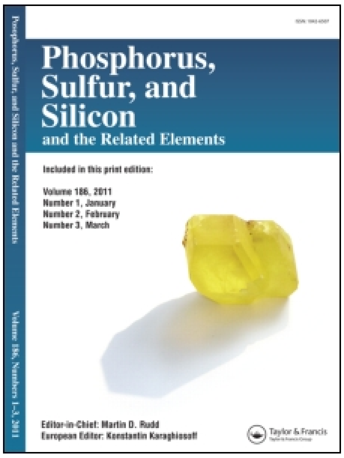

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Specificity of ^{13}C NMR Shielding Calculations in Thiocarbonyl Compounds

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Specificity of ^{13}C NMR Shielding Calculations in Thiocarbonyl Compounds

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Isotropic ^{13}C nuclear magnetic shielding values (σ_{iso}) and corresponding chemical shift magnitudes (δ_C) have been calculated for the large series of the thiocarbonyl compounds using DFT (RI-BP86 and B3LYP) and ab initio (RHF and MP2, with or without resolution of the identity approximation) levels of theory and different basis sets. As expected, the Hartree–Fock method and hybrid B3LYP approach essentially overestimate deshielding of the C=S carbon nuclei. The RI-BP86 level of approximation provides a noticeably better agreement with the experiment and can be used for calculations of the theoretical ^{13}C NMR spectra for the most classes of the thiocarbonyl compounds. Geometry optimizations and the nuclear magnetic shielding calculations using the MP2 level of theory provide the most reliable results. The resolution of the identity algorithm implemented into the TURBOMOLE program set does not affect the calculated σ_{iso} and δC values compared to the strict MP2 nuclear magnetic shielding calculations (using the GAUSSIAN-03 program packet). A poor agreement with the experiment found in the case of the thiourea and thiosemicarbazide derivatives is referred to the different conformations of these species in the gas phase, solid state, and solution.

Supplementary materials are available for this article. Please go to the publisher's online edition of Phosphorus, Sulfur, and Silicon *to view the free supplemental resource.*

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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Keywords Ab initio; DFT; ^{13}C NMR; MP2; nuclear magnetic shielding calculations; shielding tensor; thiocarbonyl compounds

INTRODUCTION

Over the last few decades, NMR spectroscopy remains the main analytical instrument for chemists working in the area of the organic synthesis. A number of magnetically active nuclei and a variety of the special techniques are used for the identification of the reaction products. In spite of the rapid progress of the X-ray crystallographic methods, some structural problems can still be solved only by NMR techniques. A good example is the identification of the short-living species. Since the 1970s, as Fourier NMR spectroscopy and superconductive magnets saw wide usage, a practical role of NMR spectroscopy of the nuclei other than ^{1}H, ^{19}F, or ^{31}P has been constantly increasing. Among these, ^{13}C NMR spectroscopy is of a fundamental importance for organic chemistry.[1] A broad chemical shift scale as well as the simplicity of the spectra made this method unique for solving structural problems. But despite the mentioned advantages, there is still no reliable approach to the spectrum interpretation, in order to make a choice between two or more guessed structures. Basing on the known data for structurally similar objects, numerous additive schemes[2] have been created that allow us to predict the ^{13}C NMR chemical shift values. But they are more or less reliable when congeners are present in the data base that are structurally similar to the guessed species, and mostly fail when only rather distant relatives can be used for the additive calculation routine.

A quite new approach to the solution of the problem is theoretical calculations of the NMR spectra based on ab initio and density functional theory (DFT)[3] and known GIAO,[4] LORG,[5] or IGLO[6] schemes. In the most cases, they provide a good agreement between theory and experiment. In the last few years, it even became possible to choose the correct structure based on the theoretically calculated NMR spectra of the several alternatives.[7] At the same time, a large number of the "difficult cases" are known for the nuclear magnetic shielding calculations. In these cases, a good agreement with the experiment could not be achieved at the Hartree–Fock level of theory, even if the large basis sets are used for the calculations. Unfortunately, the DFT functionals, which practically made revolution in the area of structure modeling, did not manage the same for the magnetic shielding calculations.[8,9] In general, difficulties by the NMR chemical shift calculations arise for the species involving third or higher period element(s) with one or two lone pairs and forming the multiple bond(s). In such cases, calculations predict an overestimated deshielding for the both nuclei participating on the multiple bond. This is due to the overestimation of the paramagnetic contribution inherent to the Hartree–Fock level of approximation. Already in 1991, Kutzelnigg and co-authors in the known review[10] noted the poor results of ^{13}C NMR magnetic shielding calculations for CS_2 or COS. Numerous difficult cases were also found for the phosphorus compounds involving multiple bonds. These were, for instance, low-coordinated phosphorus (III) compounds,[11–13] for which the good description of the isotropic magnetic shielding for the ^{31}P nuclei (σ_{iso}(P)) could not be achieved, even at the MP2 level of approximation.[14] In order to improve the agreement of the ^{31}P NMR calculated data with the experiment, Chesnut[15] proposed to employ an empirical correction for the σ_{iso}(P) values calculated at the MP2 level. The further improvement of the calculation results is only possible by taking into account electron correlation effects at the considerably high level of theory. Such high demands are often unrealizable even for rather small structures, due to the computational restrictions. On the other hand, the procedures of the NMR magnetic shielding calculations, which operate with the electron correlation at the high level of theory, have been practically developed only in the last years,[16–22] and to date are still not implemented into the known commercial and free quantum chemical program packets. An increasing interest to the calculations of the NMR magnetic shielding is also demonstrated in a new monograph.[3]

In the last few years, a development of the modern effective procedures has significantly reinforced the capabilities of the quantum chemistry programs. An example of one such successful innovation is the resolution of the identity (RI) algorithm,[23] which provides an approximate calculation of the majority of the many-center integrals. This makes it possible to perform geometry optimizations for rather large structures at the RI-MP2 level of approximation and to perform more rapid DFT calculations for the very large structures, including the calculations of the NMR chemical shifts. But the RI is still an approximation, and to date it is not clear how the inaccuracies in the geometry and density matrix created using the RI influence the calculated NMR magnetic shielding values. Another question was if the ^{13}C shielding can be analyzed using this approximation for the calculation of the difficult cases and the satisfactory agreement with the experiment can be achieved. To date, a number of continuum models have been included in the modern quantum chemistry program packets; hence the solvent effect on the NMR chemical shifts could be also analyzed by the calculations.

