

Planar 1,3,4,8-tetrafluoro-2,4-benzodithiadiazine and Its Nonplanar 5,6,7,8-Tetrafluoro Derivative: Gas-Phase Structures Studied by Electron Diffraction and Ab Initio Calculations

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Abstract: The gas-phase molecular structures of 1,3,4,8-tetrafluoro-2,4-benzodithiadiazine and 5,6,7,8-tetrafluoro-1,3,4,8-tetrafluoro-2,4-benzodithiadiazine have been investigated by ab initio calculations and electron diffraction using the SARACEN method of structural analysis. Important structural parameters (r_{hl} structure) for the parent compound were found to be: $\langle r(\text{S}=\text{N}) \rangle > 1.546(3)$,

$r(\text{S}-\text{N})$ 1.697(5), $r(\text{C}-\text{S})$ 1.784(5), and $r(\text{C}-\text{N})$ 1.393(6) Å. For the tetrafluoro derivative, these are (r_{hl} structure): $\langle r(\text{S}=\text{N}) \rangle > 1.552(3)$, $r(\text{S}-\text{N})$ 1.723(8), $r(\text{C}-\text{S})$ 1.812(9), and $r(\text{C}-\text{N})$ 1.396(7) Å. Furthermore, the GED ex-

periment (Gas Electron Diffraction) quite convincingly demonstrates the nonplanarity of the former and the planarity of the latter in agreement with DFT calculations; but the results contradict calculations at the MP2 level. The effect of the fluorine atoms on the conformations of the molecules is discussed.

Keywords: ab initio calculations • electron diffraction • heterocycles

Introduction

Mixed heterocyclic–carbocyclic compounds that combine true aromaticity in the all-carbon part ($4n + 2\pi$ -electrons) with a nonaromatic heteroatom part, which give an antiaromatic structure ($4n\pi$ -electrons), are interesting because they display properties, which are markedly different from those of the corresponding benzenoid systems. One of the representative compounds of this fairly new class is 1,3,4,8-tetrafluoro-2,4-benzodithiadiazine (**1**),^[1] combining a benzene ring and a S_2N_2 unit in a 12π -electron system. The present study deals with the molecular geometries of this compound and one of its derivatives, 5,6,7,8-tetrafluoro-1,3,4,8-tetrafluoro-2,4-benzodithiadiazine (**2**),^[2] determined by gas electron diffraction. The crystal structures of both have been described, and these

indicate that **1** is planar in the solid phase,^[3] whereas the structure of **2** deviates from planarity, and the molecule is bent along the N11–S14 line.^[2] However, ab initio calculations at the B3LYP/6-31G* level suggest that for the free molecules the geometrical situations are *reversed*: **1** has a nonplanar geometry, in which the heterocyclic ring is bent along the N11–S14 line, and S14 lies out of the plane of the benzene ring, while **2** is planar. At the MP2/6-31G* level, however, **2** seems to display the same deviation from planarity in its structure as **1**. These observations justify the investigation of the gas-phase structures of both compounds.

Experimental Section

Electron scattering intensities were recorded on Kodak Electron Image plates using the Edinburgh gas electron diffraction apparatus,^[4] operating at approximately 40 kV. Six plates (three from the long and three from the short camera distance) for **1** and six (three long, three short) for **2** were recorded and converted into digital format using a computer-controlled PDS microdensitometer at the Royal Greenwich Observatory (Cambridge) that employed a 200 μm pixel size.^[5] Standard programs were used for the data reduction with the scattering factors of Ross et al.^[6] Sample and nozzle temperatures, nozzle-to-plate distances, weighting functions used to set up the off-diagonal weight matrix, correlation parameters, final scale factors k , and electron wavelengths λ for the measurements of both compounds are collected in Table 1.

Geometry optimizations, frequency, and force-field calculations: The calculations on **1** were performed using Gaussian98,^[7] those on **2** were performed using Gaussian94.^[8] A graded series of calculations was performed for each compound in order to gauge the effects of basis set

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Table 1. Experimental parameters for GED analyses of **1** and **2**.

	d [mm]	$T_{\text{sample}}^{[a]}$	$T_{\text{nozzle}}^{[a]}$	$\Delta s^{[b]}$	$s_{\text{min}}^{[b]}$	$sw_1^{[b]}$	$sw_2^{[b]}$	$s_{\text{max}}^{[b]}$	corr. par.	k	λ [pm] ^[c]
1	97.18	144	154	0.4	10.0	12.0	30.4	35.6	0.3864	0.687(33)	6.0155
	249.94	141	162	0.2	2.0	4.0	13.0	15.2	0.4390	0.796(10)	6.0155
2	95.08	132	164	0.4	10.0	12.0	30.4	35.6	0.3015	0.686(21)	6.0155
	250.32	126	138	0.2	2.0	4.0	13.0	15.2	0.4841	0.796(9)	6.0155

[a] In °C. [b] In Å⁻¹. [c] Determined by reference to the scattering patterns of benzene vapor.

size and electron correlation treatments on the optimized structures. For **1**, calculations were performed using standard gradient techniques at the HF level of theory using the 3-21G*^[9–11] and 6-31G*^[12–14] basis sets on all atoms, at the B3LYP level using 6-31G* on all atoms, at the B3LYP level with 6-31G* on C and H and 6-31 + G* on N and S, at the B3LYP level with 6-31G* on C and H and 6-311 + G*^[15, 16] on N and S, and at the MP2 level using 6-31G* on C and H and 6-311 + G* on N and S. The calculations for **2** were performed analogously, the more extensive basis sets were applied to F, as well as to N and S; the calculation at the MP2/6-31G* level was performed using the GAMESS program.^[17] Vibrational frequencies were calculated at the B3LYP/6-311 + G* level (6-31G* on C and H) for **1** and at the B3LYP/6-31G* level for **2**. For each compound, the force field described in Cartesian coordinates was transformed into one described in a set of pseudosymmetry coordinates using the program ASYM40,^[18] and was then used to calculate the amplitudes of vibration, u , after scaling (see below). Furthermore, perpendicular amplitudes of vibration, k , were calculated according to the methods of Sipachev,^[19, 20] by treating the force field in terms of coordinates more closely approximating the true curvilinear motions of the atoms in the molecule.

Results and Discussion

Ab initio calculations: The molecular framework and atomic numbering of **1** and **2** are shown in Figures 1 and 2, respectively. Force fields calculated at the HF level with the

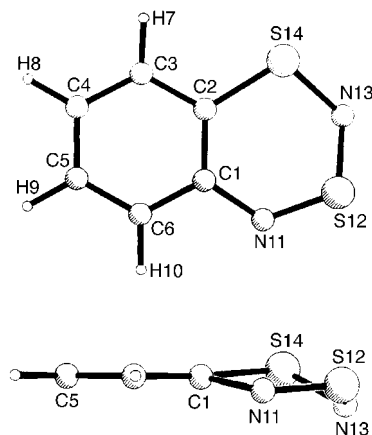


Figure 1. Molecular structure and atomic numbering of 1,3λ⁴δ²,2,4-benzodithiadiazine (**1**) (top) and view of **1** along the C1–C2 bond (bottom).

3-21G* and 6-31G* basis sets for compound **1** in C_s symmetry yielded one imaginary frequency, and a force-field calculation at the B3LYP/6-311 + G* (6-31G* on C and H) level confirmed that **1** has C₁ symmetry. Table 2 shows the calculated geometries for **1** at the different levels of theory

Table 2. Molecular geometries [r_c in Å and angles in °] calculated for **1** (X = H) and **2** (X = F) by a range of ab initio methods.

