UNIVERSITY OF PLOVDIV
“PAISII HILENDARSKI”

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DEPARTMENT “ANALYTICAL CHEMISTRY AND COMPUTER CHEMISTRY”

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NMR and vibrational spectra assignment for verification and elucidation of the structures of aromatic organic and metal-organic coordination compounds

SYNOPSIS

for acquiring the educational and scientific degree „doctor”
in the field of higher education: 4. Natural sciences, mathematics and informatics;
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The dissertation was discussed and suggested for defense at an extended meeting of department “Analytical chemistry and Computer chemistry”, Faculty of Chemistry, University of Plovdiv “Paisii Hilendarski”.

The dissertation contains 144 pages, from which 133 in its main part and 11 pages for bibliography. The bibliography list includes 157 sources, from which 4 are written in Cyrilic alphabet and 153 are written in Latin alphabet.

The list with publications is consisted of 4 titles.

The defense of the dissertation will be held on 05.11.2025 г. from 11.00 h. in the meeting room of the Rectorate of Plovdiv University “Paisii Hilendarski”, str. „Tsar Assen “24, Plovdiv. The materials for the defense are available at the department “Development of scientific staff and PhD programs” and are published on the website of Plovdiv University “Paisii Hilendarski” – https://procedures.uni-plovdiv.bg.

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CONTENTS

INTRODUCTION

Spectral assignments find application in two main directions. One of them is the enrichment of scientific literature with spectral data assigned for novel or known compounds from different classes for which there are no or there are only partial and/or insufficiently reliable spectral assignments. The other direction is the development and enrichment of spectral databases which can be used for structure search and/or spectra simulation. In both cases, structures of interest should be reliably verified or elucidated due to which the assignment of 1D and 2D NMR spectra appears to be one of the main approaches applied for reliable structure determination.

Aim and tasks

The aim of the thesis is to provide fully assigned NMR data, supported by partially assigned vibrational data, for novel and known organic compounds from different classes, for which there is not or there is only partially and/or mistakenly assigned NMR and vibrational data in the literature.

For achieving the aim, the following tasks were completed:

1. To fully assign *1D (^{1}H and ^{13}C)* and *2D (^{1} H- ^{1}H COSY, HMQC, HMBC and ^{1}H-^{1}H NOESY*) NMR spectra for verifying the structures of three substituted fluorenylspirohydantoins - *1',3'-bis(hydroxymethyl)-2'H,5'H-spiro[fluorene-9,4'-imidazolidine]-2',5'-dione (I) and 2-bromo-2'H,5'H-spiro[fluorene-9,4'-imidazolidine]-2',5'-dione. (II), 5'-oxospiro-(fluorene-9,4'-imidazolidine)-2'-thione (III).*
2. To fully assign *1D (^{1}H and ^{13}C)* and *2D (^{1} H- ^{1}H COSY, HSQC, HMQC, HMBC*) NMR spectra for verifying the structures of three substituted naphtopyranones - *3-[(4-methoxyphenyl)methylidene]-1H,3H-naphtho[1,8-cd]-pyran-1-one (IV), 3-[(4-fluorophenyl)methylidene]-1H,3H-naphtho-[1,8-cd]-pyran-1-one (V) and 3-[(thiophen-3-yl)methylidene]-1H,3H-naphtho[1,8-cd]-pyran-1-one (VI).*
3. To fully assign *1D (^{1}H and ^{13}C)* and *2D (^{1} H- ^{1}H COSY, HSQC, HMBC*) NMR spectra for verifying the structures of 2,4-dithiouracil *(VII)* and 2-thiouracil *(VIII).*
4. To fully assign *1D (^{1}H and ^{13}C)* and *2D (HSQC*) NMR spectra for elucidating the structures of some metal complexes of *Cu(II) (X) and Au(III)(IX) with 2,4-dithiouracil (VII) and its oxoderivatives (2-thiouracil (VIII) and uracil).*
5. To fully assign *1D (^{1}H and ^{13}C)* and *2D (^{1} H- ^{1}H COSY, HSQC, HMBC*) NMR spectra for verifying the structures of four dispiroimidazolidines - *3-(2'-oxospiro[1,2,3,4-tetrahydro-1,4-diazepine-7,3'-indoline]-5-yl)spiro[imidazolidine-5,1'-tetralin]-2,4-dione (XI), 3-(2'-oxospiro[5H-1,5-benzothiazepine-4,3'-indoline]-2-yl)spiro[imidazolidine-5,1'-tetralin]-2,4-dione (XII), 3'-(2'-oxospiro[5H-1,5-benzothiazepine-4,3'-indoline]-2-yl)spiro[fluorene-9,5'-imidazolidine]-2',4'-dione (XIII), 4-(8-propyl-2,4-dithioxo-1,3-diazaspiro[4.5]decan-3-yl)spiro[1,5-dihydro-1,5-benzodiazepine-2,3'-indoline]-2'-one (XIV)*
6. To fully assign *1D (^{1}H and ^{13}C)* and *2D (^{1} H- ^{1}H COSY, HSQC, HMQC, HMBC*) NMR spectra for verifying the structures of *2-[2,2,2-trichloroacetyl]amino]benzamide (XV)* and its six derivatives *(XVI - XXI).*
7. To fully assign *1D (^{1}H and ^{13}C)* and *2D (^{1} H- ^{1}H COSY, HSQC, HMBC*) NMR spectra for verifying the structures of *2-amino-1H-benzo[d]isoquinoline-1,3(2H)-dione (XXII) and 2-(2-hydroxyethyl)-1H-benzo[d]isoquinoline-1,3(2H)-dione (XXIII).*
8. To assign the characteristic vibrational bands from *FT-IR, ATR and Raman spectra,* confirming the presence of some functional groups in the structures of compounds.