This work is the first attempt to model systematically the structure and ^{13}C NMR magnetic shielding for the large series of the compounds involving C=S double bond using different quantum chemistry methods. The results obtained using the GIAO[4] method at the different levels of approximation are compared. The Hartree–Fock level of theory, two different DFT methods (the "pure" BP86[24,25] and the popular hybrid B3LYP[26] functionals) as well as the Møller–Plesset perturbation theory,[27] have been tested, both within the RI approximation and without it. The choice of the structures for investigation was determined by our wish to perform calculations for the different classes of the known thiocarbonyl compounds. On the other hand, we were restricted by the available experimental ^{13}C NMR chemical shift values. We knowingly analyzed the calculated chemical shift magnitudes (δ_C), in contrast to the directly computed isotropic magnetic shielding values (σ_{iso}). The experimental $\sigma_{iso}(^{13}C)$ values are known only for the few number of the chemical compounds and, thus, a clear comparison of the calculated data with the experiment could not be provided. An additional stimulus was the fact that the numerous thio-analogues of the carbonyl compound are still not synthesized and remain a challenge for the chemists.[28] The calculated ^{13}C NMR data could help to discover and to identify some short-living species if they are generated in solution and stable enough long for the registration of the ^{13}C NMR spectra.

EXPERIMENTAL

^{13}C NMR Spectra

^{13}C spectral data were taken from the Aldrich/ACD Library of FT-NMR Spectra[29] or from the literature.[30–33] A spectrum for thioacetamide was recorded using the Bruker AVANCE 400 NMR spectrometer (B_0 = 9.4 T; 100.4 MHz for the carbon nuclei) in DMSO-d_6 as a solvent. The following acquisition parameters were used: a 30 degrees acquisition pulse (4.6 μs), a relaxation delay 10 sec, and the WALTZ-16 impulse proton decoupling.[34] The chemical shift values were measured relatively to the central peak of the DMSO-d_6 multiplet (39.45 ppm in the δ scale from tetramethylsilane). The ^{13}C-MAS NMR spectra were recorded using the Bruker AVANCE 400 NMR spectrometer and 4 mm zirconium dioxide rotors for the sample preparation. A standard HPDEC one-pulse acquisition sequence was used for the data accumulation. The 90 degree pulse (4 μs) was used for the FID acquisition, the relaxation time 60 sec was chosen. The speed of the rotor rotation was 5 kHz. A high power decoupling modus was used. The chemical shift values were transformed into δ scale from tetramethylsilane using the high-frequency signal from the adamantan powder sample (38.56 ppm, CH_2).[35]

Details of Calculations

All investigated structures were optimized using the TURBOMOLE[36] program set without any symmetry restrictions. The TZV basis sets[37] of triple-zeta quality were used: (14s9p)/[5s4p] for S, with contraction {73211/6111}; (11s6p)/[5s3p] for C, N, O and F contracted as {62111/411} and (5s)/[3s] for H with contraction {311}]. The basis sets were additionally expanded by addition of the polarization functions as in the standard TZVP basis sets (TURBOMOLE). These meant the above-mentioned TZV basis sets plus one set of three p-functions for hydrogen and one set of five d-functions for other elements. Such a choice was determined by the relatively high quality of the TZVP basis sets, which, on the other hand, can still be used for calculations of the fairly large structures. The structures were first optimized using the DFT RI-BP86[24,25] and B3LYP approaches. The latter involved the three-parameter hybrid functional involving the correlation functionals from Becke,[26] Lee, Yang, and Parr,[38] and VWN5.[39] The high integration accuracy (grid = 5) and convergence criterion 1×10^{-8} (scfconv = 8) were used for calculations using both mentioned methods. The resulted equilibrium structures were re-optimized at the RI-MP2 level of theory[40] (using the frozen core approximation) within the symmetry point group achieved at the DFT level of theory. In order to check the structures to be the local minima in energy, the vibrational analyses were performed at the RI-BP86 level of theory [and sometimes also at the B3LYP and/or RIMP2(fc) level of approximation], calculating the first and second derivatives analytically (see Supplementary Material). Finally, all the structures were re-optimized at the MP2(fc) approximation level using the GAUSSIAN-03 program set.[41] The 6-311+G(d,p) basis sets were used by default [meaning the 6-311G Pople basis sets[42] for hydrogen and the second period atoms (C, N, O, F) and the (12s,9p) McLean–Chandler[43] basis sets for sulfur and chlorine extended with the corresponding polarization and diffuse Gauss functions].