Parameter	1				2			
	B3LYP/6-31G*	B3LYP/6-31 + G*	B3LYP/6-311 + G*	MP2/6-311 + G*	B3LYP/6-31G*	B3LYP/6-31 + G*	B3LYP/6-311 + G*	MP2/6-31G*
C1–C2	1.4116	1.4113	1.4117	1.4085	1.4163	1.4170	1.4171	1.4109
C2–C3	1.3873	1.3886	1.3886	1.3966	1.3774	1.3778	1.3784	1.3880
C3–C4	1.4052	1.4051	1.4053	1.4000	1.4061	1.4054	1.4071	1.3980
C4–C5	1.3894	1.3903	1.3903	1.3979	1.3812	1.3808	1.3822	1.3890
C5–C6	1.3996	1.3994	1.3996	1.3961	1.4040	1.4033	1.4051	1.3951
C6–C1	1.3979	1.3987	1.3986	1.4025	1.3965	1.3967	1.3975	1.4002
C1–N11	1.4120	1.4131	1.4114	1.4110	1.4031	1.4038	1.4018	1.4060
C2–S14	1.8134	1.8095	1.8097	1.7791	1.8201	1.8221	1.8237	1.7834
N13–S14	1.7234	1.7231	1.7208	1.7345	1.7068	1.7017	1.6987	1.7368
S12–N13	1.5743	1.5762	1.5708	1.6006	1.5706	1.5700	1.5649	1.6060
N11–S12	1.5683	1.5706	1.5665	1.5949	1.5670	1.5677	1.5638	1.5928
C–X	1.0862	1.0862	1.0862	1.0875	1.3365	1.3407	1.3338	1.3415
C6–C1–C2	118.7	118.8	118.8	119.4	117.9	117.9	118.0	119.0
C5–C6–C1	120.9	120.8	120.8	120.1	121.9	122.0	122.0	121.0
C4–C5–C6	119.9	120.0	120.0	120.2	119.6	119.5	119.5	119.8
X10–C6–C1	117.8	117.9	117.9	118.2	120.3	120.3	120.3	120.5
X9–C5–C6	119.7	119.6	119.6	119.7	119.7	119.9	119.9	120.1
X8–C4–C5	120.7	120.6	120.6	120.3	121.2	121.1	121.0	120.3
X7–C3–C4	119.9	120.0	120.0	120.7	118.1	117.9	118.0	117.8
N11–C1–C2	124.5	124.3	124.2	123.9	125.7	125.6	125.5	124.8
S14–N13–S12	120.2	119.9	120.2	115.8	124.1	124.7	125.1	117.4
N13–S14–C2	104.2	103.5	103.4	100.7	104.2	104.1	104.0	101.7
S14–C2–C1	122.2	121.7	121.6	119.7	124.7	124.5	124.4	121.7
N11–C1–C2–S14	–9.1	–9.7	–9.7	–13.4	0.0	0.0	0.0	–12.4
S12–N13–S14–C2	–25.9	–30.0	–30.0	–44.4	0.0	0.0	0.0	–37.9
N13–S14–C2–C1	27.6	31.3	31.2	46.3	0.0	0.0	0.0	39.8
S14–C2–C1–C6	175.1	174.9	175.0	174.5	180.0	180.0	180.0	176.8

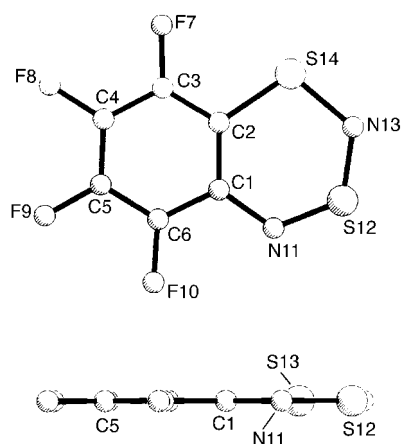


Figure 2. Molecular structure and atomic numbering of 5,6,7,8-tetrafluoro-1,3λ⁴δ²,2,4-benzodithiadiazine (**2**) (top) and view of **2** along the C1–C2 bond (bottom).

used in this study. There is a convincing agreement between the DFT calculations with different basis sets: neither the introduction of diffuse functions nor the addition of a triple- ξ valence basis set seems to have much effect on the bond lengths in the carbocycle part of **1**, even though the bond lengths in the heterocycle seem to decrease slightly when going to the B3LYP/6-311 + G* level. This is reflected in the valence angles: while the differences in CCC and HCC angles are negligible, the largest variation in the angles of the heterocycle can be found in N13–S14–C2, which decreases by 0.8° on increasing the basis set size. The variation in torsional angles is most pronounced, and is more than 4° for N13–S14–C2–C1.

However, even this marked difference is small when compared with the changes that occur when MP2 is introduced as the method of calculation. Again the variation in the bond lengths and valence angles of the carbocycle is small; the variations amount to no more than 0.008 Å and about 0.6°, respectively. In contrast, the differences in the heteroatomic section of the molecule are large: we calculated the largest difference in bond length to be more than 0.03 Å for N11–S12 and for the S14–N13–S12 angle we found a variation of 4.4°. All of the latter differences are due to the disagreement between DFT and MP2 on the exact conformation of the heteroatomic six-membered ring of **1**, which is most clearly expressed in the torsional angles that define the deviation from planarity of the structure, where the differences amount to more than 15° in N13–S14–C2–C1.

In contrast, in the case of compound **2**, the force-field calculations for the planar conformation at the HF level with the 3-21G* and 6-31G* basis sets yielded no imaginary frequencies, and the assignment of the symmetry of **2** as C_s was confirmed by a calculation at the B3LYP/6-31G* level. Further geometry optimizations were

performed with larger basis sets, all in C_s symmetry. Again the DFT calculations with different combinations of basis sets were found to agree quite well on the various parameters in the molecule: the bond lengths in the heteroatomic part shortened somewhat with the incorporation of triple- ξ basis functions, and the values were similar in magnitude to those observed for **1**. The largest variation in the angles amounted to 1.0° for the S14–N13–S12 angle.

But here, too, these differences are small when compared with what happens when the results of the MP2 calculation are included. Not only are larger differences observed in the carbocycle than in the case of **1** (up to 0.01 Å for the bond lengths and 1.0° for the valence angles), but as a result of the fact that the conformation of the heterocycle has been twisted away from the planar arrangement (stabilizing the molecule by 4.66 kJ mol⁻¹), the values of the corresponding distances and angles change dramatically. While the C–N distance and the CCN angle remain virtually unaffected by the change in conformation, the C–S distance drops by more than 0.04 Å, and the various S–N bonds elongate by an equally large amount. Correspondingly, the CCS and the N13–S14–C2 angles shrink by 2.7° and 2.3°, respectively; the value of the S14–N13–S12 angle decreases by 7.7°. The change in the torsional angles is straightforward, but we do wish to emphasize that both S14 and N11 are moved out of the plane of the carbocycle in *different* directions, exactly as was observed in **1**.

We can conclude that both molecules are described differently by the two correlated methods used, and that experimental determination of the gas-phase structures of both compounds is warranted: in the end it will allow us to gauge the accuracy of both methods in calculating geometries for these types of compounds.

