Role of C−H···S and C−H···N Hydrogen Bonds in Organic Crystal Structures—The Crystal and Molecular Structure of 3-Methyl-2,4-diphenyl-(1,3)-thiazolidine-5-spiro-2′-adamantane and 3-Methyl-2,4,5,5-tetraphenyl-(1,3)-thiazolidine

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Received: June 28, 2002; In Final Form: February 17, 2003

The crystal and molecular structures of 3-methyl-2,4-diphenyl-(1,3)-thiazolidine-5-spiro-2′-adamantane and 3-methyl-2,4,5,5-tetraphenyl-(1,3)-thiazolidine are investigated showing the existence of C(sp^2)−H···S and C(sp^2)−H···N intramolecular contacts. The use of the Bader theory shows that C−H...S interactions existing in crystal structures may be treated as weak H bonds. The C−H...N and C−H...S interactions are also analyzed here for simple modeled complexes of (1,3)-thiazolidine as the proton acceptor and simple proton donators: HF, H_2O, C_2H_4, and C_2H_2 molecules. The calculations for these complexes were performed within the DFT method, B3LYP/6-311++G** level of theory. The bond critical points (BCPs) were found for these modeled systems and the analysis of the electron densities and their Laplacians at BCPs was performed.

1. Introduction

It is well-known that hydrogen bonding is one of the most important interactions influencing on the arrangement of molecules in molecular organic crystals.[1−3] The studies on this interaction have shown that the proton donating and accepting abilities of molecules determine the architecture of crystals. In recent years, the role of H bonds with the C−H proton donating bond in the crystal engineering has been extensively studied.[3−5] Among them C−H···O interactions are the most often investigated because of their frequency of occurrence in crystals.[3] In earlier studies, Taylor and Kennard [6] have shown that for C−H···X contacts H bonds with the oxygen atom accepting center (X = O) are of the most frequent occurrence; it is 54% the full sample of C−H···X systems taken from the Cambridge Structural Database.[7] The occurrence of the other C−H···X (X = N, P, Cl, Br, S, C) interactions is much smaller, the C−H···Y systems for which H···X distance is smaller than the corresponding sum of van der Waals radii ($r_H^{vdW} + r_X^{vdW}$) have been investigated.[6]

The problem of the role of C−H···X H bonds in crystals is the aim of this study, but special attention is paid to C−H···S and C−H···N interactions because they occur in the crystal structures investigated here. The above-mentioned contacts have been investigated previously both theoretically as well as experimentally;[3] the C−H···S hydrogen bonds are not well-known because of their rare occurrence in crystals.[3,6] Taylor and Kennard in their early study on C−H···X interactions have found only four C−H···S contacts, three of them being intramolecular.[6] More recently, the hydrogen bond proton accepting ability of sulfur in C═S bonds has been investigated using crystallographic data retrieved from the Cambridge Structural Database and using ab initio calculations.[8,9]

There are early reports on individual crystal structures showing the presence of X−H···S hydrogen bonds; among them the C−H···S interactions are considered. The H bond with C≡C−H alkyne terminal group as a proton donator is an example of such interaction.[10] The C(sp^2)−H···S(sp^3) and C(sp^2)−H···N(sp^3) intramolecular contacts are analyzed in this paper because they occur within the crystal structures of 3-methyl-2,4-diphenyl-(1,3)-thiazolidine-5-spiro-2′-adamantane (**1**) and 3-methyl-2,4,5,5-tetraphenyl-(1,3)-thiazolidine (**2**) investigated here. Compounds **1** and **2** were synthesized within the more extensive studies on derivatives of (1,3)-thiazolidines;[11−13] some of these heterocycles may be used in synthesis of immunomodulating drugs or antibiotics.[14−16]

The studies on intermolecular C−H···S systems are not often reported. The same is in force for the corresponding intramolecular systems. For example, the possibility of the existence of intramolecular C−H···S hydrogen bonding despite a strongly bent angle (∼105°) has been discussed for the crystal structure of 4-(methylthio)-4-nitro-1-(pyrrolidin-1-yl)buta-1,3-diene.[17]

The studies of intramolecular H bonds mentioned above are supported in this paper by DFT calculations on the related modeled systems. The atoms in molecules theory (AIM) of Bader [18] is also applied here to find bond critical points (BCPs) and to analyze them in terms of their electron densities and Laplacians.

The calculations on very simple systems containing C(sp^3)−H···X hydrogen bonds have been performed previously showing the low S(sp^3) sulfur ability as proton acceptor and low ability of C(sp^3)−H bond as proton donor. For example, the calculations on CH_4···OH_2,[19] CH_4···NH_3,[20] and CH_4···SH_2 [21] complexes performed at MP2/6-311++G** level of theory, corrected by BSSE, show the binding energies of 0.34, 0.31, and 0.07 kcal/mol, respectively. It is in line with other investigations