The NMR magnetic shielding calculations were performed using the GIAO routine[4] implemented into the TURBOMOLE program set,[44–46] the TZVPP basis sets, and the RI-BP86, B3LYP, and RI-MP2(full) levels of approximation. The TZVPP basis sets were the products of extension of the above-mentioned TZV basis via addition of two sets of the p-type and one set of the d-type polarization functions for hydrogen and two sets of the d-type and one set of the f-type polarization functions for all heavy atoms. The geometries obtained at the same level of theory but with the smaller (TZVP) basis set were used for the magnetic shielding calculations. In the cases of the especially high molecular symmetry, the latter was reduced to the nearest Abel's group (due to the peculiarities of the GIAO routine implemented into the TURBOMOLE packet). Additionally the magnetic shielding calculations were performed with the GAUSSIAN-03 program set at the MP2(full)/6−311+G(2d,p)//MP2(fc)/6-311+G(d,p) level of theory. For **25**, the orientation of the principal axes of the magnetic shielding was analyzed using the IOp33(10=1) option for the extended output. The Euler's angles were calculated as the arccos of the corresponding eigenvectors of the shielding tensor. Since the σ_{iso} magnitudes calculated at the RHF level of theory were also available from the RI-MP2 calculation data, they were also considered for completeness. The calculated σ_{iso} values were converted into δ scale using the σ_{iso} values for $Si(CH_3)_4$ corresponding to 0 ppm in the $\delta(^{13}C)$ scale and calculated at the same levels of theory as the investigated structures [194.1, 182.5, 183.7, 198.2, 197.2 ppm for the RHF/TZVPP, RI-BP86/TZVPP, B3LYP/TZVPP, RI-MP2(full)/TZVPP, and MP2(full)/6-311+g(2d,p) levels of approximation, respectively]. These values essentially differed from the experimental one [$\sigma_{\text{iso}}(C) = 188.1$ ppm].[47] The solvent effects were taken into account using the COSMO[48,49] procedure implemented into the TURBOMOLE program set.

The calculation of the density matrix was performed using the GAUSSIAN program set at the RHF/6-31G*//MP2(fc)/6-311+G** level of theory. The molecular orbitals were presented with the MOLDEN program.[50] The VMD program packet[51] was used for the graphical presentation of the calculated structures.

RESULTS AND DISCUSSION

The investigated structures in their favored conformations, obtained by geometry optimization, the experimental δ_C values for the C=S carbon nuclei, and those calculated at the RI-MP2 и RI-BP86 level of approximations are shown in Figure 1. The plots of the calculated [δ_C(calc.)] versus observed [δ_C(exp.)] chemical shift values are presented in Figure 2.

The complete experimental and calculated data are collected in Table S1 of the Supplementary Material. The scale of the ^{13}C NMR chemical shifts for the usual organic compounds covers approximately 250 ppm. Taking into account the above-mentioned specificity of the

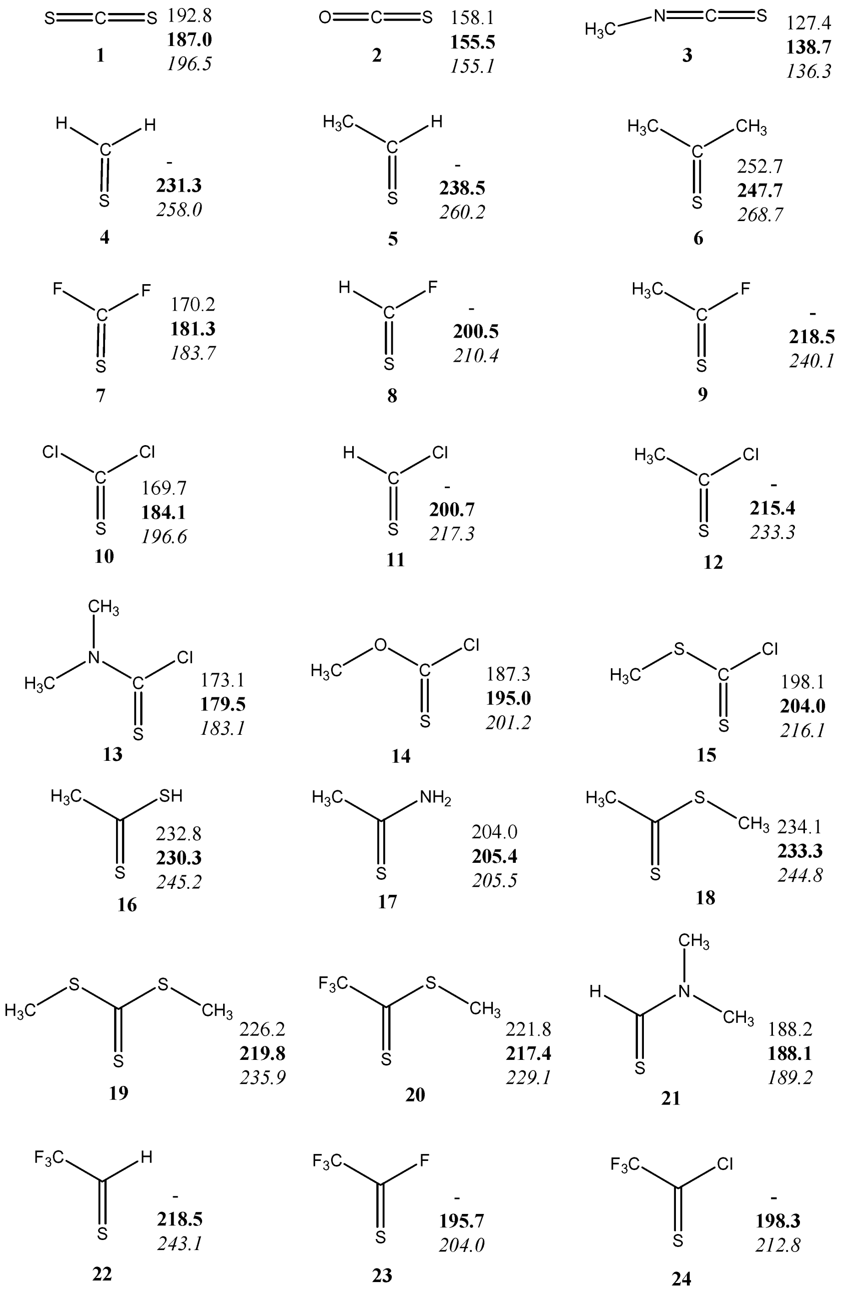
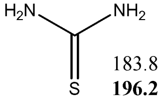
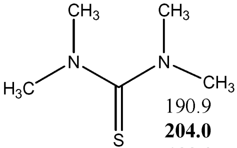