9. To verify ^{13}C chemical shifts assigned for the signals of the carbons in naphtopyranones, 2-thiouracil, 2,4-dithiouracil and benzamides with the ^{13}C chemical shifts predicted with *HOSE* coding implemented in the online *NMRShiftDB* database.
10. To simulate the spectra of *AA'XX'*, *AA'BB', AA'BB'X*, *AA'MM'X* and *ABX* systems with the option *Spin Simulation in the MestreNova software as well as with Python NMRSim*, to predict their coupling constants and to verify the ^{1}H chemical shifts of protons in the corresponding systems.
11. To import the structures of fluorenylspirohydantoins and naphtopyranones together with the ^{1}H and ^{13}C chemical shifts assigned for their corresponding signals, ^{1}H signal multiplicity and raw 1D and 2D NMR spectra in *NMRShiftDB database (https://nmrshiftdb.nmr.uni-koeln.de/)*.

The publications on the dissertation topic along with their supplementary files containing the registered NMR and vibrational spectra of the compounds, as well as the simulated ^{1}H spectra for the three-, four- and five-spin systems can be found in **Appendix**. For each class of compounds, individual directory was made, containing the corresponding spectra and/or articles. The Appendix is presented in digital format on compact disc, attached to the dissertation.

RESULTS FROM SPECTRAL ASSIGNMENTS

Only the most interesting NMR assignments for each of the presented structures, accompanied by their assigned vibrational bands, were briefly described in the synopsis.

1.1. Methods and materials

Apparatus and conditions for registration of vibrational spectra

All vibrational spectra were measured in the Laboratory of Molecular Spectroscopy, Department of Analytical chemistry and Computer chemistry, Faculty of Chemistry, University of Plovdiv "Paisii Hilendarski". A part of them were measured by Prof. DSc Plamen Penchev and the other by Chief Assistant Dr. Slava Tsoneva.

IR spectra were registered in KBr tablets on *VERTEX 70 FT-IR (Bruker Optics)* spectrometer in the range 4000 cm^{-1} to 400 cm^{-1} at the following resolution and number of scans:

- 4 cm^{-1} and 9 scans for fluorenylspirohydantoins;
- 2 cm^{-1} and 25 scans for naphtopyranones and benzamides.

Raman spectra (stirred crystals placed in aluminium discs) were measured on *RAM II (Bruker Optics)* spectrometer with a resolution of 2 cm^{-1} and 25 scans. The power of the laser (Nd:YAG laser, 1064 nm) was:

- 50 mW for fluorenylspirohydantoins, except for compound III, where the power was 500 mW;
- 100 mW, 40 mW, 10 mW correspondingly for naphtopyranones;
- 700 mW for 2,4-dithiouracil, 300 mW for Au(III) complex and 150 mW for Cu(II) complex;

Raman spectra of benzamides were measured at resolution of 1 cm^{-1}, laser power of 200 mW and 100 scans.

Partially assigned Raman and IR data was presented in the range (4000 – 400) cm^{-1} for the corresponding compounds.

ATR spectra of the compounds I, II and III were measured from 4000 cm^{-1} to 600 cm^{-1} with *VERTEX 70 FT-IR (Bruker Optics)* spectrometer at the following resolution and number of scans:

- 2 cm^{-1} and 16 scans for I and II;
- 2 cm^{-1} and 25 scans for III, 2,4-dithiouracil, metal complexes and dispiroimidazolidines.

The ATR instrument is MIRacle™ with a one-reflection ZnSe element (Pike Technology) as the crystals were pressed by an anvil to the reflection element.

Apparatus and conditions for registration of NMR spectra

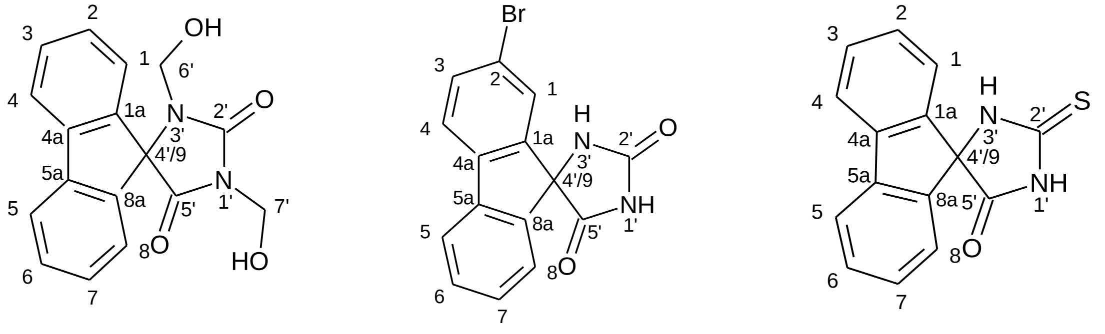
^{1}H, ^{13}C and 2D NMR spectra of fluorenylspirohydantoins, naphtopyranones, 2-thiouracil, 2,4-dithiouracil and benzamides were measured with Bruker Avance II + 600MHz NMR spectrometer with operating frequencies 600.130 MHz (^{1}H) and 150.903 MHz (^{13}C), utilizing TMS as internal standard and DMSO-d$_6$ as solvent. The measurements were conducted in the *NMR laboratory, Institute of Organic Chemistry with Centre of Phytochemistry – BAS*. NMR measurements were conducted at ambient temperature of 293.0K. Chemical shifts (δ) were expressed in ppm whereas the coupling constants (J) in Hz. 1D and 2D NMR spectra were registerd using standard Bruker pulse programs.