Vibrational spectra: For both **1** and **2**, partial IR spectra can be found in the literature.^[2, 3] These published frequencies were used to scale the calculated force fields to obtain the most realistic estimates for the amplitudes of vibration; for **2** the original data were re-examined, and the published series of wavenumbers expanded by ten values. Table 3 lists the experimental values for **1** as well as the scaled calculated ones; the latter were obtained by scaling down the CH stretching modes by 0.9, the CC stretching modes by 0.92, and the CS, CN, and SN stretching modes by 0.98. The rms difference is then 13 cm⁻¹, while the largest difference is 27 cm⁻¹. Table 4 lists the corresponding data for **2**; by scaling down the CC

Table 3. Observed and scaled calculated vibrational data for **1** (see text for scaling factors).^[a]

ν_{calcd} (I_{calcd})	ν_{expt}	ν_{calcd} (I_{calcd})	ν_{expt}	ν_{calcd} (I_{calcd})	ν_{expt}	ν_{calcd} (I_{calcd})	ν_{expt}
3060 (12)		1278 (3)	1271 w	948 (5)	937 m	506 (9)	
3051 (12)		1230 (23)	1219 s	882 (1)		452 (3)	
3039 (5)	3045 w	1181 (0)	1159 w	792 (15)	783 m	416 (4)	415 w
3027 (1)		1115 (1)		770 (55)	754 vs	363 (4)	
1584 (1)		1076 (51)	1097 vs	721 (2)	700 m	346 (16)	357 m
1576 (2)	1576 w	1044 (28)	1049 m	676 (8)	649 m	309 (4)	309 m
1474 (37)	1466 vs	1020 (16)		657 (3)	656 m	241 (5)	246 w
1461 (12)	1437 vs	985 (0)		596 (28)	623 m	144 (0)	
1293 (2)		956 (0)		541 (3)		84 (1)	98

[a] Wavenumbers ν in cm⁻¹ and intensities I in km mol⁻¹. w weak; m medium; s strong; vs very strong.

Table 4. Observed and scaled calculated vibrational data for **2** (see text for scaling factors).^[a]

ν_{calcd} (I_{calcd})	ν_{expt}	ν_{calcd} (I_{calcd})	ν_{expt}	ν_{calcd} (I_{calcd})	ν_{expt}	ν_{calcd} (I_{calcd})	ν_{expt}
1633 (25)	1632 m	1061 (43)	1051 m	573 (0)		281 (1)	
1603 (6)	1609 m	1010 (55)	999 s	534 (2)	536 vw	279 (1)	
1513 (345)	1497 vs	909 (39)	906 s	498 (8)	502 w	264 (0)	
1489 (307)	1471 vs	811 (21)	818 m	436 (5)	434 w	207 (1)	
1397 (3)	1382 w	792 (7)	785 w	418 (3)	418 w	197 (1)	
1318 (7)	1330 w	647 (0)		366 (1)		166 (0)	
1261 (11)	1282 m	639 (20)	642 m	362 (1)	367 vw	127 (0)	
1192 (72)	1176 s	618 (1)	619 vw	356 (4)	358 w	99 (0)	
1131 (141)	1110 s	594 (31)	611 m	324 (14)	326 m	32 (0)	

[a] Wavenumbers ν in cm^{-1} and intensities I in km mol^{-1} . w weak; m medium; s strong; vs very strong.

stretching modes by 0.94 and the CS, CN, and SN stretching modes by 0.98, we obtained an rms difference of 11 cm^{-1} , with the largest difference of 21 cm^{-1} . The tables show that there is reasonable agreement between the experiment and the calculations, both in the values of the wavenumbers and in the intensities of the signals.

In each case, the lowest-energy vibrational mode describes the folding of the heteroatomic section of the molecule along the N11–S14 line, but this folding is slightly different for the two molecules. For **2**, starting from the calculated planar conformation, the folding along the N11–S14 line can be described by a single folding parameter, in which only N13 and S12 move (see below), while N11 and S14 remain stationary in the plane of the carbon ring. For **1**, where in the calculated nonplanar geometry S14 and N11 are displaced out of the plane of the carbocycle, each to a different side, the folding motion is more complex and involves moving not only S12 and N13 but also N11 and S14 from their original positions. Despite these differences, it is still this “floppy” internal motion that shows how the molecules deform from their equilibrium structures and determines the differences between observed conformations of both molecules in different phases.

A. GED study of 1,3λ⁴δ²,2,4-benzodithiadiazine (**1**)

GED model: The molecular framework and atomic numbering of **1** are shown in Figure 1. For this compound, a model was constructed in C_1 symmetry; the C_6H_4 fragment of the molecule was assumed to be planar, but four torsional angles were introduced to describe the out-of-plane movements of the four heteroatoms. In total, 27 independent geometrical parameters were defined, as documented in Table 5. Eleven bond angles and the four torsional angles were introduced as independent parameters, and the four C–H distances in **1** were replaced by one parameter (p_8), which described the average C–H distance. The rest of the bond lengths (eleven) were recombined in eleven new independent parameters, which are also listed in Table 5. Three parameters were found to shape clearly the main feature of the radial distribution curve: p_1 is defined as the mean of all C–C and the C–N bond lengths, p_9 as the mean of the C2–S14 and N13–S14 distances, which have a similar magnitude according to the calculations (Table 2), and p_{11} as the mean of the S12–N13 and N11–S12 distances, again reflecting their similarity (Table 2). Accordingly, parameters p_{10} and p_{12} are defined as the differences

between the latter two pairs of distances. Parameters p_2 to p_7 describe various means of and differences between groups of CC and CN distances. From these independent parameters, the eleven separate bond lengths were calculated as dependent parameters (p_{28} to p_{38} in Table 5).

GED structural refinement: In the model described above

there is in fact one parameter more than is needed; the distance N11–S12 is determined by other bond lengths and angles in its ring. Both parameters in which it was used (p_{11} and p_{12}) were therefore restrained, and the restraints were applied to the mean and difference of r_a distances. In the end, all parameters except for p_1 were restrained. Parameters relating to the carbocycle section of the molecule were subjected to fairly tight restraints, since the different calculations provided us with fairly reliable predictions of these values. The starting values for the distance parameters for this part of the molecule were taken from the B3LYP calculation, while those for the angle parameters were taken from the MP2 calculation. More credibility was given to the B3LYP values for the distance parameters, since the variation between the different DFT calculations was far smaller than between DFT and MP2. The variation in the angles between both correlated methods was far smaller, and the MP2 values were chosen by default. At the end of the refinement, all experimental parameters for this section of the molecule returned values that lay well within the boundaries set by the restraints, except for p_2 , which confirmed the agreement that exists between the two types of calculations. The calculated values for all CCC and HCC angles at the B3LYP level fall within one esd of the experimental values, while for the distances, only p_{29} , p_{31} , and p_{32} are within one esd of the data calculated by both methods; p_{28} , p_{30} , and p_{33} are shorter than expected. It is also interesting to note that the set of alternating double–single C–C bonds, which is predicted by the calculations, is lost in the experimental data.

The eight parameters describing distances and valence angles in the heteroatomic ring, for which there exists an evident disagreement between the two correlated methods, were dealt with differently. Since it became clear early on in the refinement that the experimental data (especially the bond lengths) were leaning towards the B3LYP predictions, starting values for these parameters were taken from the B3LYP calculations alone, and the sizes of the uncertainties of the restraints were chosen disregarding the results of the MP2 calculation. While the refinement finally yielded values for parameters p_{10} and p_{12} (the redefined form of the C–S and N–S distances, see above) that lay well within the applied restraints, p_9 and p_{11} (the redefined forms, see above) returned values that are both about 0.02 \AA shorter than expected from the B3LYP calculation. The difference between the experimental value of p_{11} —a difference between two S–N bonds—and the MP2 value is striking; this will be commented on later.

Table 5. Experimental geometrical parameters from the SARACEN gas-phase study of 1,3,λ⁴δ²,2,4-benzodithiadiazine (**1**) [r_{hi} in Å and angles in °]. For definition of parameters and details of the refinement, see text.