FIGURE 1 The experimental ^{13}C NMR chemical shift values (above) and δ_C magnitudes calculated at the RI-MP2/TZVPP (in the middle) and RI-BP86/TZVPP level of approximation (below) for the investigated series of thiocarbonyl compounds. *(Continued)*



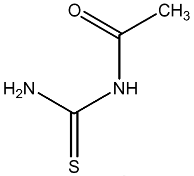
183.8
196.2
188.8

25



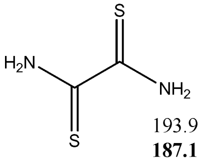
190.9
204.0
199.0

26



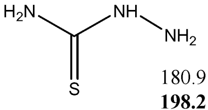
181.5
187.3
182.9

27



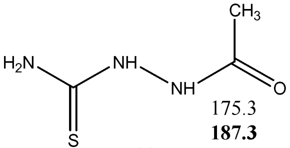
193.9
187.1
188.1

28



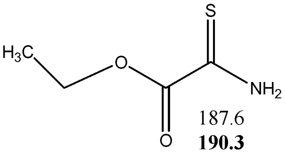
180.9
198.2
191.9

29



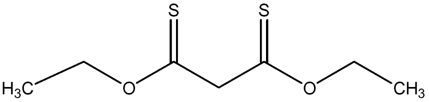
175.3
187.3
189.6

30



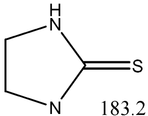
187.6
190.3
188.6

31



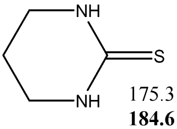
213.1
214.2, 218.0
218.9, 223.2

32



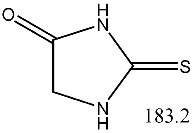
183.2
194.6
188.9

33



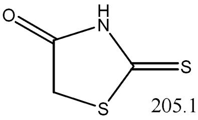
175.3
184.6
179.1

34



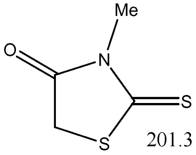
183.2
188.8
183.2

35



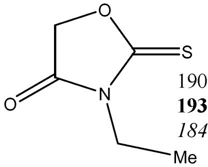
205.1
199.8
204.4

36



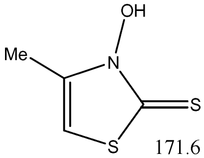
201.3
200.9
205.8

37



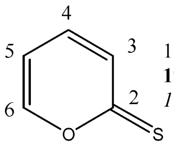
190.5
193.8
184.7

38



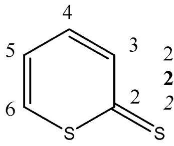
171.6
171.3
175.8

39



196.9
197.1
198.4

40



205.2
203.3
209.9

41

FIGURE 1 (Continued.)