NMR spectra of Au(III) and Cu(II) complexes, dispiroimidazolidines and 2-amino-1*H*-benzo[*d*]isoquinoline derivatives, were measured on Bruker Avance III HD spectrometer in *NMR laboratory, Department of Organic chemistry and Pharmacognosy, Faculty of Chemistry and Pharmacy, University of Sofia, „St. Climent Ohridski" with operating frequencies* 500.130 MHz (^{1}H) and 125.76 MHz (^{13}C), respectively. Solid phase CP-MAS and CPPI-MAS spectra of complexes were measured at the same instrument with ^{13}C frequency of 500.13 MHz. α-glycine was applied as external reference (α-glycine carbonyl C-176.03 ppm) as the applied MAS speed was 15 kHz. All NMR spectra were measured at room temperature.

MestReNova software (*version 6.0.2-5475*) was used for the NMR data processing and assignment.

1.2. NMR data assignment for substituted fluorenylspirohydantoins

I, II, III (Figure 1) were synthesized by the team of Assoc. Prof. Dr. Marin Marinov and coworkers (Agricultural University – Plovdiv).



I II III

Figure 1. Suggested structures for I, II and III

^{1}H and ^{13}C NMR data assignment for I

Molecular formula of compound I is $C_{17}H_{14}N_2O_4$. DEPT 135 spectrum shows two negative signals at δ_C 63,83 ppm and 61,89 ppm, confirming the presence of methylene groups in the structure (Table 1).

Table 1. ^{1}H and ^{13}C NMR data assignment for I[a]

Atom	δ (^{13}C), ppm	DEPT	δ (^{1}H), ppm	Multiplicity (J, Hz)	^{1}H-^{1}H COSY [b]	HMBC[b]
2' (C=O)	155.34	C				
5' (C=O)	171.10	C				
6'	63.83	CH_2	4.40	d (6.7)	OH (C-6')	2', 4'/9
7'	61.89	CH_2	4.91	d (7.0)	OH (C-7')	2', 5'
4'/9	73.71	C				
1/8	124.27	CH	7.37[c]	m	2	3, 4a, 4'/9
1a/8a	140.68	C				
2/7	128.15	CH	7.35[c]	m	1.3. 4[e]	1[e], 1a, 3[d], 4
3/6	130.08	CH	7.51	td (7.4; 1.4)	2, 4	1, 2[d], 4[e], 4a
4/5	120.86	CH	7.93	d (7.6)	2[e], 3	1[e], 2, 1a
4a/5a	141,15	C				
OH (C-7')			6,57	t (7,1)	7'	7'
OH (C-6')			5,77	t (6,8)	6'	6'

[a] *In DMSO-d_6 solution. All assignments were in agreement with COSY, HMQC and HMBC spectra.*

[b] *For brevity, these correlations were given only for one of the benzene rings.*

[c] *Assigned from HMQC.*

[d] *Weak correlations.*

[e] *Extremely weak correlations.*

HMQC, (δ_{H} 4,40 ppm – δ_{C} 63,83 ppm) and (δ_{H} 4,91 ppm- δ_{C} 61,89 ppm), as well as HMBC correlations for each of the signals at δ_{H} 4,40 ppm (with δ_{C} 73,71 ppm and δ_{C} 155,34 ppm) and δ_{H} 4,91 ppm (with δ_{C} 155,34 ppm and δ_{C} 171,10 ppm), indicated that δ_{H} 4,40 ppm and δ_{C} 63,83 ppm were for the protons and carbon in $C^{6'}H_2$ групата, whereas δ_{H} 4,91 ppm and δ_{C} 61,89 ppm were for the protons and carbons in $C^{7'}H_2$ групата. Based on the strong COSY and HMBC correlations - (δ_{H} 4,40 ppm - δ_{H} 5,77 ppm), (δ_{H} 4,91 ppm - δ_{H} 6,57 ppm), (δ_{H} 5,77 ppm – δ_{C} 63,83 ppm) and (δ_{H} 6,57 ppm - δ_{C} 61,89 ppm), δ_{H} 5,77 ppm and δ_{H} 6,57 ppm were assigned respectively for the protons in OH (C-6') and OH (C-7') groups.

Vibrational data assigned for I

IR bands(KBr, cm^{-1}): 3377 (υ(CO-H)), 3331 (υ(CO-H)), 3063 (υ(C-H), arom.), 3010 (υ(C-H), arom.), 2948 ($\upsilon_{as}(CH_2)$), 2925 ($\upsilon_{as}(CH_2)$), 2900 ($\upsilon_{s}(CH_2)$), 2853 ($\upsilon_{s}(CH_2)$), 1770 (υ(C=O)), 1704 (υ(C=O)), 1081(υ(CH_2-OH), 1066, 1042, 1032 (υ(CH_2-OH))

Raman bands, (cm^{-1}): 3086 (υ(C-H), arom.), 3071 (υ(C-H), arom.), 3043 (υ(C-H), arom.), 2949 ($\upsilon_{as}(CH_2)$), 1769 (υ(C=O)), 1080 (υ(CH_2-OH)), 1023 (υ(CH_2-OH))