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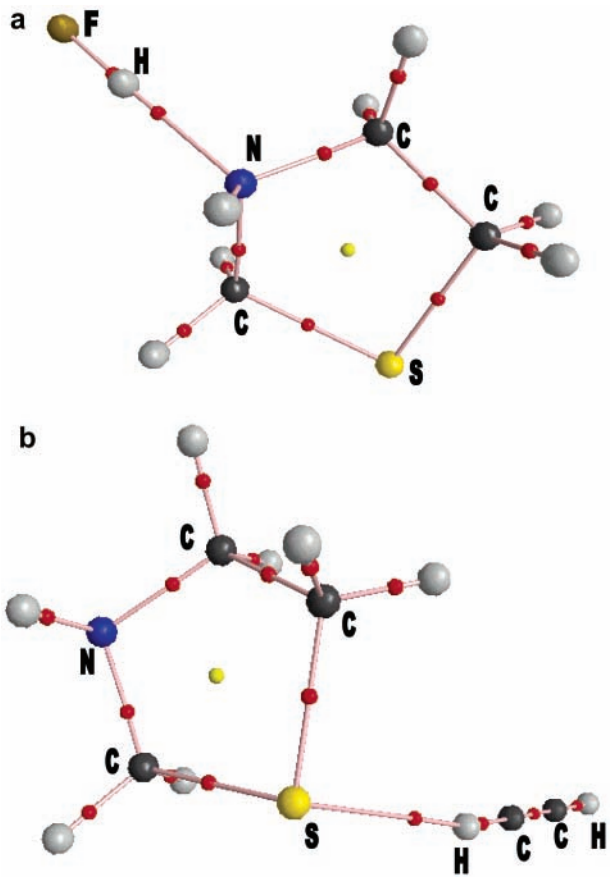
10.1021/jp021520e CCC: $25.00
Published on Web 03/20/2003

SCHEME 1: (a) Complex of 1,3-Thiazolidine and HF; Nitrogen as Proton Acceptor; (b) the Complex of 1,3-Thiazolidine and C_2H_2; Sulfur as Proton Acceptor, where Molecular Graphs Show Attractors Which Correspond to Atomic Positions, Bond Paths Connecting Atoms, and Critical Points



since it has been pointed out that C−H···S interactions are weaker than C−H···O hydrogen bonds.[3]

2. Computational Details

The complexes analyzed here were chosen to investigate interactions similar to those existing within crystal structures of **1** and **2**. The (1,3)-thiazolidine molecule being the heterocyclic ring with the sulfur and nitrogen atoms was chosen as the proton acceptor for H bridges. The same ring exists within 3-methyl-2,4-diphenyl-(1,3)-thiazolidine-5-spiro-2′-adamantane (**1**) and 3-methyl-2,4,5,5-tetraphenyl-(1,3)-thiazolidine (**2**) molecules. HF, H_2O, C_2H_2, and C_2H_4 molecules are chosen here as proton donors. Hence, for each complex analyzed here, there are two types of dimers with the sulfur or nitrogen atoms, respectively, as acceptors. Scheme 1 presents molecular graphs of two dimers analyzed in this study: (1,3)-thiazolidine + HF with F−H···N hydrogen bonding and (1,3)-thiazolidine + HCCH with C−H···S H bond. For two dimers of (1,3)-thiazolidine + C_2H_4 investigated here, there are interactions of the same type as those existing for structures **1** and **2**: $C(sp^2)$−H···N and $C(sp^2)$−H···S.

The calculations have been performed using Gaussian 98 sets of codes [22] within the density functional methods (DFT). The B3LYP functional and 6-311++G** basis set were used. Interaction energies were computed as the difference in energy between the complex on one hand and the sum of isolated monomers on the other hand. The geometries of the complexes and of the isolated molecules were fully optimized during the calculations. Basis set superposition error (BSSE) was corrected by the counterpoise procedure of Boys and Bernardi.[23] Charges on individual atoms were computed using the natural population scheme. The additional calculations on the modeled complexes described above have been performed at MP2/6-311++G** level of theory.

The H-bonding characteristics of the complexes studied have been investigated through the use of the atoms in molecules (AIM) theory of Bader.[18] For this purpose, the bond critical points (BCPs) have been located,[24] i.e., the points where the charge density function $\rho(r)$ is a minimum along the bond path and maximum in the other two directions. The Laplacians of the electron density functions at BCPs were also calculated. Scheme 1 shows the molecular graphs of the mentioned above complexes; the localization of bond and ring critical points (BCPs and RCPs) is visible.

3. Experimental Section

The colorless single crystals [0.15 × 0.25 × 0.50 mm (**1**) and 0.2 × 0.4 × 0.5 mm (**2**)] were chosen for structure determination, at room temperature.

The diffraction data have been collected on AFC5S Rigaku diffractometer with graphite monochromatized Cu Kα radiation for **1** and Mo Kα radiation for **2**, with ω scan. After each group of 150 reflections, three standard intensities were monitored, and no evidence of crystal decay was observed both for **1** and **2**.

In the data reduction step,[25,26] intensities were corrected for Lorentz and polarization factors and the absorption correction was applied for **1**: minimum and maximum transmission factors were 0.5898 and 0.8155.[27]

The structures were solved by direct methods[28] and refined on F^2 by full-matrix least-squares calculation.[29] All non-hydrogen atoms for both structures were located and refined with anisotropic thermal displacement parameters. The hydrogen atoms of structure **1** were introduced in the last step of the refinement procedure for calculated positions and refined isotropically. For structure **2**, the H atoms were located from difference Fourier map and refined isotropically (except of H251) with the C−H distance restrained geometrically. The crystal data and details of the X-ray analysis are given in Table 1. Atomic coordinates and equivalent isotropic displacement coefficients U_{eq} for **1** and **2** are given in Table 2, parts a and b (supplementary Tables).