Parameter		GED	B3LYP ^[a]	MP2 ^[b]
Independent				
p_1	av of $r(\text{C}-\text{C})$ and $r(\text{C}-\text{N})$	1.3911(11)	1.4008	1.4018
p_2	av of $r[\text{C}1-\text{C}2]$, $r[\text{C}3-\text{C}4]$, $r[\text{C}1-\text{C}6]$, and $r[\text{C}1-\text{N}11]$ – av of $r[\text{C}2-\text{C}3]$, $r[\text{C}4-\text{C}5]$, and $r[\text{C}5-\text{C}6]$	– 0.009(9)	0.0139	0.0086
p_3	$r[\text{C}5-\text{C}6]$ – av. of $r[\text{C}2-\text{C}3]$ and $r[\text{C}4-\text{C}5]$	0.008(6)	0.0101	– 0.0012
p_4	$r[\text{C}2-\text{C}3]$ – $r[\text{C}4-\text{C}5]$	– 0.003(11)	– 0.0017	– 0.0013
p_5	$r[\text{C}1-\text{C}2]$ – av. of $r[\text{C}3-\text{C}4]$, $r[\text{C}1-\text{C}6]$, and $r[\text{C}1-\text{N}11]$	0.005(6)	0.0066	0.0040
p_6	$r[\text{C}1-\text{N}11]$ – av. of $r[\text{C}3-\text{C}4]$ and $r[\text{C}1-\text{C}6]$	0.009(6)	0.0094	0.0097
p_7	$r[\text{C}3-\text{C}4]$ – $r[\text{C}1-\text{C}6]$	0.010(12)	0.0067	– 0.0025
p_8	av. $r[\text{C}-\text{H}]$	1.087(2)	1.0862	1.0875
p_9	av. of $r[\text{C}2-\text{S}14]$ and $r[\text{N}13-\text{S}14]$	1.740(4)	1.7653	1.7568
p_{10}	$r[\text{C}2-\text{S}14]$ – $r[\text{N}13-\text{S}14]$	0.087(6)	0.0889	0.0446
p_{11}	av. of $r[\text{S}12-\text{N}13]$ and $r[\text{S}12-\text{N}11]$	1.546(3)	1.5687	1.5978
p_{12}	$r[\text{S}12-\text{N}13]$ – $r[\text{S}12-\text{N}11]$	0.0057 f ^[c]	0.0043	0.0057
p_{13}	C6–C1–C2	119.4(6)	118.8	119.4
p_{14}	C5–C6–C1	120.9(7)	120.8	120.1
p_{15}	C4–C5–C6	120.1(5)	120.0	120.2
p_{16}	H10–C6–C1	117.8(6)	117.9	118.2
p_{17}	H9–C5–C6	119.67(12)	119.64	119.67
p_{18}	H8–C4–C5	120.4(6)	120.6	120.3
p_{19}	H7–C3–C4	120.4(12)	120.0	120.7
p_{20}	N11–C1–C2	123.3(7)	124.2	123.9
p_{21}	S14–N13–S12	119.9(5)	120.2	115.8
p_{22}	N13–S14–C2	101.5(7)	103.4	100.7
p_{23}	S14–C2–C1	122.7(6)	121.6	119.7
p_{24}	N11–C1–C2–S14	– 17(3)	– 9.7	– 13.4
p_{25}	S12–N13–S14–C2	– 41(3)	– 30.0	– 44.4
p_{26}	N13–S14–C2–C1	26.2(23)	31.2	46.3
p_{27}	S14–C2–C1–C6	174.6(12)	175.0	174.5
dependent				
p_{28}	C1–C2	1.391(6)	1.4117	1.4085
p_{29}	C2–C3	1.392(8)	1.3886	1.3966
p_{30}	C3–C4	1.388(8)	1.4053	1.4000
p_{31}	C4–C5	1.395(8)	1.3903	1.3979
p_{32}	C5–C6	1.402(7)	1.3996	1.3961
p_{33}	C6–C1	1.378(7)	1.3986	1.4025
p_{34}	C1–N11	1.393(6)	1.4114	1.4110
p_{35}	C2–S14	1.784(5)	1.8097	1.7791
p_{36}	N13–S14	1.697(5)	1.7208	1.7345
p_{37}	S12–N13	1.548(3)	1.5708	1.6006
p_{38}	N11–S12	1.543(3)	1.5665	1.5949

[a] Refers to B3LYP/6-311 + G* (6-31G* on C and H) calculation. [b] Refers to MP2/6-311 + G* (6-31G* on C and H) calculation. [c] f indicates that the parameter was kept fixed.

The starting values for parameters p_{24} to p_{27} , which describe the folding of the ring, were chosen as the means of the values at the B3LYP level and those at the MP2 level, and very loose restraints were applied in order to let these parameters take a very wide range of values; the range meant that we did not exclude either computational method at the outset. We should note that during the course of the refinement these torsional parameters varied over a wide range of values that reflect the floppiness of this part of the molecule; the values reported in Table 5 are those at the lowest R factor, even though the latter did not change very much with varying torsional angles. The values of the bond angles of this part of the molecule, which are closely related to those of the torsional angles, seemed to settle down more quickly and, as mentioned above, are slightly in favor of the B3LYP results. The small difference between results obtained by the two methods for p_{20} is reflected in the fact that both are within one esd of the experimental value; the experimental value of p_{22} also lies between those of the calculations, but the values for p_{21} and p_{23} definitely tend more to the B3LYP values. This is especially

true for the SNS angle, for which the difference between the methods is substantial. The CSN angle (p_{22}) lies the farthest outside its restraint, but ends up between the predictions of the two computational methods.

Ultimately, a tight restraint was applied on the C–H distance (p_8) as well, since during the course of the refinement, it had reached an unrealistic value (up to 1.23(3) Å). Once the restraint had been applied, the value returned from the experimental data lay well within the boundaries of the restraint. Restraints were also applied to amplitudes of vibration that could not be refined independently. Values for the restraints were calculated directly from the scaled force field, with uncertainty ranges of 10% of the computed values for single amplitudes or 5% of the computed values for ratios of amplitudes. With these restraints in place, all amplitudes were refined. The final R_G factor for the refinement was 0.073. A selection of interatomic distance and vibrational amplitude values for the final structure is given in Table 6, and the final radial distribution curve is shown in Figure 3.

The difference between the gas-phase and solid-state geometries of **1** is striking: while in the gas phase the nonplanarity of the compound has been well established both by the calculations and the experiment, the solid-state structure clearly displays a coplanar arrangement for the carbocycle and the heteroatomic ring.^[3] Nevertheless, taking into account what was discussed above concerning the floppiness of the heteroatomic section of the molecule, this is hardly surprising. As a result of packing effects in the crystal (in this case a relatively short interplanar separation between the molecules in the solid^[3]), the molecule will be very easily deformed in a way that is dictated by the lowest-energy vibrational mode, that is, the folding of the heteroatomic ring along the N11–S14 line. This way the molecule can be flattened without any great effort; the calculated energy difference is just 1.17 kJ mol⁻¹ at the HF/6-31G* level.

In contrast, however, the flattening of the heteroatomic part does not seem to have any great influence on the various bond lengths in the compound. In the carbocycle, the alternation of double and single C–C bonds, which was lost in the experimental gas-phase structure, is present in the solid, but, taking the esds in consideration, we found that the overall differences between gas and crystal geometries are minimal. More surprisingly, the bond lengths in the heteroatomic part

are very similar as well, except for the C–N distance, which in the crystal (1.423 Å) is much larger than either the experimental (1.393(6) Å) or the calculated (1.4114 Å at the B3LYP level) gas-phase value. The experimental C–S distance (1.796 Å) suffers from a similar elongation in the solid, but its value lies between the experimental and B3LYP calculated gas-phase values, and the larger difference must therefore be put in perspective. There is, however, surprisingly good correspondence between the two phases for the various S–N distances, all to well within one esd: the solid-state values for N13–S14, S12–N13, and N11–S12 are 1.693 Å, 1.548 Å, and 1.544 Å, respectively; the values reflect the differences in bond order for that segment of the molecule, and they can be directly compared with the gas-phase values in Table 5. This overall agreement can again be seen as an indication of the floppiness of the heteroatomic segment of **1**; the fact that the values for the bond lengths and orders remain virtually unaffected by the folding reflects the small amount of energy that is required to execute it.