ATR bands, (cm^{-1}): 3372 (υ(CO-H)), 3319 (υ(CO-H)), 3063 (υ(C-H), arom.), 3011 (υ(C-H), arom.), 2948 ($\upsilon_{as}(CH_2)$), 1768 (υ(C=O)), 1699 (υ(C=O)), 1078 (υ(CH_2-OH)), 1030 (υ(CH_2-OH))

^{1}H and ^{13}C NMR data assignment for II

Molecular formula is $C_{15}H_9O_2N_2Br$. The ^{13}C NMR spectrum of II showed 15 signals, corresponding to the number of carbons in the compound (Table 2). According to the strong HMBC correlations, (δ_{H} 8,61 ppm - δ_{C} 72,16 ppm; δ_{H} 8,61 ppm - δ_{C} 157,52 ppm; δ_{H} 8,61 ppm - δ_{C} 173,56 ppm), the signal at δ_{H} 8,61 ppm was assigned for the $N^{3'}$H proton, while that at δ_{H} 11.31 ppm – for the $N^{1'}$H proton.

Table 2. ^{1}H and ^{13}C NMR data assigned for II[a]

Atom	δ (^{13}C), ppm	DEPT	δ (^{1}H), ppm	Multiplicity (J, Hz)	^{1}H-^{1}H COSY	HMBC
3' (NH)			8,61	s		2', 5', 4'/9
2' (C=O)	157,52	C				
1' (NH)			11,31	s		
5' (C=O)	173,56	C				
4'/9	72,16	C				
1	126,83	CH	7,75	s		2, 3, 4a, 4'/9[b]
1a	145,12	C				
2	121,08	C				
3	132,76	CH	7,70	dd (8,2; 1,2)	4	1, 2, 4a
4	122,63	CH	7,88	d(8,1)	3	1a, 2 , 3[b], 5a
4a	140,00	C				
5	121,05	CH	7,92	d (7,5)	6	4a, 8a, 7
5a	139,52	C				
6	130,00	CH	7,50	d(7,5)	5, 7[b]	5a, 8
7	128,81	CH	7,40	t(7,4)	6[b], 8[b]	5, 8a
8	123,54	CH	7,48	d(7,5)	7[b]	5a, 6, 4'/9
8a	142,85	C				

[a] In DMSO-d_6. solution. All assignments were in agreement with COSY, HMQC and HMBC spectra.

[b] Weak correlations.

DEPT 135 spectrum did not show signals at δ_{C} 121,08 ppm, 139,52 ppm, 140,00 ppm, 142,85 ppm and 145,12 ppm. Based on the strong meta (vicinal) interactions in benzene rings, the signals at δ_{H} 7,48 ppm and δ_{H} 7,75 ppm were assigned for H-8 and H-1 protons, whereas those at δ_{C} 130,00 ppm, δ_{C} 132,76 ppm, δ_{C} 139,52 ppm and δ_{C} 140,00 ppm were for C-6, C-3, C-5a and C-4a. Only one COSY correlation, (δ_{H} 7,70 ppm - δ_{H} 7,88 ppm), was found for H-3.

One strong HMBC correlation was found between H-3 and C-4a, (δ_H 7,70 ppm - δ_C 140,00 ppm), as well as other two strong HMBC correlations, (δ_H 7,88 ppm – δ_C 139,52 ppm) and (δ_H 7,88 ppm – δ_C 145,12 ppm), indicating the interaction of H-4 with C-5a and C-1a. There was one NOESY correlation between H-3 and H-4, (δ_H 7,70 ppm - δ_H 7,88 ppm), confirming the hypothesis that the bromine is bonded to the carbon, C-2, whose signal is at δ_C 121,08 ppm.

The NMR data fully assigned for the first two compounds was published in Special Issue *D* of *Bulgarian Chemical Communications* journal [7].

Vibrational data assigned for II

IR bands (KBr, cm^{-1}): 3349 (υ(N-H)), 3194 (υ(N-H)), 3069 (υ(C-H), arom.), 1782 (υ(C=O)), 1756 (υ(C=O)), 1717 (υ(C=O))

Raman bands, (cm^{-1}): 3071 (υ(C-H), arom.), 3050 (υ(C-H), arom.), 1763 (υ(C=O))

ATR bands, (cm^{-1}): 3354 (υ(N-H)), 3185 (υ(N-H)), 3073 (υ(C-H), arom.), 1779 (υ(C=O)), 1713 (υ(C=O))

^{1}H and ^{13}C NMR data assignment for III

Only ^{1}H and ^{13}C NMR data assigned from 1D NMR spectra exists for the structure of III that was presented in previous publication [8].

Table 3. ^{1}H and ^{13}C NMR data assigned for III.[a]

Atom	δ (^{13}C), ppm	DEPT	δ (^{1}H), ppm	Multiplicity (J, Hz)	^{1}H-^{1}H COSY[b]	HMBC[b]
3′ (NH)			10.64	s	1′	2′, 5′, 4′/9
2′ (C=S)	183.60	C				
1′ (NH)			12.39	s	3′	2′, 5′, 4′/9
5′ (C=O)	174.80	C				
4′/9	74.84	C				
1/8	123.76	CH	7.42 [c]	m	2	2,3,4a,4′/9, 5′[e]
1a/8a	141.40	C				
2/7	128.64	CH	7.39 [c]	m	1, 3	1, 1a, 3, 4, 4′/9
3/6	130.27	CH	7.52	m	2, 4	1, 2, 4, 4a, 4′/9[e]
4/5	121.07	CH	7.93	d (7.6)	3	1, 2, 3, 4′/9[d], 1a
4a/5a	140.79	C				