4. Results and Discussion

4.1. Crystal and Molecular Structures. The crystal and molecular structures of 3-methyl-2,4-diphenyl-(1,3)-thiazolidine-5-spiro-2′-adamantane (**1**) and 3-methyl-2,4,5,5-tetraphenyl-(1,3)-thiazolidine (**2**) are the subject of the present study. Table 1 collects the crystal data and structure refinement details for these compounds; Table 2 shows the atomic coordinates and equivalent isotropic displacement coefficients U_{eq}; Table 3 shows the selected bond lengths and angles. Figure 1 shows the molecular structures of **1** and **2** with the atom-labeling scheme; Figure 2 presents the unit cell contests for both crystal structures.

The molecular structures for these compounds differ in the substituent for the C5 carbon atom within the heterocyclic ring. It is the adamantane for **1** and two phenyl rings for **2**. As it is well-known, directional interactions such hydrogen bonds mostly influence on the crystal architecture.[1−3] There are not typical proton donating and proton accepting groups for the crystal

TABLE 1: Crystal Data and Structure Refinement Details for Compounds 1 and 2

	1	2
formula	$C_{25}H_{29}NS$	$C_{28}H_{25}NS$
M	375.55	407.55
T (K)	293	293
wavelength	CuKα	MoKα
crystal system	monoclinic	orthorombic
space group	$P2_1/n$	$Pna2_1$
a (Å)	11.931(1)	20.744(2)
b (Å)	15.305(1)	8.923(1)
c (Å)	12.164(1)	12.194(2)
α (deg)	90.00	90.00
β (deg)	112.75(1)	90.00
γ (deg)	90.00	90.00
V (Å^3)	2048.4(2)	2257.1(5)
Z	4	4
D_x (g cm^{-3})	1.218	1.199
μ (mm^{-1})	1.447	0.158
absorpcion correction	analytical	none
$T_{min} = 0.5898$, $T_{max} = 0.8155$		
F(000)	808	864
no. of collected data	3659	4422
no. of data with $I > 2\sigma(I)$	2455	3824
no. of parameters varied	275	333
S	0.885	1.035
R/wR	0.0358/0.0912	0.0295/0.0761
R (all data)/wR (all data)	0.0620/0.0965	0.0396/0.0799

TABLE 3: Selected Bond Lengths (Å) and Angles (deg) for 1 and 2 (Parts a and b, Respectively)

		Part a	
S1−C2	1.830(2)	C2−S1−C5	94.5(1)
S1−C5	1.850(2)	N3−C2−S1	104.5(1)
C2−N3	1.459(3)	C2−N3−C31	112.1(2)
N3−C31	1.465(3)	C2−N3−C4	110.0(2)
N3−C4	1.472(3)	C31−N3−C4	114.0(2)
C4−C5	1.546(3)	N3−C4−C5	105.5(2)
		C4−C5−S1	102.7(1)
		Part b	
S1−C2	1.838(2)	C2−S1−C5	93.9(1)
S1−C5	1.853(2)	N3−C2−S1	104.6(1)
C2−N3	1.452(2)	C2−N3−C31	112.8(2)
N3−C31	1.466(2)	C2−N3−C4	109.7(1)
N3−C4	1.469(2)	C31−N3−C4	114.7(1)
C4−C5	1.549(2)	N3−C4−C5	105.0(1)
		C4−C5−S1	102.6(1)

structures investigated here. There are accepting centers for heterocyclic rings: nitrogen and sulfur atoms, but both are not strong acceptors. The short review of the literature concerning accepting abilities of sulfur was presented in the Introduction. There is also the sp^3 nitrogen atom within the heterocyclic rings. This acceptor center is not so strong; in the previous investigations, it was pointed out that sp^3 nitrogen atom is not a good proton acceptor.[30] The similar situation is present for donators; there is no typical OH or NH proton donating bonds for the crystal structures **1** and **2**. It was pointed out early on that "good proton donors" and "good proton acceptors" are always used in hydrogen bonds.[31] The rules concerning the architecture of molecules in crystals have been extended later by Etter,[32] who claimed that if there is no "good donors"; thus, C−H bonds are involved in hydrogen bonds. Such situation occurs for the present structures since there are only C(sp^2)−H bonds which may be proton donators. However, it should be pointed out that the acidity of donators decrease as follows: C(sp)−H > C(sp^2)−H > C(sp^3)−H.[33]

Table 4 presents the parameters of D−H···A contacts of **1** and **2** which are possible hydrogen bonds; D and A designate the proton donator and the proton acceptor, respectively. We have to take into account the fact that some of the geometrical