In conclusion we can say that the applied DFT method describes the gas-phase structure of 1,3,λ⁴δ²,2,4-benzodithiadiazine (**1**) more correctly than the MP2 method, and that the differences are most markedly seen in the various S–N distances. The fact that MP2 calculations often overestimate the lengths of these types of bonds has been noticed before.^[21, 22] These observations were subsequently used in the structural refinement of the tetrafluoro derivative of **1** by assuming from the start of the refinement that the B3LYP calculated values would be closer to the experimental ones.

Table 6. Selected interatomic distances [r_a in Å] and amplitudes of vibration [u in Å] derived from the SARACEN study of 1,3,λ⁴δ²,2,4-benzodithiadiazine (**1**).

Atom pair	Distance	Amplitude	Atom pair	Distance	Amplitude
S14...S12	2.798(6)	0.069(5)	S12...C5	4.980(11)	0.097(8)
S12–N11	1.542(3)	0.051(4)	N13...N11	2.548(20)	0.063(7)
N13–S12	1.547(3)	0.051(4)	N11...C6	2.351(12)	0.058(7)
S14–N13	1.693(5)	0.069(7)	C4...C2	2.423(12)	0.052(4)
S14–C2	1.781(5)	0.069(6)	C5...C2	2.771(9)	0.067(7)
S12...C1	2.585(9)	0.065(6)	N11...C5	3.640(13)	0.066(7)
S12...C2	3.033(12)	0.071(6)	N13...C3	3.944(20)	0.099(12)
N11–C1	1.391(6)	0.049(3)	N13...C6	4.323(22)	0.099(9)
S12...C6	3.793(11)	0.082(8)	H10...C1	2.103(9)	0.109(10)
H7–C3	1.082(2)	0.077(8)	H8...C2	3.398(15)	0.085(10)
S12...C3	4.412(11)	0.094(8)			

B. GED study of 5,6,7,8-tetrafluoro-1,3,λ⁴δ²,2,4-benzodithiadiazine (**2**)

GED model: The molecular framework and atomic numbering of **2** are shown in Figure 2. A model was constructed for **2** in C_1 symmetry (allowing the heteroatomic part of the molecule to be twisted away from the planar geometry predicted by B3LYP). Again, the C₆F₄ fragment was assumed to be planar. Four torsional angles, describing the out-of-plane movements of the four heteroatoms, and eleven bond angles were introduced as independent parameters. The four CF distances were assumed to be equal, since the calculated differences between the four distances are small, and they were replaced by a single parameter, p_8 , that describes the average CF distance. Eleven new independent parameters describe the rest of the bond lengths and are similar to the ones defined for **1**; all of these are listed in Table 7. From these independent parameters, the eleven separate bond lengths were calculated as dependent parameters (p_{28} to p_{38} in Table 7).

GED structural refinement: From the outset, more credibility was given to the B3LYP structure and, in line with a planar conformation for **2**, the four parameters describing the out-of-plane motions of the atoms in the heteroatomic segment of the molecule, p_{24} , p_{25} , p_{26} , and p_{27} , were kept fixed at 0°, 0°, 0°, and 180°, respectively. Again, the model contained one parameter more than is needed (the N11–S12 distance) and in

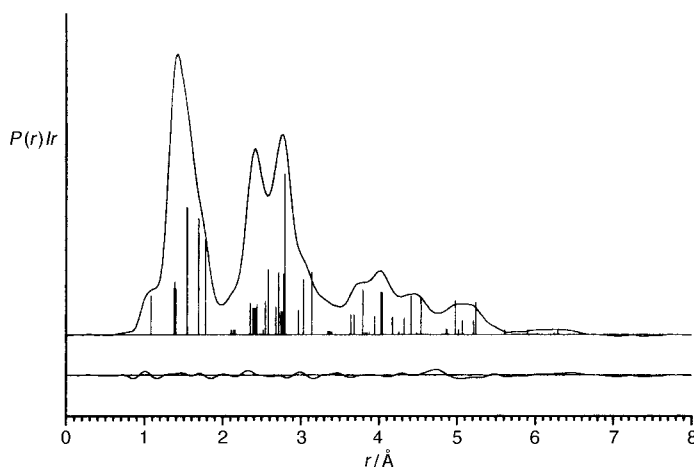


Figure 3. Experimental and difference (experimental – theoretical) radial distribution curves for 1,3,λ⁴δ²,2,4-benzodithiadiazine (**1**). Before Fourier inversion, the data were multiplied by $s \cdot \exp(-0.002s^2)/(Z_s - f_s)(Z_N - f_N)$.

Table 7. Experimental geometrical parameters from the SARACEN gas-phase study of 5,6,7,8-tetrafluoro-1,3,4,8-tetrahydro-2,4-benzodithiadiazine (**2**) [r_{hi} in Å and angles in °]. For definition of parameters and details of the refinement, see text.

Parameter		GED	B3LYP ^[a]	MP2 ^[b]
Independent				
p_1	av of $r[C-C]$ and $r[C-N]$	1.390(3)	1.3985	1.3982
p_2	av of $r[C1-C2]$, $r[C3-C4]$, $r[C5-C6]$, and $r[C1-N11]$ – av of $r[C2-C3]$, $r[C4-C5]$, and $r[C1-C6]$	0.019(10)	0.0217	0.0101
p_3	$r[C1-C6]$ – av of $r[C2-C3]$, and $r[C4-C5]$	0.027(10)	0.0172	0.0117
p_4	$r[C2-C3]$ – $r[C4-C5]$	–0.002(5)	–0.0038	–0.0010
p_5	$r[C1-C2]$ – av of $r[C3-C4]$, $r[C5-C6]$, and $r[C1-N11]$	0.009(9)	0.0124	0.0112
p_6	$r[C1-N11]$ – av of $r[C3-C4]$ and $r[C5-C6]$	0.000(5)	–0.0043	0.0094
p_7	$r[C3-C4]$ – $r[C5-C6]$	0.0020(11)	0.0020	0.0029
p_8	av $r[C-F]$	1.330(5)	1.3338	1.3415
p_9	av of $r[C2-S14]$ and $r[N13-S14]$	1.767(5)	1.7612	1.7601
p_{10}	$R[C2-S14] - r[N13-S14]$	0.089(14)	0.1250	0.0466
p_{11}	av of $r[S12-N13]$ and $r[S12-N11]$	1.552(3)	1.5644	1.5994
p_{12}	$r[S12-N13] - r[S12-N11]$	0.0011 f ^[c]	0.0011	0.0132
p_{13}	C6–C1–C2	116.2(5)	118.0	119.0
p_{14}	C5–C6–C1	122.3(5)	122.0	121.0
p_{15}	C4–C5–C6	119.1(6)	119.5	119.8
p_{16}	F10–C6–C1	120.2(7)	120.3	120.5
p_{17}	F9–C5–C6	119.5(8)	119.9	120.1
p_{18}	F8–C4–C5	120.9(8)	121.0	120.3
p_{19}	F7–C3–C4	117.4(8)	118.0	117.8
p_{20}	N11–C1–C2	125.4(7)	125.5	124.8
p_{21}	S14–N13–S12	122.8(5)	125.1	117.4
p_{22}	N13–S14–C2	104.5(3)	104.0	101.7
p_{23}	S14–C2–C1	124.6(6)	124.4	121.7
p_{24}	N11–C1–C2–S14	0.0	0.0	–12.4
p_{25}	S12–N13–S14–C2	0.0	0.0	–37.9
p_{26}	N13–S14–C2–C10	0.0	0.0	39.8
p_{27}	S14–C2–C1–C6	180.0	180.0	176.8
dependent				
p_{28}	C1–C2	1.405(8)	1.4171	1.4109
p_{29}	C2–C3	1.370(8)	1.3784	1.3880
p_{30}	C3–C4	1.397(6)	1.4071	1.3980
p_{31}	C4–C5	1.372(8)	1.3822	1.3890
p_{32}	C5–C6	1.395(6)	1.4051	1.3951
p_{33}	C6–C1	1.398(8)	1.3975	1.4002
p_{34}	C1–N11	1.396(7)	1.4018	1.4060
p_{35}	C2–S14	1.812(9)	1.8237	1.7834
p_{36}	N13–S14	1.723(8)	1.6987	1.7368
p_{37}	S12–N13	1.553(3)	1.5649	1.6060
p_{38}	N11–S12	1.552(3)	1.5638	1.5928