[a] *In DMSO-d$_6$. solution. All assignments were in agreement with COSY, HMQC and HMBC spectra.*
[b] *For brevity, these correlations were given only for one of the benzene rings.*
[c] *Assigned from HMQC.*
[d] *Weak correlations.*
[e] *Extremely weak correlations.*

Molecular formula of III is $C_{15}H_{10}N_2OS$. Both signals at δ_C 183.60 ppm and δ_C 174.80 ppm, were assigned to the thiocarbonyl and carbonyl carbon, respectively $C^{2\prime}$=S and $C^{5\prime}$=O (Table 3). In article [8] the signals at δ_C 183.60 ppm and δ_C 174.80 ppm were assigned mistakenly, as the signal at δ_C 183.60 was assigned for $C^{5\prime}$=O and that at δ_C 174.80 ppm was for $C^{2\prime}$=S. The signal at δ_C 74.84 ppm was assigned to spirocarbon, C-4′/9. The $N^{1\prime}$H proton is located between the thiocarbonyl and carbonyl group, $C^{2\prime}$=S and $C^{5\prime}$=O, thus, it will be more strongly deshielded due to their magnetic anisotropy [4] [5][10]. Consequently, the singlet at δ_H 12.39 ppm was assigned to the $N^{1\prime}$H proton, whereas that at δ_H 10.64 ppm - for the $N^{3\prime}$H proton. The NMR data fully assigned for compound III was published in *Molbank, MDPI, section Structure Determination* [18]. The structures of the three fluorenylspirohydantoins, together with the assigned ^{1}H and ^{13}C chemical shifts and ^{1}H signal multiplicity, were sent to *NMRShiftDB* database [15][16], where they were reviewed, accepted and imported.

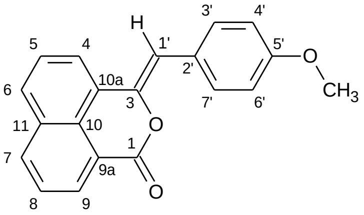
Assigned vibrational data for III

ATR bands (υ, cm^{-1}): 3244 (sh., υ_{NH}), 3153 (υ_{NH}), 3091 (υ_{CH}), 1729 (υ_{CO}), 1249 (υ_{CS})

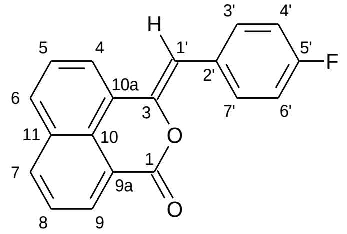
Raman bands (υ, cm^{-1}): 3067 (υ_{CH}), 3050 (υ_{CH}), 1728 (υ_{CO}), 1233 (υ_{CS})

1.3. NMR data assignment for naphtopyranones

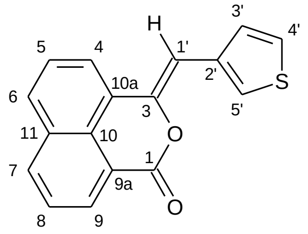
IV, V, VI were synthesized by the team of Assoc. Prof. Dr. Marin Marinov and coworkers (Agricultural University – Plovdiv) (Figure 2).



IV



V



VI

Figure 2. Suggested structures for IV, V and VI

^{1}H and ^{13}C NMR data assignment for IV

IV has a molecular formula $C_{20}H_{14}O_3$. The significantly higher intensity of the ^{13}C signals at δ_C 131,17 ppm and δ_C 114,13 ppm compared to the intensities of the other ^{13}C signals indicated that they should be assigned for carbons, C-3'/7' and C-4'/6' (Table 4).

Table 4. ^{1}H and ^{13}C NMR data assigned for IV[a]

Atom	δ (^{13}C), ppm	DEPT[b]	δ (^{1}H), ppm	Multiplicity (J, Hz)	^{1}H-^{1}H COSY [b]	HMBC[b]
1(C=O)	*159.80*	*C*				
3	*144.61*	*C*				
4	*121.57*	*CH*	*8.26*	*dd(7.6; 0.5)*	*5, 6*^{d}	*3, 10, 11*^{c}
5	*127.42*	*CH*	*7.70*	*t (7.9)*	*4,6*	*4*^{c}*, 10*^{d}*, 10a, 11*
6	*127.74*	*CH*	*8.03*	*d (8.1)*	*4*^{d}*, 5*	*4,7, 10, 10a*^{c}*, 11*^{c}
7	*134.35*	*CH*	*8.31*	*dd(8.3; 0.8)*	*8*	*9,9a*^{d}*,10a*^{d}*,10, 11*^{d}
8	*126.85*	*CH*	*7.75*	*dd (8.2; 7.3)*	*7, 9*	*9*^{c}*, 9a, 11*
9	*128.99*	*CH*	*8.29*	*dd (7.2; 1.1)*	*8*	*1, 7, 10*
9a	*119.21*	*C*				
10	*127.47*	*C*				
10a	*124.08*	*C*				
11	*132.11*	*C*				
1'	*108.19*	*CH*	*6.98*	*s*	*3'/ 7'*^{c}	*1*^{c}*,2'*^{c}*,3, 10a, 3'/ 7'*
2'	*126.79*	*C*				
3'	*131.17*	*CH*	*7.89*	*m*	*1'*^{c}*, 4'*	*1',2'*^{d}*,4'*^{c}*, 5', 7'*
4'	*114.13*	*CH*	*7.03*	*m*	*3'*	*2',5', 6', 7'*^{d}
5'	*158.75*	*C*				
6'	*114.13*	*CH*	*7.03*	*m*	*7'*	*2', 3'*^{d}*, 4', 5'*
7'	*131.17*	*CH*	*7.89*	*m*	*1'*^{c}*, 6'*	*1', 2'*^{d}*, 3', 5', 6'*^{c}
OCH$_3$	*55.18*	*C*	*3.80*	*s*		*5'*