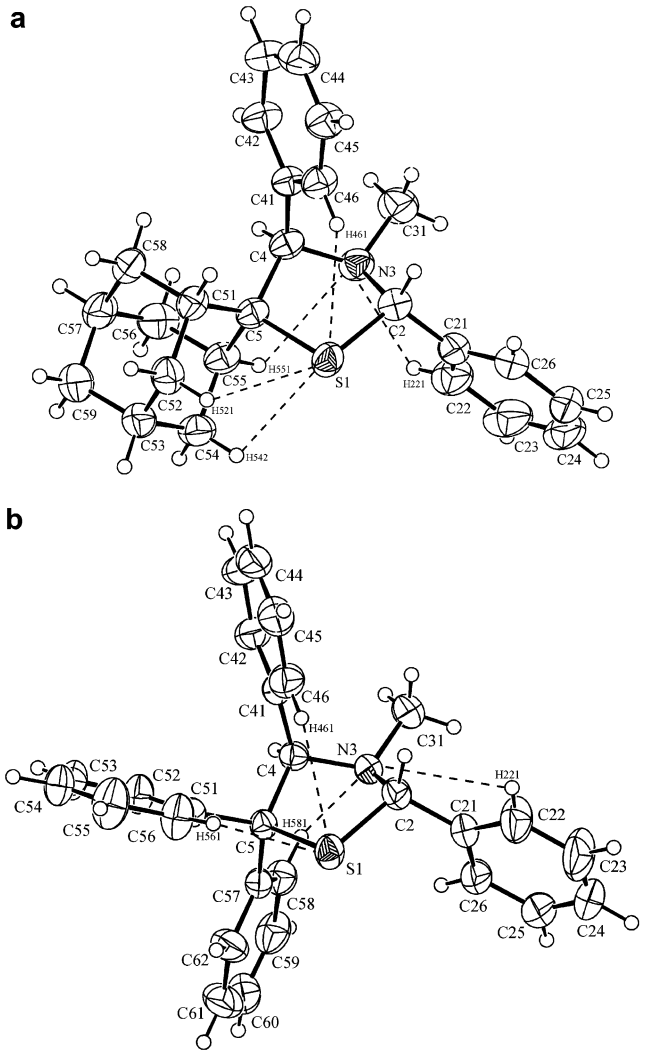


Figure 1. Molecular structures of **1** (Figure 1a) and **2** (Figure 1b) compounds

parameters presented in Table 4 are not accurate because of the positions of H atoms. The structures of **1** and **2** were determined using X-ray diffraction, and it is well-known that H-atom positions are not accurate within this technique of measurement. Neutron diffraction is a much better approach for the investigations of hydrogen bridges. Despite the above-mentioned restrictions, we can give some conclusions based on the results of Table 4. We see that all D−H···A bonds are strongly bent systems because D−H···A angles are far from 180° (96−127°). It may suggest that these contacts exist only because of the steric effects but not because of the creation of H bonds. The contacts are intramolecular what may confirm that the steric effects are dominant. The H···N distances of **1** and **2** are slightly greater or are approximately equal to the sum of van der Waals radii, whereas the H···S distances are smaller than the sum of van der Waals radii; the Pauling radii of S, N, and H amount to 1.85, 1.5, and 1.2 Å respectively. We see that the proton donators are C(sp^2)−H bonds. There are not short intermolecular contacts for structures **1** and **2**.

4.2. Results of Calculations. The B3LYP/6-311++G** calculations for modeled systems similar to those solved using X-ray diffraction techniques were performed here. The complexes of (1,3)-thiazolidine as the proton accepting molecule and the simple proton donators were analyzed. HF, H_2O, C_2H_4, and C_2H_2 were chosen as the donating molecules. For each of

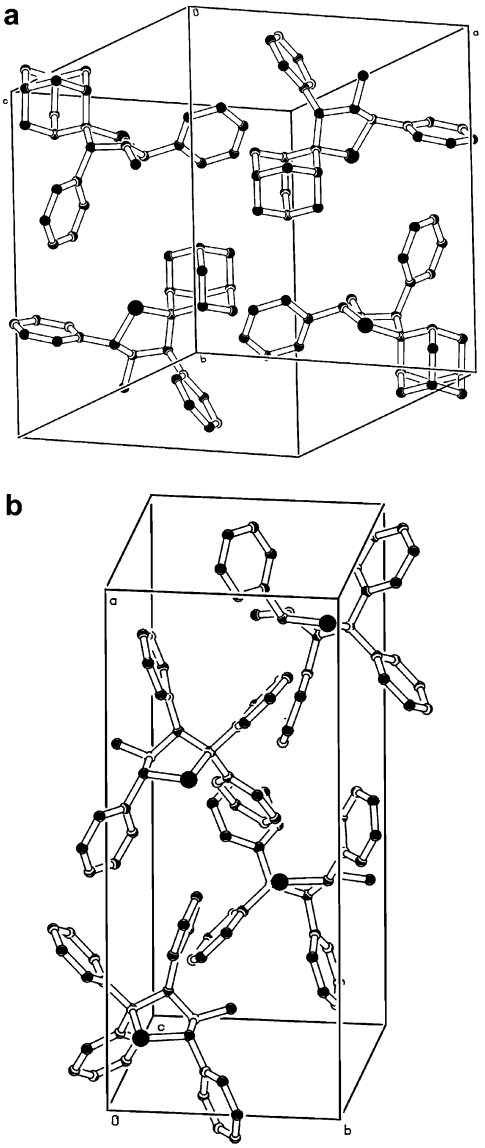


Figure 2. Unit cell contests for **1** (Figure 2a) and **2** (Figure 2b) crystal structures