[a] Refers to B3LYP/6-311 + G* (6-31G* on C and H) calculation. [b] Refers to MP2/6-31G* calculation. [c] f indicates that the parameter was kept fixed.

exactly the same manner as discussed above for **1**, parameters p_{11} and p_{12} were restrained from the outset to eliminate this redundant degree of freedom. In this case only we were able to refine parameters p_1 , p_8 , p_9 , and p_{10} freely; all others were restrained, and the uncertainties for the latter were chosen based on the values determined in the series of B3LYP calculations. The refined values of the parameters describing the carbocycle were again found to compare well with those calculated at the B3LYP level. All the angles p_{14} to p_{19} are within one esd of the calculated values, and well within the boundaries set by the restraints. Only p_{13} deviates slightly from the calculated value, but more importantly, the values of the two angles deviating most from the ideal 120° , p_{13} and p_{14} , are mirrored very well by the calculations. For the distance parameters, all parameters except p_1 lie within one esd of the calculated values. The experimental value of p_1 indicates an overall shortening of the C–N and C–C bonds relative to the theoretical values; in contrast, the C–F distance compares well. Here also, the alternating single–double C–C bond

scheme in the benzene ring, which is clear in the results of the calculations, is less pronounced in the experimental structure.

The parameters describing the heteroatomic part of the molecule again proved more interesting. The mean of the S–N and S–C distances, p_9 , was refined to a value slightly longer than was calculated. This is mostly due to N13–S14 being considerably longer than the calculations predicted, so p_{10} also differs quite substantially from the calculated value. A similar effect is found in p_{11} , but here it is due to the fact that both S=N distances are again overestimated by the calculations. The result is that even though a fairly tight restraint was set on this parameter, the refined value falls well outside the restraint. As was the case for **1**, both the experimental CCN and CCS angles correspond nicely to the predicted values, and larger discrepancies are found for SNS and CSN; for SNS the difference is more than 2° , even with a tight restraint in place.

Restraints were also applied to amplitudes of vibration that could not otherwise be refined independently. Values for the

restraints were calculated directly from the scaled force field, with uncertainty ranges of 10% of the computed values for single amplitudes or 5% of the computed values for ratios of amplitudes. With these restraints in place, all amplitudes were refined. The final R_G factor for the refinement of **2** in a planar conformation was 0.084. A selection of interatomic distance and vibrational amplitude values for the final structure is given in Table 8, and the final radial distribution curve is given in Figure 4.

Finally, to confirm the planarity of the molecule unequivocally, we combined the four torsional parameters describing the out-of-plane motions of the atoms in the heteroatomic segment of the molecule into one new parameter describing the lowest-energy folding mode of the N=S=N-S fragment out of the plane of the carbocycle. This was achieved by calculating the four torsional angles in a nonplanar conformation of **2**, which was obtained by deforming the planar geometry according to the displacements of the atoms in the computed lowest normal mode of the compound. One of the torsional angles was chosen to represent the folding of the N=S=N-S fragment, and the other three were linked to the new one by their respective calculated ratios, which are 2.50, -2.83, and -0.36, respectively. This new folding parameter

Table 8. Selected interatomic distances [r_a in Å] and amplitudes of vibration [u in Å] derived from the SARACEN study of 5,6,7,8-tetrafluoro-1,3λ⁴δ²,2,4-benzodithiadiazine (**2**).

Atom pair	Distance	Amplitude	Atom pair	Distance	Amplitude
F7–C3	1.329(5)	0.046(3)	S14...F8	4.99(4)	0.105(8)
S14...S12	2.848(7)	0.064(4)	S12...C6	3.81(7)	0.064(6)
S12–N11	1.55(9)	0.047(4)	S14...F9	5.870(10)	0.086(6)
N13–S12	1.552(3)	0.047(4)	F10...C5	2.326(10)	0.061(3)
S14–N13	1.717(8)	0.056(6)	S12...C3	4.362(11)	0.074(7)
S14–C2	1.806(9)	0.056(6)	N11...N13	2.67(9)	0.061(7)
S12...C1	2.57(5)	0.054(5)	N11...C6	2.410(9)	0.060(6)
S14...N11	3.20(5)	0.074(7)	F9...F7	4.669(15)	0.073(10)
S12...F10	4.25(9)	0.094(9)	C5...C3	2.400(10)	0.061(5)
F10...F9	2.660(20)	0.090(9)	F7...C5	3.581(10)	0.069(4)
N11–C1	1.398(7)	0.051(4)			

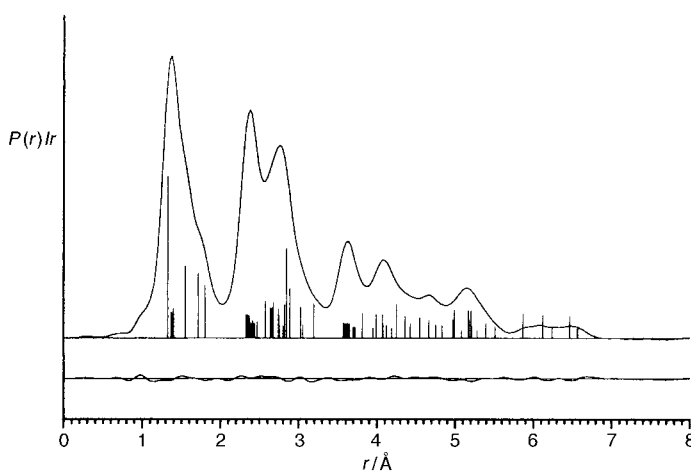


Figure 4. Experimental and difference (experimental – theoretical) radial distribution curves for 5,6,7,8-tetrafluoro-1,3λ⁴δ²,2,4-benzodithiadiazine (**2**). Before Fourier inversion, the data were multiplied by $s \cdot \exp(-0.002s^2)/(Z_S - f_S)(Z_F - f_F)$.

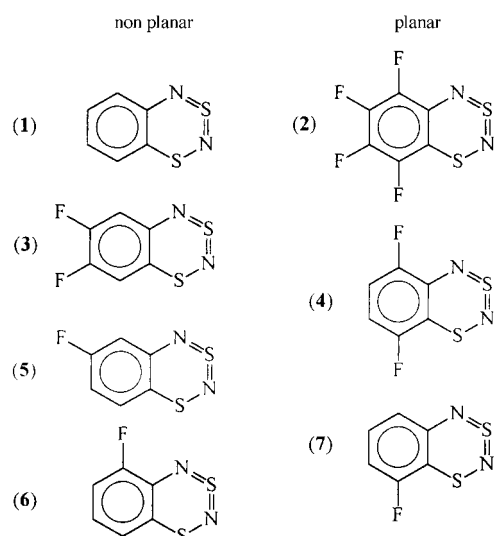
was then fixed at various nonzero values, and all remaining parameters for the resulting structures were completely refined. At a folding of 5° the R factor rose slightly to 0.086, and at 10° this became 0.097; at 15° the R factor was found to be 0.110 and at 20° 0.217, and at 30° we were no longer able to refine the resulting structure against the experimental data. From this we conclude that **2** is essentially planar to within about 10°; the experimental data and the fact that the heteroatomic part of the molecule displays a low-energy low-frequency motion preclude the possibility of defining the equilibrium conformation of **2** more precisely.