[a] *In DMSO-d$_6$ solution. All assignments were in agreement with COSY, HMQC and HMBC spectra.*

[b] *Abbreviations: DEPT, Distortionless Enhancement by Polarization Transfer spectrum; ^{1}H-^{1}H COSY – proton-proton homonuclear correlation spectrum; HMQC, Heteronuclear Multiple Quantum Correlation experiment; HMBC, Long range ^{1}H-^{13}C Heteronuclear Multiple Bond Correlation experiment.*

[c] *Weak correlations.*

[d] *Extremely weak correlations.*

Coupling constants for the signals of the protons, H-3'/7' and H-4'/6', were determined by simulating the AA' and XX' parts of AA'XX' spectrum. Thus, the *Spin Simulation* option from MestreNova software as well as the *Python NMRSim* package were used for the simulation. The best similarity between the simulated and real AA'XX' spectrum was achieved with the following set of parameters - (δ_H 7.03 ppm for H-4'/6' (AA' part); δ_H 7.89 ppm for H-3'/7' (XX' part); $J^4_{AA'}$ = 3.8 Hz, $J^4_{XX'}$ = 3.0 Hz, J^3_{AX}= $J^3_{A'X'}$ = 7.8 Hz, $J^5_{AX'}$=$J^5_{A'X}$= 0.45 Hz). Strong HMBC correlations were found between the signals of H-3'/7' and C-1', as well as between the signals of H-1'and C-3'/7'. Also, there was an extremely weak HMBC correlation (δ_H 7.89 ppm - δ_C 126.79 ppm), due to which the signal at δ_C 126.79 ppm was assigned to carbon, C-2’. This conclusion was supported additionally by the strong HMBC correlations between the signals of the protons, H-4’ and H-6’, and the signal of carbon, C-2’. For the ^{1}H singlet at δ_H 3.80 ppm with area 2.73 the following HMQC and HMBC correlations were found, respectively, (δ_H 3.80 ppm – δ_C 55.18 ppm) and (δ_H 3.80 ppm - δ_C 158.75 ppm). The signals at δ_H 3.80 ppm and δ_C 55.18 ppm were assigned to the protons and carbon in methoxy group, -OCH_3, as the signal at δ_C 158.75 ppm – to the carbon, C-5’.

Vibrational data assigned for IV

IR bands (cm^{-1}): 3058 ((υ(C-H), arom.)), 2838 (υ(-OCH_3)), 1726 (υ(C=O)), 1626 (υ(C=C)), 1605 (υ(C=C), arom.), 1513 ((υ(C=C), arom.)), 768 (γ(C-H), arom.)

Raman bands (cm^{-1}): 3067 (υ(C-H), arom.), 1728 ((υ(C=O)), 1627 (υ(C=C)), 1604 ((υ(C=C), arom.)), 1509 (υ(C=C), arom.), 703 (γ(C-H), arom.).

^{1}H and ^{13}C NMR data assigned for V

The molecular formula of V is $C_{19}H_{11}O_2F$. It was found that F caused doubling of the signals of the carbons, C-2’, C-3’/7’, C-4’/6’ and C-5’, as well as splitting of the signal of C-3 that appeared almost as a doublet. Thus, the chemical shifts of the signals of carbons, C-3, C-2’, C-3’/7’, C-4’/6’ and C-5’, were presented as average from two values in Table 5.

Table 5. ^{1}H and ^{13}C NMR data assigned for V[a]

Atom	δ (^{13}C), ppm	DEPT[b]	δ (^{1}H), ppm	Multiplicity (J, Hz)	^{1}H-^{1}H COSY [b]	HMBC[b]
1(C=O)	159.61	C				
3	145.93^{c}	C				
4	122.18	CH	8.33	dd(7.5; 0.5)	5, 6^{d}	3, 6
5	127.42	CH	7.73	t (7.9)	4,6	10a, 11
6	128.36	CH	8.08	d (8.1)	4^{d}, 5	4, 7, 10, 11^{d}
7	134.49	CH	8.35	dd (8.3; 0.8)	8	9, $9a^{e}$, 11^{d}
8	126.91	CH	7.77	dd (8.2; 7.2)	7, 9	9^{e}, 9a, 11
9	129.29	CH	8.34	dd (7.2; 1.1)	8	1, 7
9a	119.09	C				
10	127.52	C				
10a	123.68	C				
11	132.05	C				
1'	107.03	CH	7.06	s	$3'/7'^{d}$	1, 3, 4^{e}, 10a, 3'/ 7'
2'	130.78^{c}	C				
3'	131.60^{c}	CH	7.96	m	$1'^{d}$, 4'	1', 5', 7'
4'	115.57^{c}	CH	7.30	m	3'	2', 5', 6'
5'	161.25^{c}	C				
6'	115.57^{c}	CH	7.30	m	7'	2', 4', 5'
7'	131.60^{c}	CH	7.96	m	$1'^{d}$, 6'	1' , 3', 5'

[a] *In DMSO-d_6 solution. All assignments were in agreement with COSY, HSQC and HMBC spectra.*