TABLE 4: Geometry of Possible Hydrogen Bonds (Å, deg) for 1 and 2 for Some of Contacts the BCPs Were Found and hence the Electron Densities and Their Laplacians at BCPs (in au) Are Given[a]

D−H···A	*d*(D−H)	*d*(D···A)	*d*(H···A)	<(DHA)
Structure **1**				
C22−H221···N3	0.93(1)	2.90(1)	2.62(1)	99(1)
C46−H461···S1	**0.93(1)**	**3.48(1)**	**2.86(1)**	**126(1)**
($\rho_{H...S}$ = 0.0108 au; $\nabla^2\rho_{H...S}$ = 0.0335)				
C52−H521···S1	0.97(1)	3.14(1)	2.69(1)	109(1)
C54−H542···S1	0.97(1)	3.15(1)	2.71(1)	109(1)
C55−H551···N3	0.98(1)	3.10(1)	2.78(1)	100(1)
Structure **2**				
C22−H221···N3	0.93(1)	2.94(1)	2.70(1)	96(1)
C46−H461···S1	**0.93(1)**	**3.42(1)**	**2.77(1)**	**127(1)**
($\rho_{H...S}$ = 0.0128 au; $\nabla^2\rho_{H...S}$ = 0.0388)				
C56−H561···S1	**0.92(3)**	**3.10(1)**	**2.64(3)**	**111(2)**
($\rho_{H...S}$ = 0.0151 au; $\nabla^2\rho_{H...S}$ = 0.0522)				
C58−H581···N3	0.93(1)	3.16(1)	2.68(1)	113(1)

[a] The designations correspond to those applied for crystal structures.

the complexes, there are two conformations differing in the proton acceptor: the nitrogen or sulfur atom.

Table 5 presents the selected geometrical parameters being the results of calculations. There are the results of (1,3)-thiazolidine and its complexes in the table. The designations of atoms for calculated systems correspond to those of Figure 1 and to those of Tables 3 for **1** and **2** structures. We see that the geometrical parameters of calculated systems approximately correspond between themselves (Table 5); the similar situation is observable for these parameters for **1** and **2** structures (Tables 3). However, the differences between experimental and theoretical results are not negligible. It may be easily interpreted because the experimental data (Tables 3) concern much greater and complicated molecules which may be additionally affected by the packing effects in crystals. Additionally, there are usually differences between different ab initio and DFT results of calculations and various experimental measurements.

Table 5 presents for comparison the parameters of (1,3)-thiazolidine not involved in H-bond formation. We see that the molecular geometries of (1,3)-thiazolidine within H-bonded complexes are much more deformed for the stronger proton donators such as the HF molecule and for nitrogen as a stronger proton acceptor center. In other words, the stronger H bonds may more efficiently influence on the geometry. Table 6 shows the energetic, geometrical, and topological parameters characterizing H-bonded systems calculated in this study. These results show that the nitrogen atom is a stronger accepting center than the sulfur atom. For the first kind of complexes, for which D−H···N bonds exist, the H···N distances are much smaller than the corresponding sum of van der Waals radii. The same effect is not so strong for D−H···S bonds. One can see that for the D−H···N systems there is the greater elongation of the proton donating bonds than for D−H···S systems. The results of B3LYP/6-311++G** calculations for the isolated proton donators are given in Table 7; the geometrical and topological parameters are presented. Comparing the parameters of Table 6, we also see that the D−H···N systems are closer to linearity than the corresponding D−H···S bonds. All these data show evidently that the nitrogen atom is the stronger acceptor than the sulfur one. The similar insight in Table 6 shows the following order of the strength of proton donators: HF, H_2O, C_2H_2, and C_2H_4.

The binding energies (E_{bin}) corrected for BSSE are also given in Table 6. Two complexes of (1,3)-thiazolidine + C_2H_4 with the sulfur and nitrogen atoms as proton acceptors are the most similar systems to the experimental ones (structures **1** and **2**). We have C−H···N and C−H···S contacts and C(sp^2)-H donators for them; the similar contacts exist for **1** and **2** structures. The binding energies calculated for (1,3)-thiazolidine + C_2H_4 dimers amount to 0.6 and 0.4 kcal/mol, for C−H···N and C−H···S contacts, respectively. It means that for corresponding intramolecular contacts existing within crystal structures such interactions may be weaker, and hence, the existence of hydrogen bonds is problematic.

To get the more reliable insight into the nature of H-bond interactions, the additional MP2/6-311++G** calculations on the modeled complexes considered here have been also performed. The binding energies obtained with this level of theory and corrected for BSSE are included in Table 6. However, for three systems with C−H donating bonds, the local minima were not obtained; hence, the main analysis of hydrogen bonds is based on the results of DFT method.