In any case, even though the DFT calculations cannot completely reproduce the experimental gas-phase structure, Table 7 clearly shows that this method is much more satisfactory than MP2, not only for the heterocyclic part but for the entire molecule, as was anticipated from the results of the refinement of **1**.

The difference between the gas-phase and solid-state geometries of **2** is just as surprising as in the case of **1** but for the opposite reason. In the gas phase, the planarity of the compound has been predicted by the B3LYP calculations—which we expect to be correct based on the results of the refinement of **1**—and confirmed by the experiments. On the other hand, the solid-state structure clearly displays a slightly non-coplanar arrangement for the carbocycle and the heteroatomic ring.^[2] A folding of 5.5(1)° was found, in which the S14 and N11 atoms clearly deviated from the plane of the carbon ring, but in this case both to the same side. In this case too, the deformation of **2** in the solid state is easily accomplished as a result of the floppiness of the heterocyclic segment, even more so than in the case of **1** when the lowest vibrational wave-numbers are considered. Again we find that the changes going from the gas phase to the solid in the carbocycle part of **2** are minimal. The larger differences observed in the gas phase for p_{13} and p_{14} are also found in the solid. Surprisingly, the C–N distance (1.432(4) Å) is found to be much larger in the gas phase than in the solid here as well, while the C–S distance is considerably shorter in the solid (1.781(5) Å). In contrast to **1**, the correspondence of the S–N distances for **2** in the solid and gas phases is much less satisfactory; while the value for S12–N13 (1.553(4) Å in the solid) is exactly the same in both phases, the other two are considerably shorter (1.651(4) Å and 1.513(3) Å for N13–S14 and N11–S12, respectively).

C. Geometrical differences between **1** and **2**: influence of the fluorine atoms

Based on the information gathered above, it is clear that the B3LYP method described the geometries of the differently substituted benzodithiadiazines more accurately than the MP2 method, especially with regard to the planarity of the heteroatomic ring of the compounds. We have therefore examined the precise influence of the fluorine atoms on the planarity of the heteroatomic part of the compounds. We extended our series of calculations on **1** and **2** at the B3LYP/6-31G* level to some mono- and difluorobenzodithiadiazines, of which the structural formulas are given in Scheme 1. Since the parent compound (**1**), 6-fluoro- (**5**) and 6,7-difluoro-1,3λ⁴δ²,2,4-benzodithiadiazine (**3**) proved to have nonplanar geometries and 5,8-difluoro- (**4**) and 5,6,7,8-tetrafluoro-1,3λ⁴δ²,2,4-benzodithiadiazine (**2**) did not, the flattening of

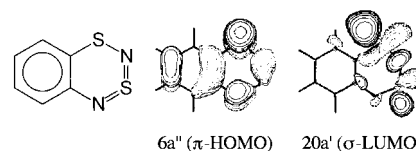


Scheme 1. Structural formulas of 1,3 $\lambda^4\delta^2$,2,4-benzodithiadiazines (**1**), 5,6,7,8-tetrafluoro-1,3 $\lambda^4\delta^2$,2,4-benzodithiadiazine (**2**), 6,7-difluoro-1,3 $\lambda^4\delta^2$,2,4-benzodithiadiazine (**3**), 5,8-difluoro-1,3 $\lambda^4\delta^2$,2,4-benzodithiadiazine (**4**), 6-fluoro-1,3 $\lambda^4\delta^2$,2,4-benzodithiadiazine (**5**), 5-fluoro-1,3 $\lambda^4\delta^2$,2,4-benzodithiadiazine (**6**), and 8-fluoro-1,3 $\lambda^4\delta^2$,2,4-benzodithiadiazine (**7**); for **2**, **4**, and **7**, Cartesian coordinates and energies of the refined geometries are given in the Supporting information.

the heteroatomic section of the molecule is clearly due to the presence of the fluorine atoms in the 5- and 8-positions. A further discrimination between the latter two was made by calculations on 5- (**6**) and 8-fluoro-1,3 $\lambda^4\delta^2$,2,4-benzodithiadiazine (**7**) separately. These indicated that the fluorine atom in the 8-position (F7, i.e., the one closest to S14) is alone responsible for the flattening of the heteroatomic ring.

The distortion of **1** away from C_s symmetry, observed in the calculations and confirmed by the experiments, reflects the tendency of the molecule to minimize the thermodynamic destabilization associated with antiaromaticity by means of a pseudo-Jahn–Teller effect.^[23] A quick glance at the molecular orbital scheme for **1** allows the identification of the orbital interactions responsible for the reduction of the molecular symmetry from C_s to C_1 . In C_s symmetry, the molecular ground state is a π^2 -state of $^1A'$ symmetry. The calculations indicate that for both **1** and 1,3 $\lambda^4\delta^2$,2,4-dithiadiazine **8** the planar structure is a transition state in the molecular bending motion (Table 9). The transition to C_1 symmetry is possible through a vibronic interaction between excited $^1A''$ states, generated by $\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ excitations. For **1**, the lowest-energy excitation of these types is $6a'' \rightarrow 20a'$. The mixing of $6a''$ (i.e. the π -HOMO) with $20a'$ (i.e. the σ -LUMO, which is the lowest virtual σ^* molecular orbital, closest to $7a''$ or the π -

LUMO, see Scheme 2) folds the molecule along the N11–S14 line in accordance with the results of the calculations and the GED data. According to the contributions of the atomic orbitals to the $6a''$ and $20a'$ molecular orbitals, the density of the one-electron transition under consideration is localized mainly on S14. The energy gain on going from C_s to C_1 symmetry is about 1 kJ mol^{-1} at the HF level of theory; at the MP2 level, however, this energy increases by a factor of nine, as can be seen in Table 9.



Scheme 2. Selected molecular orbital representations of **1** (see text for details).

Obviously, the orbital interaction mentioned above should be sensitive to the energy difference between the contributing molecular orbitals. This allows us to explain why only the fluorine atom located in the 8-position (F7) is responsible for the flattening of the heterocyclic ring on going from **1** to **2**. One can easily see that the substitution of any hydrogen atom in **1** by a fluorine atom does not affect the energy of the $20a'$ (σ^*) orbital, which is localized on the S–N bonds (see Scheme 2). In contrast, replacing a hydrogen atom by a fluorine in position 8 leads to an inductive stabilization of the $6a''$ (π -HOMO) orbital, an effect which must be *inductive*, since C3 does not contribute to this molecular orbital. In all other cases, that is, substitution in positions 5, 6, and 7, this effect will be compensated for to a great extent by mesomeric destabilization due to the nonzero contributions of C4, C5, and C6 to the $6a''$ molecular orbital, as can be seen in Scheme 2. Thus, F7 enlarges the energy difference mentioned above (and F8, F9, and F10 do not), counteracts the pseudo-Jahn–Teller distortion of the molecule, and so allows it to assume C_s symmetry.

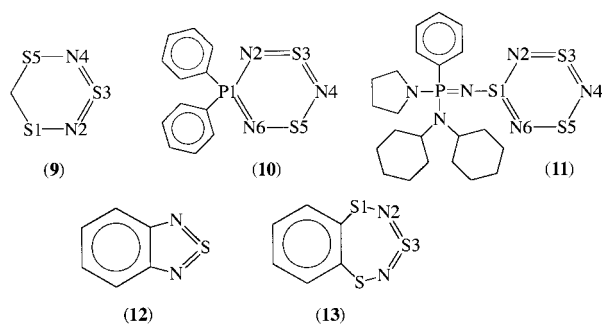
D. General overview of cyclic compounds containing S–N units:

As mentioned in the introduction, the class of compounds containing an $-\text{N}=\text{S}=\text{N}-\text{S}-$ fragment linked to a benzene ring is fairly new, but the chemistry concerning inorganic (anti)aromatic six-membered rings containing S–N units is not. Many compounds have been synthesized and of these several have had their (crystal) structures reported. One of their most important features, and the one that interested us in the context of this paper, is the precise conformation of the heterocycle.