[b] *Abbreviations: DEPT, Distortionless Enhancement by Polarization Transfer spectrum; ^{1}H-^{1}H COSY – proton-proton homonuclear correlation spectrum; HSQC, Heteronuclear Single Quantum Correlation experiment; HMBC, Long range ^{1}H-^{13}C Heteronuclear Multiple Bond Correlation experiment.*

[c] *Average from two values.*

[d] *Weak correlations.*

[e] *Extremely weak correlations.*

Coupling constants ($^{n}J_{CF}$) in benzene ring were found - $^{1}J_{CF}$ (246.1 Hz), $^{2}J_{CF}$ (21.4 Hz), $^{3}J_{CF}$ (8.0 Hz), $^{4}J_{CF}$ (3.2 Hz). Fluorine and benzene protons form five-spin *AA’MM’X* system. The *Spin Simulation* option from *MestreNova* was used to simulate the *AA’* and *MM’* spectra, based on the following parameters: (δ_H 7.96 ppm за H-3’/7’ (AA’ part); δ_H 7.30 ppm for H-4’/6’ (MM’ part); δ_F -59 254.16 ppm (X part)); $J^{3}_{MX}=J^{3}_{M'X}=$ 11.0 Hz, $J^{4}_{AX}=J^{4}_{A'X}=$7.5 Hz, $J^{4}_{AA'} = J^{4}_{MM'} =$ 3.25 Hz, $J^{3}_{AM}= J^{3}_{A'M'} =$ 10.5 Hz, $J^{5}_{AM'}=J^{5}_{A'M}=$ 0.35 Hz). Strong HMBC correlations were found between the signals of H-3’/7’ and C-1’, as well as between the signals of H-1’ and C-3’/7’, confirming the assignment of the signals at δ_H 7.96 ppm and δ_H 7.30 ppm for H-3’/7’ and H-4’/6’.

Vibrational data assigned for V

IR bands (cm^{-1}): 3056 (υ(C-H), arom.), 1747(υ(C=O)), 1630 (υ(C=C)), 1599 (υ(C=C), arom.), 1506 (υ(C=C), arom.), 1466 (υ(C=C), arom.), 765 (γ(C-H), arom.), 711(γ(C-H), arom.)

Raman bands (cm^{-1}): 3069 (υ(C-H), arom.), 1736 (υ(C=O)), 1630 (υ(C=C)), 1600 (υ(C=C), arom.), 1507(υ(C=C), arom.), 1468 (υ(C=C), arom.)), 703 (γ(C-H), arom.)

^{1}H and ^{13}C NMR data assignment for VI

The molecular formula of VI is $C_{17}H_{10}O_2S$. The three thiophene protons form ABX system that produced complex spectrum. To ensure the correct assignment of the signals of thiophene protons, the ABX spectrum was simulated using the *Spin Simulation* option from MestreNova. The best similarity between the simulated and real ABX spectrum was achieved by the following parameters: δ_H 7.92 ppm for H-3' ($^3J_{HH}$ = 2.8 Hz, $^4J_{HH}$ = 1.3 Hz), as well as δ_H 7.655 ppm and δ_H 7.664 ppm for H-4' ($^4J_{HH}$ = 4.8 Hz, $^3J_{HH}$ =2.8 Hz) and H-5'($^4J_{HH}$ = 4.8Hz, $^4J_{HH}$ =1.3 Hz). Additionally, the simulation was supported by the weak COSY and HMBC correlations - (δ_H 7.664 ppm – δ_H 7.18 ppm), (δ_H 7.92 ppm – δ_H 7.18 ppm), (δ_H 7.664 ppm – δ_C 103.35 ppm) and (δ_H 7.92 ppm – δ_C 103.35 ppm).

Table 6. ^{1}H and ^{13}C NMR data assigned for VI[a]

Atom	δ (^{13}C), ppm	DEPT[b]	δ (^{1}H), ppm	Multiplicity (J, Hz)	^{1}H-^{1}H COSY [b]	HMBC[b]
1(C=O)	159.75	C				
3	144.95	C				
4	121.62	CH	8.26	dd (7.5; 0.5)	5, 6^{c}, $1'^{c}$	3, 5, 6, $9a^{d}$, 11^{d}
5	127.48	CH	7.72	t (7.8)	4,6	10a, 11
6	128.05	CH	8.07	d (8.1)	4^{c}, 5, 7^{d}	4, 7, 10, 11^{c}
7	134.44	CH	8.34	dd (8.3; 0.8)	6^{d},8	9, $9a^{d}$, 11^{c}
8	126.95	CH	7.78	dd (8.2; 7.2)	7, 9	9^{c}, 9a, 11
9	129.20	CH	8.32	dd (7.2; 1.1)	8	1, 7, 10
9a	119.23	C				
10	127.51	C				
10a	123.69	C				
11	132.11	C				
1'	103.35	CH	7.18	s	4^{c}, $3'^{c}$,$5'^{d}$	1, 3, 10a, $2'^{d}$, 3', 4', 5'
2'	135.07	C				
3'	125.64	CH	7.92	m	$1'^{c}$, 4'	$1'^{d}$, $2'^{c}$, $4'^{c}$, $5'^{c}$
4'	128.90	CH	7.66 (7.655)*	m	3'	2', 3', 5'
5'	126.27	CH	7.66 (7.664)*	m	$1'^{d}$	$1'^{d}$, 2', 3', $4'^{c}$

[a] *In DMSO-d_6 solution. All assignments were in accordance with COSY, HMQC and HMBC spectra.*

[b] *Abbreviations: DEPT, Distortionless Enhancement by Polarization Transfer spectrum; ^{1}H-^{1}H COSY – proton-proton homonuclear correlation spectrum; HMQC, Heteronuclear Multiple Quantum Correlation experiment; HMBC, Long range ^{1}H-^{13}C Heteronuclear Multiple Bond Correlation experiment.*

[c] *Weak correlations.*

[d] *Extremely weak correlations.*

**The chemical shifts in the brackets were obtained from the simulation of the ABX spectrum.*

The NMR data fully assigned for the three structures (Table 6) was published in *Crystals, MDPI* [17]. The structures of IV, V and VI, together with the assigned ^{1}H and ^{13}C chemical shifts and ^{1}H signal multiplicities, were sent to *NMRShiftDB* database, where they were reviewed, accepted and imported.