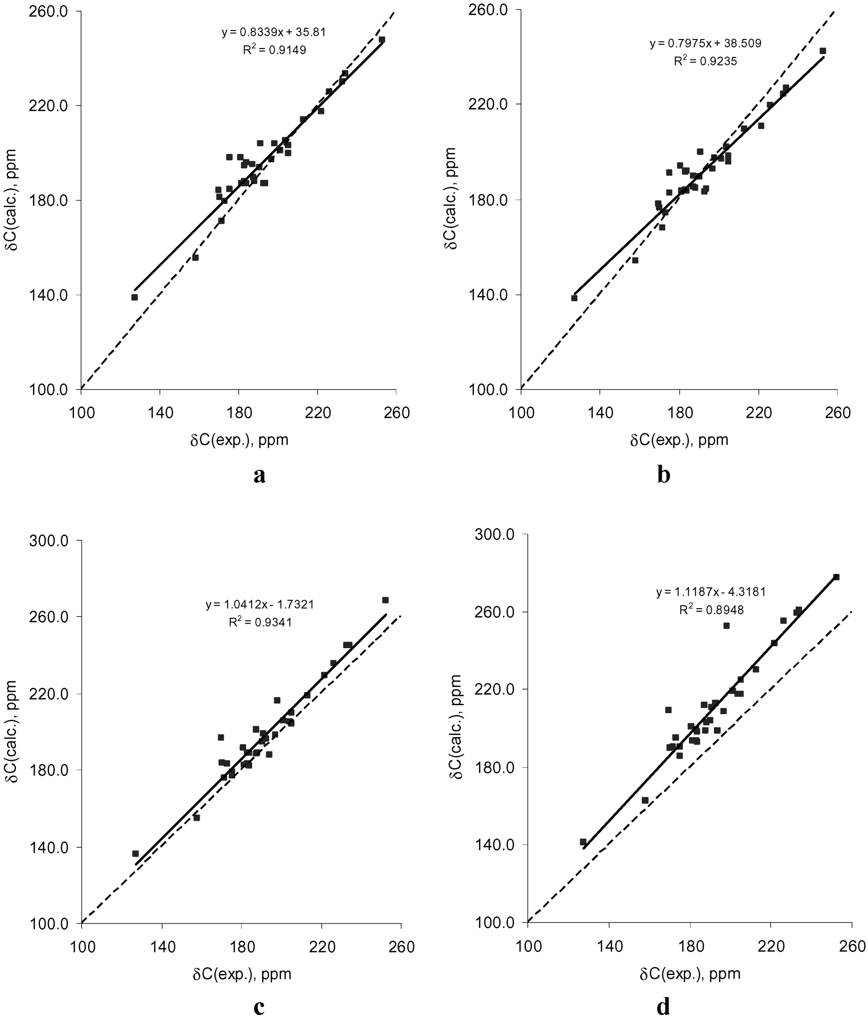


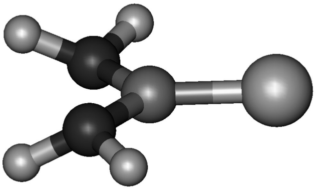
FIGURE 2 Calculated (δ_C(calc.)) versus observed (δ_C(exp.)) chemical shift values for thiocarbonyl carbon nuclei [RI-MP2/TZVPP (**a**), MP2/6-311++G(2d,p) (**b**), RI-BP86/TZVPP (**c**), B3LYP/TZVPP (**d**)]. The $y = x$ lines reflecting the desired fit are also added.

thiocarbonyl compounds and the level of the approximations used for the calculations (neglecting the solvent and vibration effects on the NMR resonance, low level of the electron correlation treatment, etc.), declinations below 5 ppm (approximately 2% from the total δ scale) have been considered to be acceptable. The magnitudes calculated with the error within the range of 5–10 ppm (2–4%) are marked in Table S1 with italics. The deflection exceeding 10 ppm (more than 4%) are shown with bold/italics.

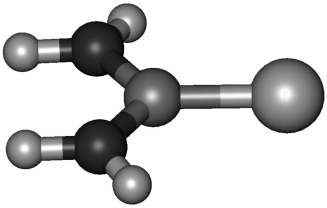
The NMR magnetic shielding values have been calculated at the RHF level using the structural parameters optimized with the RI-MP2 method (see Table S1). Significant discrepancies have been found for these data in comparison with the experimental values. As expected, the largest overestimations of the δ_C magnitudes are inherent to the thiocarbonyl carbon nuclei. The error grows with the increasing absolute δ_C. This is a feature of the RHF approximation level overestimating systematically the paramagnetic contribution into the ^{13}C magnetic shielding values (for instance, this exceeds 65 ppm for compound **7**). The usage of the "pure" (BP86) and hybrid (B3LYP) DFT functionals yields essentially different results. For the latter method, the significant overestimation of the δ_C values is also obvious (all the data points are above the $y = x$ line in Figure 2a). The HF exchange interaction term being the part of the B3LYP functional is probably responsible for the observed discrepancy with the experiment. At the same time, the "pure" BP86 method, even by using the RI algorithm, better describes the δ_C values (Figure 2b) and in general provides a satisfactory agreement with the experimental data (Figure 1). But in some cases, the RI-BP86 method also yields big differences between the calculated and observed δ_C values. This is not unexpected because of the poor description of the correlation effects within the DFT approximation. Especially large deviations of the calculated data have been found for the cases with the most deshielded carbon nuclei (as for example for **4–7**). Changing to the more superior RI-MP2 method (both for the structure optimization and for the magnetic shielding calculation) significantly improves the results also for these cases. This is noteworthy—for the majority of the thiocarbonyl compounds (in particular, for thioketones, thioesters, dithioesters, and thioamides) the deviations of the calculated data from the experimental chemical shift magnitudes do not exceed 5 ppm. Too large chemical shifts have been predicted at all investigated levels of theory for the halogen derivatives $Hal_2C(=S)$ (**7,10**). However, it should be noted that the experimental data obtained for $F_2C=S$ **(7)** and $Cl_2C=S$ **(10)**[52] are referred to the neat liquids diluted only by 30–40% of $CFCl_3$, which was used as the internal standard for the δ_C measurement. Something of better coincidence with the experiment seems to be achieved at the RI-free MP2(full)/6311++G(2d,p)//MP2(fc)/6-311++G(d,p) level of approximation. However, the σ_{iso} values calculated under the same conditions and with the same geometrical parameters but using the TZVPP basis sets (σ_{iso} = 17.7 and 13.7 ppm for structures **7** and **10,** respectively) were close to those obtained at the RI-MP2/TZVPP level of theory (16.9 and 14.1 ppm). Hence, the combination of the MP2 routine with the 6-311++G(2d,p) basis sets accidentally compensates the shortcomings arising from both of them. The even worse agreement with the experiment has been found for the data calculated at the DFT levels of theory for X-C(=S)-Hal (structures **7, 10, 13–15**). These methods are probably not suitable for calculations of the NMR parameters for such structures.

The deshielding for the C=S carbon nuclei for the thiourea **(25–27, 33, 34)** and thiosemicarbazide **(29,30)** derivatives are significantly overestimated at all used levels of theory. The most critical cases are structures **29,30**, for which the absolute errors exceed, respectively, 18 and 22 ppm. The recalculation made for these species at the MP2(full)/6-311+G(2d,p)//MP2(fc)/6-311+G(d,p) level of approximation only slightly decreases the discrepancy down to 14 and 16 ppm, respectively. Since the 6-311+G(d,p) and TZVP basis sets as well as the 6-311+G(2d,p) and TZVPP are comparable in size and quality, the geometry calculations using the pure MP2 method demonstrate no advantages in comparison with the RI approximated approach. The former something better describes magnetic shielding for the thioureas and thiosemicarbazides but yields the worse results for some other cases (for instance, for **4–6**). Taking the solvent effect into consideration (using COSMO routine implemented into the TURBOMOLE program set[49]) only on the step of the magnetic shielding calculations does not improve the agreement as well. At the same time, the δ_C values calculated for the predetermined planar (C_{2v} symmetrical) structures [187.1 and 183.6 ppm at the RI-MP2/TZVPP//RI-MP2(fc)/TZVP and MP2(full)/6-311+G(2d,p)// MP2(fc)/6-311+G(d,p), respectively] agree well with the experiment ($\delta_C = 183.8$ ppm).[53] Gas phase calculations at the all used levels of theory (up to the RI-CCSD/TZVP) yielded C_2 symmetrical structure with the pyramidalized amino groups [the sum of the valence angles at nitrogens for the structure calculated at the RI-MP2/TZVP is 345.6°; see Figure 3].