The topological parameters obtained from the Bader theory[18] support the mentioned above conclusions based on the results of calculations obtained at B3LYP/6-311++G** level of theory. It was detected that the kinetic energy density at BCP of the H-bonded contact ($V(rCP)$) roughly corresponds to the H-bond energy $-E_{HB}$; $E_{HB} = {}^1/_2V(\mathrm{rCP})$.[34] $V(rCP)$ values may be directly obtained from the AIM theory.[24] In other words, it is

TABLE 5: Molecular Geometry of (1,3)-Thiazolidine (Th) and Its Complexes Obtained after the Optimization within the B3LYP/6-311++G Level of Theory (in Å)[a]**

parameter	Th	Th + HF[b]	Th +H_2O[b]	Th + C_2H_2[b]	Th + C_2H_4[b]	Th + HF[c]	Th + H_2O[c]	Th + C_2H_2[c]	Th+C_2H_4[b]
S1−C2	1.895	1.912	1.911	1.900	1.896	1.869	1.880	1.886	1.892
S1−C5	1.844	1.849	1.848	1.846	1.844	1.848	1.846	1.846	1.845
C2−N3	1.439	1.429	1.430	1.437	1.439	1.458	1.450	1.446	1.442
N3−C4	1.462	1.459	1.459	1.462	1.462	1.475	1.471	1.466	1.464
C4−C5	1.548	1.555	1.553	1.548	1.548	1.539	1.542	1.544	1.546
C2−S1−C5	90.9	90.5	90.5	90.9	91.0	91.6	91.3	91.2	91.0
N3−C2−S1	107.9	107.1	107.3	107.7	107.8	107.6	107.8	107.9	107.8
C2−N3−C4	107.8	108.1	107.9	108.0	107.9	107.5	107.5	107.6	107.7
N3−C4−C5	109.4	109.8	109.7	109.3	109.4	108.9	109.1	109.2	109.3
C4−C5−S1	105.7	106.1	106.0	105.7	105.7	105.8	105.8	105.7	105.7

[a] The designations correspond to those applied for crystal structures. [b] For complexes with C−H···S bonds. [c] For complexes with C−H···N bonds.

TABLE 6: Geometrical (Å, deg), Energetic (kcal/mol), and Topological (au) Parameters for Complexes of (1,3)-Thiazolidine Obtained after the Optimization within the B3LYP/6-311++G Level of Theory[a]**

	Th + HF[b]	Th + H_2O[b]	Th + C_2H_2[b]	Th + C_2H_4[b]	Th + HF[c]	Th + H_2O[c]	Th + C_2H_2[c]	Th + C_2H_4[c]
H-bond type	F−H···S (N−H···F)	O−H···S (N−H···O)	C−H···S	C−H···S (C−H···S)	F−H···N	O−H···N	C−H···N	C−H···N
d(D−H)	0.952 (1.016)	0.974 (1.017)	1.069	1.085 (1.085)	0.965	0.977	1.073	1.086
D(H···A)	2.106 (2.719)	2.401 (2.314)	2.762	3.339 (3.630)	1.655	1.956	2.280	2.704
<(DHA)	161.6 (125.3)	145.7 (137.1)	169.4	130.8 (118.9)	177.7	166.3	178.5	178.8
ρ_{D-H}	0.3292 (0.3393)	0.3506 (0.3387)	0.2854	0.2804 (0.2801)	0.3142	0.3469	0.2837	0.2811
$\nabla^2\rho_{D-H}$	−2.327 (−1.554)	−2.405 (−1.580)	−1.036	−0.9624 (−0.9599)	−2.144	−2.386	−1.030	−0.9686
$\rho_{H\cdots A}$	0.0364 (0.0054)	0.0196 (0.0119)	0.0098	0.0032 (0.0017)	0.0594	0.0300	0.0157	0.0076
$\nabla^2\rho_{H\cdots A}$	0.0566 (0.0210)	0.0469 (0.0416)	0.0251	0.0097 (0.0063)	0.1100	0.0857	0.0463	0.0188
E_{bin} (DFT)	−8.7	−5.8	−0.4	−0.4	−11.7	−5.5	−2.5	−0.6
BSSE (DFT)	0.8032	0.7307	1.5741	0.0216	1.2291	0.8006	0.5293	0.1776
E_{bin} (MP2)	−10.4	−5.7	−3.3		−6.8	−5.7		
BSSE (MP2)	2.9066	2.2086	1.5809		2.2880	2.3599		

[a] The topological parameters obtained from the B3LYP/6-311++G** wave functions. The designations correspond to those applied for crystal structures and those within Table 5. The binding energies obtained at the MP2/6-311++G** level of theory and corrected for BSSE (in kcal/mol) are also included. [b] For complexes with C−H···S bonds. [c] For complexes with C−H···N bonds.

TABLE 7: Geometrical (in Å) and Topological (in au) Parameters for Proton Donating Bonds of Monomers Optimized within the B3LYP/6-311++G Level of Theory**

parameter/ molecule	HF	H_2O	HCCH	Th (N−H bond)	C_2H_4
D−H bond length	0.922	0.962	1.063	1.016	1.085
ρ_{D-H}	0.3698	0.3663	0.2880	0.3395	0.2798
$\nabla^2\rho_{D-H}$	−2.803	−2.491	−1.044	−1.511	−0.9579

possible to calculate "the topological H-bond energy" using the appropriate wave function or the electron density. Figure 4 presents the relationship between E_{HB} and $^1/_2V(rCP)$ showing that for some of cases the agreement is not good. It refers to complexes of (1,3)-thiazolidine with HF and H_2O molecules with sulfur atom as an accepting center The binding energies are usually obtained within ab initio or DFT techniques and are treated as H-bond energies. They seem to be too high for two mentioned above complexes. It may be simply justified because for them the proton donating HF and H_2O molecules are simultaneously proton donors and proton acceptors. N−H···F and N−H···O bonds exist for them respectively (see Table 6); the (1,3)-thiazolidine molecule is the donator for these interactions. In other words, the binding energies consist at least of two H bonds for these complexes. The similar situation is observed for the complex of (1,3)-thiazolidine with C_2H_4 connected through CH···S contacts; both H···S contacts are

