the second-order perturbative interaction energies between the donor Lewis-type NBO of the nitrogen lone pair and the acceptor non-Lewis-type antibonding NBO of the C=N group ($n_N \rightarrow \pi^*_{C=N}$). This interaction corresponds to a correction of the zero-order natural reference Lewis structure by a Lewis structure containing an electron pair which is transferred from the amino group to the aza nitrogen:

The stabilization energy which is associated with delocalization from the idealized Lewis structure description is examined by the equation E(2) = 2



7 **8**

$< n_N | \hat{F} | \sigma^*_{C=N} >^2 / (\varepsilon_j - \varepsilon_i)$. The interaction term of the corresponding Fock operator is represented by the nominator, the difference of the orbital energies ε_i and ε_j of the nitrogen lone pair and the C=N antibond by the denominator. According to the NBO calculation based on the B3LYP/6–31G* Kohn-Sham orbitals the energy lowering increases on passing from **5** (34.2 kcal/mol) through **6** (48.2 kcal/mol) and **1**, R = NH_2 (59.2 kcal/mol) to **1**, R = piperidyl (68.9 kcal/mol). The stabilizing amino-to-imine interaction is actually most large for amino-substituted trithiapentalenes. The exceptionally strong interaction is obviously reflected in the uncommon molecular geometries of **1**. The hydrogen bondings may also be discussed in terms of the NBO theory as outlined above. According to the second-order perturbative energy lowerings accompanied by the $n \rightarrow \sigma^*$ "charge transfer" interaction the hydrogen bonding to the aza nitrogen ($n_N \rightarrow \sigma^*_{NH}$) is twice as large as the hydrogen bonding to the external sulfur ($n_S \rightarrow \sigma^*_{NH}$).

The stabilization by the amidine groups is supported by the energy of the following transformation that is a homodesmic reaction.[38]

2 + 2 aniline + 2 pyridine → **1** + 4 benzene

The stabilization energy of **1** (R = NH_2) calculated by this equation provides a gain in energies with respect to the substitution of the methine group of benzene by N (formation of pyridine) and of hydrogen by NH_2 (formation of aniline). The calculated stabilization energy was relatively large and amounts to 36.1 kcal/mol. The energies of the analogous homodesmic reactions of naphthalene and benzene in **6** and **5** are 15.8 and 12.6 kcal/mol (for 2 moles in the latter case), respectively. The stabilization of **1** (R = diamino) by substitution is evidently about twice as large.

The structural peculiarities and stabilization of **1** with amino substitution might be attributed to the formation of two amidine groups. However, the amidine fragments are parts of a more delocalized π-bond system. A more appropriate description of the bonds has to consider the delocalized

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NCNCNCN substructure that is terminated by nitrogen and, in addition, by sulfur atoms. This fragment with a partial positive π-charge is completed by another fragment that has a partial negative charge. This fragment is the central sulfur atom as shown for the parent structure in Fig 1. According to the net charges (atomic charges), the sulfur atoms bear only small charges. As to be expected, the atomic charges at the ring nitrogen atoms considerably increase in passing from **1** (R = H) to **1** (R = NH_2) with charges of – 0.44 and – 0.55, respectively, which imparts the aza nitrogen of **1**(R = NH_2) a large basic character for the compound. The charge at **1**(R = piperidyl) exceeds that of the aza nitrogen atoms of **5** (- 0.51) and **6** (- 0.52).

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EXPERIMENTAL

X-ray structure of 2,5-bis(piperidyl)-3,4-diaza-1,6,6λ⁴-trithiapentalene[40]

Crystals of 2,5-bis(piperidyl) –3,4-diaza-1,6,6aλ^4-trithiapentalene **1** (R = piperidyl) were obtained by the reaction of 2,5-bis(phenoxy) –1,6,6aλ^4-trithia-3,4-diazapentalene with piperidine.[5d] Recrystallization from chloroform/toluene gave light yellow crystals suitable for X-ray determination.

Crystal data : ($C_{13}H_{20}N_4S_3$, M = 328.5); monocyclic space group $P2_1/_c$; a = 10.918(2), b = 10.6672(9), c = 14.6477(9) Å, α = 90.0, β = 109.865(9), γ = 90.0° ; z = 4; D_x = 1.360 gcm^{-3} ; cell volume 1604,5 Å^3; crystal size 0.50 × 0.22 × 0.18 mm; scan-modus : ω-2Θ; Θ = 3.43 – 23; h_{min}, h_{max} : –13.14; k_{min}, k_{max} : –14.0; 1_{min}, 1_{max} : –19.0; total reflection numbers R = 2224 [$F_o > 3\sigma(F_o)$] ; μ = 45.8 cm^{-1} ; used reflections for refinement R = 1303; structure solvation by SHELX-90[41] ; Refinement : full-matrix, last-square planes; number of refined parameters : 182; w = $1/\sigma(F)^2$; R (R_W) : 0.032 (0.077); difference electron density 0.178 e Å^{-3} ; used program system: SHELXL-93.[42]

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CONCLUSIONS

Density functional theory calculations (B3LYP/6–31G*) of **1** (R = H, NH_2) and **2** (R = H) were performed in conjunction with calculations by second-order many-body pertubation theory (MP2/6–31G*). Full geometry optimizations resulted in planar structures that are confirmed by frequency calculations. DFT(B3LYP) proved to be a useful alternative to conventional wave-function-based methods. Structures with tetravalent sulfur are not supported. The analysis in terms of resonance by natural resonance theory favours the early proposed no-bond / single-bond resonance that has to be enlarged by pairs of polar Lewis structures taking charge delocalization into account. As shown by experimental and theoretical CN bond lengths and rationalized by NBO interaction and homodesmic stabilization energies the amino-substituted 3,4-diaza-1,6,6aλ^4-trithiapentalenes display unique features. The calculated DFT(B3LYP) geometry of 2,5-bis(piperidyl)-3,4-diaza-1,6,6a^4-trithiapentalene (**1**, R = piperidyl) is in good accordance with the experimental X-ray structure although the isolated molecule is considered in the first case and the molecule in the crystal in the second one. The short CH···X (X = N, S) interactions are interpreted as intramolecular H bondings. These short contacts are excellently reproduced by theoretical methods.

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