One of the basic members of this class of compounds is 1,3 $\lambda^4\delta^2$,5,2,4-trithiadiazine (**9**);^[24] its structure is given in Scheme 3. The molecule exhibits a chair-like (puckered envelope) conformation in the solid: the plane through S3, N2, and N4 and the plane through the carbon atom, S1, and S5 make angles of 4° and 48° , respectively, with the plane defined by the S1–N2 and N4–S5 bonds. Even though the S–N=S–N–S fragment is nearly planar, the values of the bond lengths quite clearly demonstrate that the π -bonds are localized on

Table 9. Summary of calculated data for 1,3 $\lambda^4\delta^2$,2,4-benzodithiadiazine (**1**) and 1,3 $\lambda^4\delta^2$,2,4-dithiadiazine (**8**).

	HF/6-31G*			MP2/6-31G*	
	Symmetry		E_{rel} [kJ mol $^{-1}$]	E_{rel} [kJ mol $^{-1}$]	
1	C_s	trans. state	1.17	trans. state	10.17
	C_1	minimum	0.00	minimum	0.00
8	C_s	trans. state	3.60		
	C_1	minimum	0.00		



Scheme 3. Structures of several related compounds (see text for details).

N2, S3, and N4, since N2–S3 (1.549(3) Å) and S3–N4 (1.560(3) Å) are substantially shorter than S1–N2 (1.671(3) Å) and N4–S5 (1.668(3) Å). Similar differences in S–N bond lengths were observed in two derivatives of **9**,^[24] that is, the 1-oxo and the 6-(4-methoxyphenyl) derivatives. Despite the fact that the π -bonds are localized in exactly the same way as in **1** and **2**, this cyclohexane-type conformation is quite different from the folded structure found in **1**.

In 1,1-diphenyl-1-phospha-3λ⁴δ²,5-dithia-2,4,6-triazine (**10**)^[25] a P–N unit is linked to the –N=S=N–S– fragment to give a six-membered ring (see Scheme 3), in which all N and S atoms are situated in a plane (to within 0.05 Å), and the P atom is positioned 0.28 Å above it. In contrast to **9**, the values of the bond lengths in this molecule suggest p-orbital overlap between the N and S atoms and thus some sort of conjugation, which most likely is a major cause for the planarity of the system. Disregarding the P–N bond lengths, we found the following distances in the crystal: N2–S3 1.560(3), S3–N4 1.580(4), N4–S5 1.583(5), and S5–N6 1.575(3) Å. The variation in bond lengths is obviously very much smaller than in the case of **9**, and the double bonds drawn in the structure of **10** in Scheme 3 are to be seen as a limiting factor.

In 1-[(dicyclohexylamino)(phenyl)(1-pyrrolidinyl)-phosphinimino]-1,3λ⁴δ²,5,2,4,6-trithiatriazine^[26] a completely inorganic six-membered ring (see Scheme 3) is found in a conformation, which is similar to that of **10**, that is, N2, S3, N4, S5, and N6 are all arranged in a near-planar conformation, and S1 is positioned 0.658(6) Å above the plane. However, a close examination of the torsional angles in the S₃N₃ ring demonstrates that the latter is in fact slightly folded into a chair conformation. Thus, **11** can be seen as an intermediate between **9** and its derivatives, where the chair conformation is readily observable, and **10**, which exhibits planarity. The differences in S–N bond lengths reflect this too; the six distances in the S₃N₃ ring can be divided into three categories: S1–N2 (1.640(5) Å) and S1–N6, (1.622(4) Å), N2–S3 (1.599(5) Å) and N6–S5 (1.597(5) Å), and S3–N4 (1.583(6) Å) and N4–S5 (1.579(6) Å). The overall variation in bond lengths here is clearly smaller than in the case of **9**, where it was found to be more than 0.1 Å, but larger than in the case of **10**, where it was 0.02 Å. The expectation that, for this reason, **9** will be the least planar, **10** will be the most planar, and **11** will be somewhere in between, is hereby confirmed. Similar features are found in various derivatives of **11**, amongst which 1-[(diphenyl)(2-pyridyl)phosphinimino]-1,3λ⁴δ²,5,2,4,6-trithiatriazine is an example.^[27]

The two compounds under investigation here clearly separate themselves from those discussed above, since they exhibit a noncyclohexane-like ring conformation. Moreover, this is imposed not by endocyclic factors (such as π -electron delocalization), but by exocyclic influences, in this case substitution on the benzene ring. In addition, the inclusion of two *sp*²-carbons in the six-membered heterocycle seems to increase the π -electron localization even further: the difference between S–N and S=N bond lengths is considerably larger than in **9**, **10**, and **11** and amounts to 0.15 and 0.17 Å for **1** and **2**, respectively.

Within the class of inorganic S–N rings condensed with a benzene ring an interesting series of aromatic and antiaromatic compounds presents itself in 2,1,3-benzothiadiazole (**12**, a 10 π -electron aromatic compound), **1** (a 12 π -electron antiaromatic compound), and 1,3,5,2,4-benzotrithiadiazepine (**13**, a 14 π -electron aromatic compound); compounds **12** and **13** have been presented in Scheme 3. The gas-phase structure of **12** was investigated using microwave spectroscopy, and the molecule was found to be planar.^[28] In the solid state, **13** has C_{2v} symmetry, and in the inorganic ring the largest deviation from planarity is a mere 0.032 Å for S1.^[29] The larger variation in S–N bond lengths (1.538(3) Å for N2–S3 vs. 1.609(3) Å for S1–N2) also suggests localization of π -electrons in the apical S–N bonds. The planarity of the compound in the solid state is thus most likely to be a packing effect, attributable to the small interplanar separation between the molecules.^[29] The 6,7,8,9-tetrafluoro derivative of **13** was found to be planar to within about 0.018 Å in the crystal,^[30] and the difference from **2** in the solid state is clear. The lengths of the various S–N bonds in 6,7,8,9-tetrafluoro-(**13**) were found to be 1.531(5) Å for N2–S3 and 1.604(4) Å for S1–N2, and these values indicate that fluorine substitution has only a small influence. The same comment about planarity can also be made here. The C–S distances in both **13** and 6,7,8,9-tetrafluoro-(**13**) (1.731(3) and 1.737(4) Å, respectively) are considerably shorter than those found for **1** and **2**.

Other solid-state structural data on **1** substituted with a wide variety of substituents have recently been published. The 5-trifluoromethyl- and 6-fluoro derivatives of **1** are virtually planar in the crystal, while the 5-methoxy and 6-methyl derivatives show a clear folding along the N11–S14 line by 10.8(2)° and 6.9(1)°, respectively,^[31] in contrast, 7-methoxy-(**1**) is planar.^[32] These data clearly show the influence of packing effects on the conformation of the heterocycle in the solid state.

Conclusion

The present ab initio and GED study presents the first structural characterization of 1,3λ⁴δ²,2,4-benzodithiadiazine and a number of its derivatives in the gas phase. The results clearly illustrate the differences that exist between the solid-state structure and that of the free molecule, in the absence of packing effects. Furthermore, they give a clear indication of the value of the results of calculations performed on both compounds with two different correlated methods. In addition, the calculations allowed the accurate description of the

precise effect of the introduction of a fluorine substituent in the benzene ring on the conformation of the inorganic ring in the molecule.

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