The different conformations were recently discovered for thiourea in the gas phase (C_2 symmetrical structure with the pyramidalized amino groups) and in the solid state (planar),[54,55] but no reliable data exist concerning the structure of thiourea in solutions. We have optimized the thiourea molecule surrounded with six molecules of dimethylsulfoxide at the RI-BP86/TZVP level of theory. In the course of optimization, it has become clear that only four of the solvent molecules are effectively bound via NH· · ·O=S hydrogen bonds to thiourea. The latter adopts a planar structure (Figure 4).



25a



25b

FIGURE 3 VMD representation of the optimized (RI-MP2/TZVP) structure of thiourea in the gas phase approximation (**25a**) and the X-Ray determined structure[57] (**25b**). The most important structural parameters for **25a** (bond lengths in Å, angles in degrees; in parenthesis the corresponding values for **25b** are listed): C=S 1.764 (1.690); C-N 1.372 (1.328) NCS 123.5 (121.5); HNCS -12.2 (7.8) and -149.9 (178.0).

The ^{13}C NMR shielding value calculated for such adduct at the BP86/TZVPP//RI-BP86/TZVP level of approximation (184.7 ppm) is in excellent agreement with the experimental value in the DMSO-d_6 as a solvent (183.8 ppm). Geometry optimization at the MP2(fc) level of

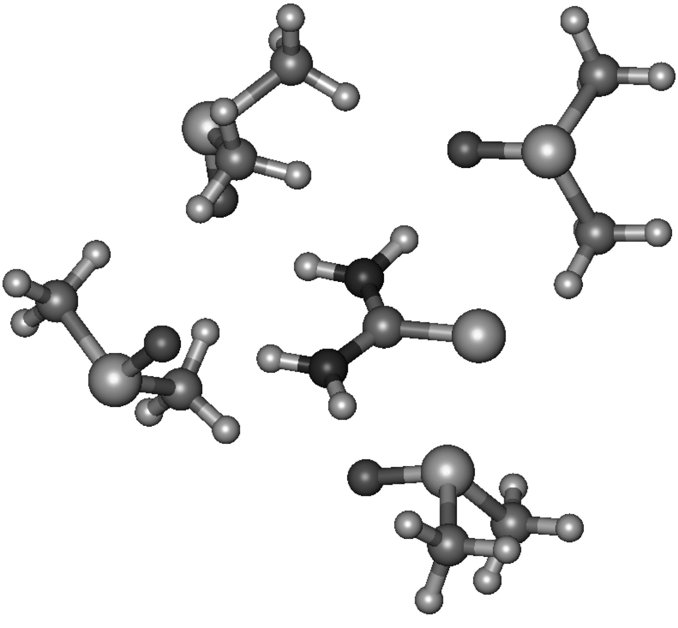


FIGURE 4 VMD representation of the optimized (RI-BP86/TZVP) structure of thiourea solvated by four molecules of DMSO.

theory, including the CPCM (COSMO)[56] procedure involved into the GAUSSIAN program set, yields an almost planar conformation, too. The δ_C value calculated for this equilibrium structure (190.2 ppm) is closer to the experimental magnitude than that found for the C_2 symmetrical conformation within the gas phase approximation (192.1 ppm), while the deviation of about 6 ppm is still significant. In the solid state, the conformation can be influenced by the intermolecular interactions and/or crystal packing effects. We have elucidated both the experimental and theoretical δ_C values for the solid state. ^{13}C NMR MAS spectra have been recorded for the powder samples of thiourea (Figure 5) and thiosemicarbazide.

The isotropic chemical shift values do not essentially differ from those obtained in DMSO-d_6. As the last step we have decided to calculate the ^{13}C chemical shifts for the molecular geometries of **25** and **29** obtained by the single-crystal X-ray investigation.[57] The calculated δ_C value for thiourea (188.2 ppm) is slightly overestimated in comparison with that found for the powder sample (181.4 ppm). The δ_C values calculated using the experimental structure for thisemicarbazide (189.5 and 187.3 ppm for RI-MP2 and MP2 approximation levels) differ even stronger from the magnitude from the ^{13}C NMR MAS experiment (177.4 ppm), but these results are in a better agreement with the experiment than those calculated for **29** within the gas phase approximation. Thus, the reason for the observed discrepancies between the calculated and experimental δ_C values is not a poor approximation level by geometry optimizations and/or by the magnetic shielding calculations, but the different structures of thiourea and thiosemicarbazide derivatives in the gas phase (nitrogens are pyramidal), solid state, and solution (a planar environment of the nitrogen atoms).

We explain the distortion of the planar structure in the gas phase as follows: for the C_{2v} symmetrical structure, the orbital energies for the highest occupied molecular orbital (HOMO) and next in energy MO (HOMO-1) (Figure 6) are practically identical. The $C_{2v} \rightarrow C_2$ distortion slightly decreases the HOMO-1 orbital energy and more significantly decreases the energy of the LUMO. Following a traditional interpretation scheme,[58,59] an observed paramagnetic shift arises due to the mixing of the HOMO that is mainly a sulfur lone pair with the low-lying π^* MO (LUMO, Figure 6). This could be achieved due to the rotational effect of the magnetic tensor component directed along the C=S bond, mixing these orbitals.