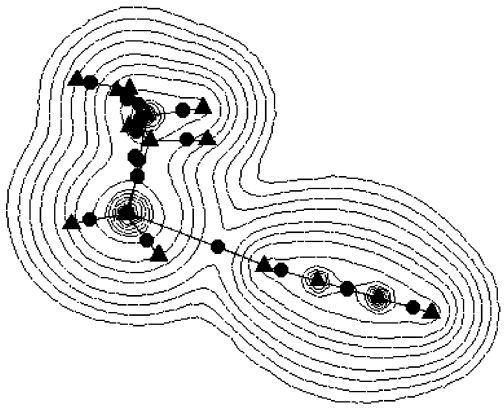


Figure 3. Contour map obtained from B3LYP/6-311++G** wave functions for (1,3)-thiazolidine−HCCH complex connected through C−H···N bond; triangles correspond to attractors and circles to the bond critical points and the ring critical point

greater than the sum of corresponding van der Waals radii. However, both slightly contribute to the binding energy because for both the bond critical points exist (Scheme 2). We see that the properties of the H···Y (Y designates the accepting center) bond critical point more properly describe the energetic parameters of H bridge than the binding energy or geometrical parameters. The application of geometrical criteria of the existence of H bonds[6] does not show hydrogen bonds for the

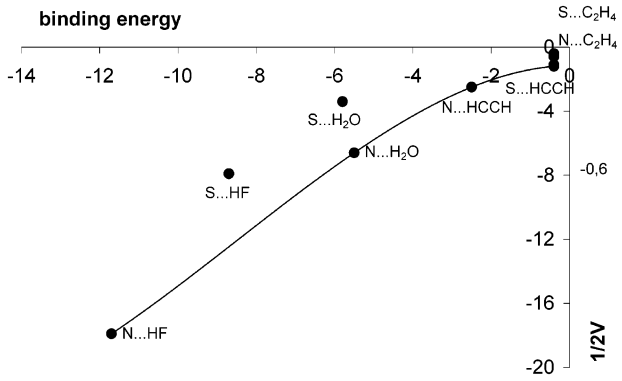


Figure 4. Binding energy versus $^1/_2V$ energy (V, potential energy density obtained within AIM theory); energies in kcal/mol

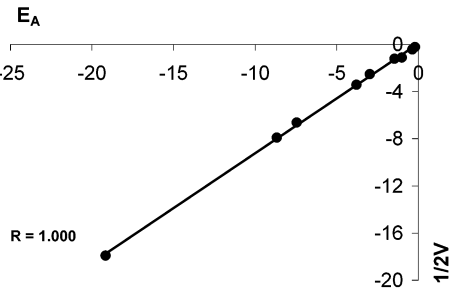
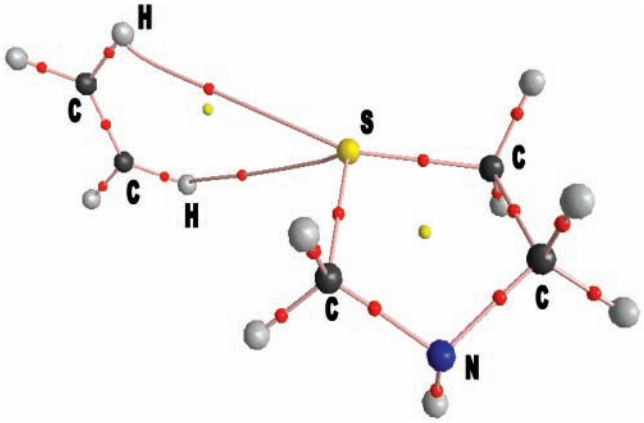


Figure 5. E_A energy (corresponding to $^1/_2V$ but obtained from the Abramov relation) vs $^1/_2V$; energies in kcal/mol; 9 points are visible because for Th + C_2H_4 complex with sulfur accepting center there are two H···S contacts.

SCHEME 2: Molecular Graph for the Complex of (1,3)-Thiazolidine with C_2H_4, where the Molecules Are Connected through H···S Contacts



complex of thiazolidine with C_2H_4; the topological parameters detect them.

Figure 5 shows additionally the relationship between $^1/_2V$ energy and the same energy obtained from the electron density at H···Y BCP. The relation to obtain V energy from $\rho_{H\cdots Y}$ was derived by Abramov.[35] The correlation between V energies obtained from AIM and those obtained from the Abramov relation (E_A) is excellent giving the value of the linear correlation coefficient R of 1.0000.