Indeed, the LUMO possesses a large contribution of the carbon atom orbitals and could be responsible for the paramagnetic deshielding. The strength of the arising paramagnetic current essentially depends

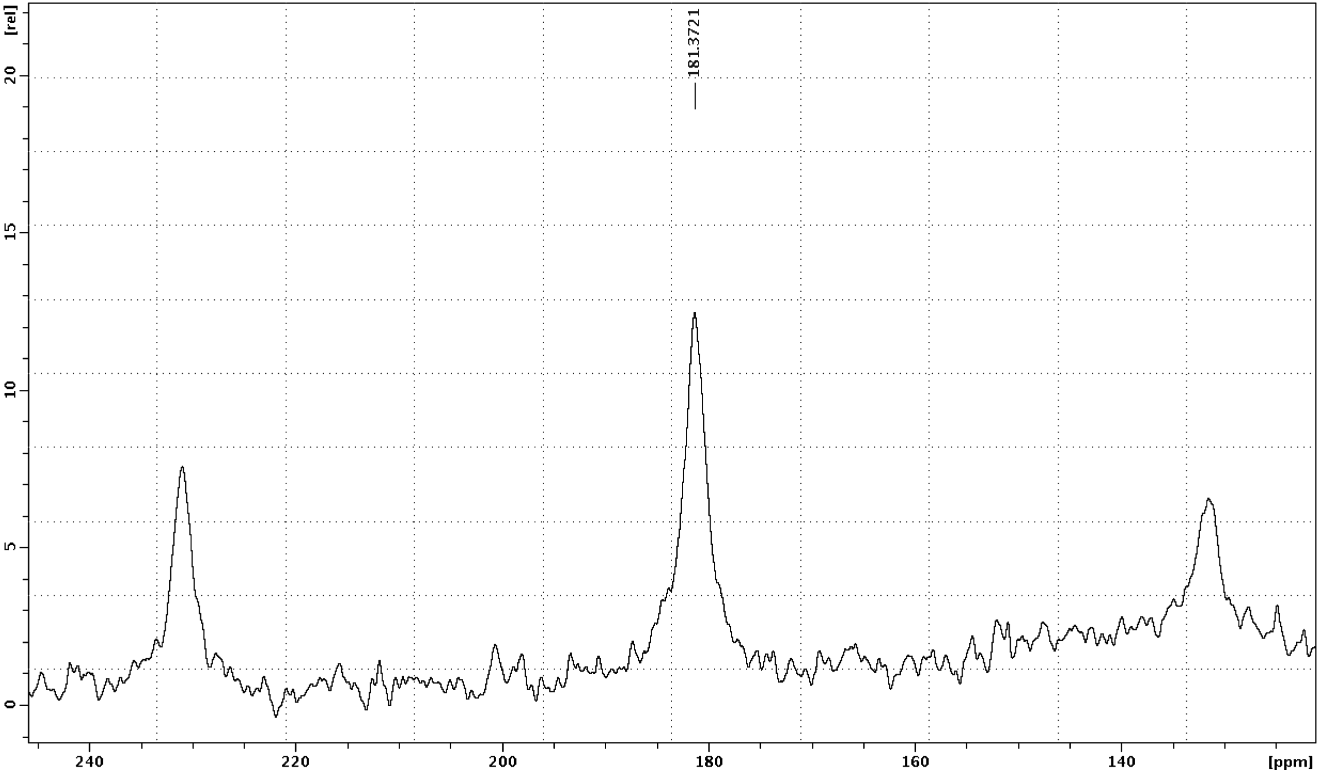


FIGURE 5 Solid state ^{13}C NMR MAS spectrum of thiourea (**25**).

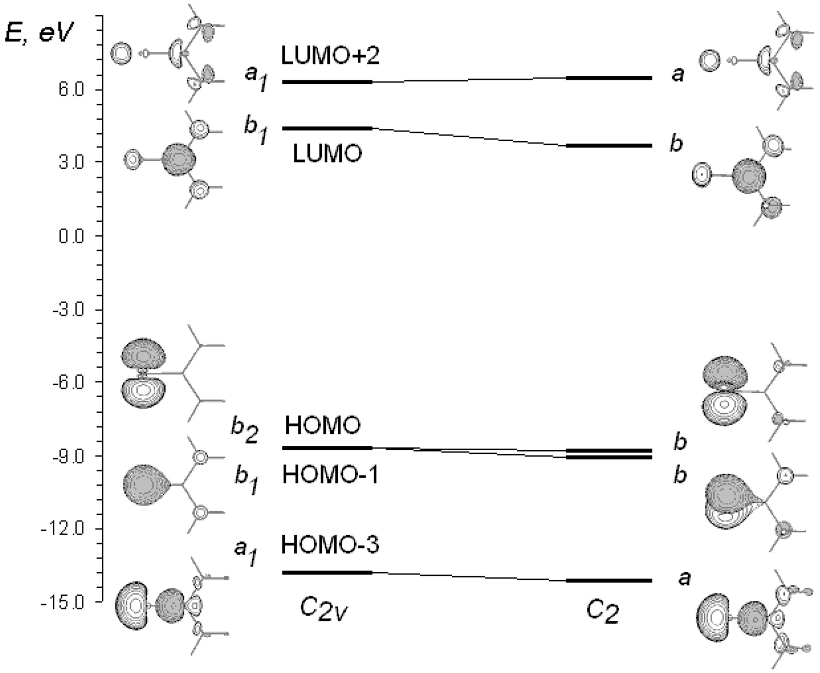


FIGURE 6 Graphical representation of the calculated (RHF/6-31G(d)//MP2(fc)/6311+G(d,p)) molecular orbitals for the C_{2v} and C_2 symmetrical structures of thiourea.

on the HOMO–LUMO energy splitting[58] that decreases by the $C_{2v} \rightarrow C_2$ structural distortion (Figure 6). However, while the contribution of the HOMO–LUMO (or LP(S)-π^*) transition into the paramagnetic deshielding can not be neglected, such an interpretation of the observed effect in thiourea is not correct, because the HOMO is strongly localized on the sulfur atom. The previous solid state NMR investigations and magnetic tensor calculations performed for the structurally similar thioamides demonstrated that the most low-field contribution (δ_{11}) came from the tensor component lying in the molecular plane and being orthogonal to the C=S bond.[35] Only the second deshielding component (δ_{22}) is directed along the C=S bond. The most shielding component (δ_{33}) is then orthogonal to the molecular plane. Our calculations yield a similar orientation of the magnetic shielding tensor components for thiourea (Table I).

Moreover, the ^{13}C nuclei deshielding arising by the C_{2v}–C_2 molecular distortion in thiourea along the δ_{11} axis (+73 ppm) is almost twice as large as that along the δ_{22} direction (+41 ppm). As suggested by Kirby

TABLE I

δ_C values[a]	C_{2v}	C_2
δ^b_{iso}	183.5	220.5
δ_{11}	309.1	382.4
Orientation	In the N_2CS plane, orthogonal to the C=S bond	Deviates by 2.9° from the N_2CS plane
δ_{22}	162.6	203.7
Orientation	Along the C=S bond	Along the C=S bond
δ_{33}	78.9	75.5
Orientation	Orthogonal to the N_2CS plane	Orthogonal to the δ_{11} and δ_{22} axes

[a] The calculated chemical shielding tensor principal components have been converted into the δ scale using the absolute ^{13}C shielding in TMS (197.2 ppm). calculated at the same level of approximation [MP2(full)/6-311+G(2d,p)//MP2(fc)/6-311+G(d,p)].

[b] $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$.

et al.,[35] the dominant contribution into the paramagnetic deshielding probably comes from the lower lying occupied σ-MOs and σ–π^* transitions (for example, HOMO-2 – LUMO, Figure 6), because both these MOs possess large contributions from the carbon atom orbitals. The C_{2v}–C_2 molecular distortion stabilizes the π^* MO (LUMO, ΔE= –0.70 eV) more than the highest σ-MO (HOMO-2, ΔE= −0.29 eV). This decreases the σ–π^* energy gap and hence yields increased paramagnetic deshielding and larger δC value for the C_2 symmetrical conformation in comparison with the ^{13}C NMR resonance for the C_{2v} symmetrical structure found in the experiment.

NMR Chemical Shift Prediction for the C=S Carbon Nuclei in the Hypothetical Thiocarbonyl Compounds

Several members of the considered series are not stable and therefore could probably be trapped only in the solution by the low temperature as the short-living compounds and characterized by means of the NMR spectroscopic methods. A successful attempt to calculate the ^{13}C NMR chemical shifts for the known thiocarbonyl compounds makes it possible to predict the δ_C values for some hypothetical and unstable derivatives, too. In the current work we content ourselves with fluoro- and chloroanhydrides of the thioformic, thioacetic, and trifluorothioacetic acids (**8,9,11,12,23,24**), as well as with the corresponding thioaldehydes (**4,5,22**) (Figure 1). Similarly to the thioketones considered above, the large differences have been found for the δ_C values calculated for the thioaldehydes using two different DFT methods (RI-BP86 and B3LYP) and both the MP2-based levels of theory. Taking into account the discussion above, the δ values calculated using the MP2 approach should be considered as the most reliable ones. The same conclusion can be derived also for the series of thiocarbonyl halogenides, because the both DFT methods poorly describe the ^{13}C NMR chemical shifts for the known derivatives of this series.

CONCLUSIONS

The calculations performed for the large series of the thiocarbonyl compounds allow us to recommend the MP2 level of approximation in combination with the mediate size basis sets as the reliable instrument for the prediction of the ^{13}C NMR chemical shifts for structures involving the thiocarbonyl group. In the most cases, the BP86 functional works enough well, too, with only exceptions for the thioaldehydes, thioketones, and halogenanhydrides of the thioacids. The inclusion of the RI approximation into the BP86 or MP2 calculations, both at the step of the geometry optimization and for the density matrix calculation used further for the magnetic shielding calculation, does not make the final results worse. The "pure" MP2 method demonstrates no advantages in comparison with the RI-MP2 routine. But the RI algorithm reduces the computational time by calculations of the real large structures. The HF approximation level in the pure form produces magnitudes with the extremely large deviation from the experimental data. Similarly, the popular hybrid functional B3LYP is not recommended for the δ_C value calculations for the thiocarbonyl compound class, because it provides the strong overestimation of the C=S carbon nuclei deshielding, too. Presumably this overestimation for the discussed hybrid functional is caused by the description of the electron exchange correlation within the Hartree–Fock approach. A bad agreement for the calculated δ_C values with the experiment found for the thiourea and thiosemicarbazide derivatives we explain by conformational effects, but not by the imperfection of the tested calculation approaches. In the gas phase thiourea possesses the C_{2v} symmetrical structure, while in solution and in solid state the C_{2v} symmetrical conformation is more stable. The paramagnetic shift observed by the C_{2v}–C_2 molecular distortion for thiourea is referred mainly to the σ–π^* transitions initialized by the rotating magnetic field and, to a lesser extent, to the LP(S)–π^* transitions. Taking into account the solvent effects significantly decreases the differences between the calculated and experimental NMR data.

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