Figure 6 presents the correlation between the electron density at H···Y BCP − $\rho_{H\cdots Y}$ and $^1/_2V$ − energy; there is the second-order polynomial regression with the correlation coefficient R of 0.999. It confirms the idea that $\rho_{H\cdots Y}$ value correspond to the H-bond strength.[36−39]

The Bader theory may be also applied as a decisive tool for detection of intramolecular hydrogen bonds for **1** and **2** crystal

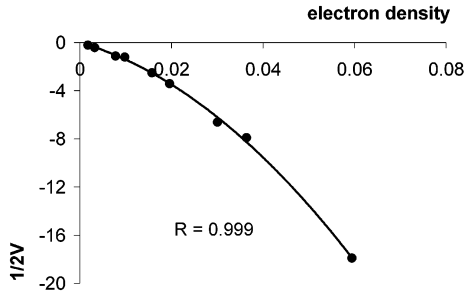


Figure 6. Electron density at H···N (or S) BCP − $\rho_{H\cdots Y}$ (in au) vs $^1/_2V$ energy (kcal/mol); 9 points for the same reasons as within Figure 5.

structures. For geometries of 3-methyl-2,4-diphenyl-(1,3)-thiazolidine-5-spiro-2′-adamantane and 3-methyl-2,4,5,5-tetraphenyl-(1,3)-thiazolidine molecules taken from the crystal structures, the wave functions were obtained at the B3LYP/6-311++G** level of theory. Further, for these results, the critical points and bond paths were analyzed. In other words, the theoretically obtained electron density for the experimental geometry was analyzed for the mentioned above molecules. The critical points were found for some of the intramolecular contacts presented in Table 4; bold lines indicate the contacts for which BCPs were detected. For the **1** crystal structure, the H···S BCP was found for C46−H461···S1 contact, and for the structure **2**, two BCPs were found for C46−H461···S1 and C56−H561···S1 contacts. Table 4 also presents the electron densities at H···S BCPs and their Laplacians ($\rho_{H\cdots S}$ and $\nabla^2\rho_{H\cdots S}$ values) for these intramolecular H bonds. These values are in agreement with the topological criteria of the existence of the hydrogen bonding given by Popelier[40] because the ranges for the electron density and its Laplacian were given for H-bond interaction; they are ⟨0.002−0.04 au⟩ for the electron density and ⟨0.02−0.15 au⟩ for Laplacian at H···A (acceptor) BCP. We see that the values given in Table 4 are within these ranges. It is also visible that the C−H···S hydrogen bonds detected for the crystal structures analyzed here are not weak since the electron density at the proton−acceptor BCP correlates with the H-bond energy.[37−39] For example, for the linear (trans) conformation of water dimer this value amount to 0.023 au for the MP2/6-311++G** wave function and 0.024 au for the B3LYP/6-311++G** wave function; the H-bond energy for the water dimer is of about 5−6 kcal/mol. For the H···S contacts presented in Table 4, the electron density values are of 0.011−0.015 au. We also see from the results for water dimer that the topological parameters do not strongly depend on the level of theory for which the wave function was obtained. B3LYP and MP2 results are approximately the same; it means that the B3LYP topological results presented here for molecules taken from crystal structures may be successfully used to discuss the nature of H-bond interactions.

The electron densities and their Laplacians presented in Table 4 may be a surprise because the topological approach does not detect the C−H···N intramolecular H bonds. Additionally, the results of calculations on modeled complexes presented in this study show that the C−H···N interactions are stronger than the C−H···S ones. However, we see that the results derived from the Bader theory are in agreement with the geometrical criteria of the existence of hydrogen bonding (Table 4). The C−H···S systems are roughly closer to the linearity than the C−H···N ones, additionally the H···S distances are shorter than the corresponding sum of van der Waals radii (3.05 Å), whereas the H···N distances are approximately close to this sum (2.7 Å). Hence, it may be concluded that the crystal packing effects

for **1** and **2** crystal structures cause that short intramolecular C−H···S contacts exist which from the geometrical and topological point of view may be treated as hydrogen bonds.

5. Conclusions

The intramolecular C−H···S and C−H···N contacts were found for the crystal structures of 3-methyl-2,4-diphenyl-(1,3)-thiazolidine-5-spiro-2′-adamantane (**1**) and 3-methyl-2,4,5,5-tetraphenyl-(1,3)-thiazolidine (**2**). According to the geometrical and topological criteria of the existence of H bonds, the C−H···S systems may be treated as such interactions.

The additional calculations on the simple related modeled complexes at B3LYP/6-311++G** level of theory have been performed showing that C−H···N and C−H···S H bonds may exist. For the complex of (1,3)-thiazolidine and acetylene, the binding energy amounts to 2.5 kcal/mol for C(sp)−H···N H bonding and only 0.4 kcal/mol for C(sp)−H···S hydrogen bond. The corresponding binding energies for the complex of (1,3)-thiazolidine with ethylene are even smaller, 0.6 and 0.4 kcal/mol, respectively. The AIM calculations were used to find the bond critical points for C−H···Y (S or N) contacts what supports the prediction of the existence of hydrogen bonding. Despite weak interactions for the modeled systems the bond paths and the bond critical points exist for appropriate H···N and H···S contacts.

Acknowledgment. The authors thank the Rector of the University of Łódź for financial support (University Research Grants).

Supporting Information Available: Atomic coordinates and equivalent isotropic displacement coefficients U_{eq} for **1** and **2** (Table 2, parts a and b). This material is available free of charge via the Internet at http://pubs.acs.org.

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