Vibrational data assigned for VI

IR bands, (cm^{-1}): 3096 (υ(C-H), arom.), 3061 (υ(C-H), arom.), 1740 (υ(C=O)), 1627 (υ(C=C)), 1516 (υ(C=C), arom.), 1464 (υ(C=C), arom.)

Raman bands, **(***cm^{-1}***):** 3100 (υ(C-H), arom.), 3064 (υ(C-H), arom.), 3006 (υ(C-H), arom.), 1736 (υ(C=O)), 1627 (υ(C=C)), 1598 (υ(C=C), arom.), 1508 (υ(C=C), arom.), 1466 (υ(C=C), arom.)

1.4. Structure elucidation of Cu(II) and Au(III) complexes with 2,4-dithiouracil and its oxoderivatives

Novel Cu(II) and Au(III) complexes with 2,4-dithiouracil and some of its oxoderivatives were synthesized by the team of Assoc. Prof. Dr. Petya Marinova and coworkers (University of Plovdiv„ Paisii Hilendarski").

Structure verification of 2,4-dithiouracil and 2-thiouracil

The structures of 2,4-dithiouracil (VII) and 2-thiouracil (VIII) are presented on Figure 3. Their molecular formulas are $C_4H_4N_2S_2$ and $C_4H_4N_2SO$.

Figure 3. Structures of VII and VIII

Table 7. ^{1}H and ^{13}C NMR data assigned for VII [600.13 MHz (^{1}H) and 150.903 MHz (^{13}C)][a]

Atom	*δ* (^{13}C) ppm	DEPT-135	*δ* (^{1}H) ppm	Multiplicity (*J*, Hz)	^{1}H-^{1}H COSY	HMBC
1 (NH)			12.90	s		
2 (C=S)	172.87	C				
3 (NH)			13.64	s		
4 (C=S)	187.81	C				
5	117.16	CH	6.50	d (7.1)	6	4, 6
6	136.69	CH	7.27	d (7.1)	5	2, 4, 5

[a] *In DMSO-d$_6$ solution. All assignments were in agreement with COSY, HSQC and HMBC spectra.*

Table 8 ^{1}H and ^{13}C NMR data assigned for VIII [600.13 MHz (^{1}H) and 150.903 MHz (^{13}C)][a]

Atom	*δ* (^{13}C) ppm	DEPT-135	*δ* (^{1}H) ppm	Multiplicity (*J*, Hz)	^{1}H-^{1}H COSY	HMBC
1 (NH)			12.29	s	$3^c,5^c,6$	
2 (C=S)	176.09	C				
3 (NH)			12.45	s	$1^c,5^b$	
4 (C=O)	161.03	C				
5	105.32	CH	5.81	ddd (7.6, 1.9, 1.3)	$1^c,3^b,6$	4^c, 6
6	142.14	CH	7.41	dd (7.6, 5.6)	1,5	2, 4, 5

[a] *In DMSO-d$_6$ solution. All spectral assignments were in agreement with COSY, HSQC and HMBC spectra.*

[b] *Weak correlations.*

[c] *Extremely weak correlations.*

The full NMR assignments for VII and VIII are presented in Table 7 and Table 8, supported by the HOSE predictions that were included in the dissertation. Due to the fact, that only 1D NMR spectra were used in publication [14], a mistake was found there in the assignment of the ^{13}C signals of the carbons, C-5 and C-6, for the structure of VII – the ^{13}C signal at 136.80 ppm was assigned for carbon, C-5, while the ^{13}C signal at 117.24 ppm was assigned for the carbon, C-6.

Structure elucidation of Au complex by NMR

The higher number of ^{1}H signals and HSQC correlations for the Au complex in comparison with their number for 2,4-dithiouracil indicate that 2,4-dithiouracil underwent desulfurization due to the used NaOH for the synthesis of Au complex producing 2-thiouracil and uracil in the reaction mixture. The HSQC pairs, (5.44 ppm – 99.94 ppm) and (5.81 ppm - 104.91 ppm) were assigned to protons and carbons, H-5 and C-5, in the respective structures of uncoordinated ligands uracil and 2-thiouracil. There were four ^{1}H signals located closely to each other at the multiplet at 7.39 ppm with area 3.48 in ^{1}H NMR spectrum of the complex. Two of these signals at 7.39 ppm were assigned to the protons, H-6, in the structures of the uncoordinated uracil and 2-thiouracil, supported by the HSQC correlations, (7.39 ppm – 142.04 ppm). The other two signals at 7.39 ppm were assigned to the protons in the tautomeric form of 2-thiouracil coordinated to Au (Figure 4). The signals at 10.81 ppm and 11.00 ppm, as well as those at 12.27 ppm and 12.43 ppm were assigned respectively to NH-1 and NH-3 protons in the uncoordinated uracil and 2-thiouracil. ^{1}H NMR data assigned for the Au complex is presented in Table 9.

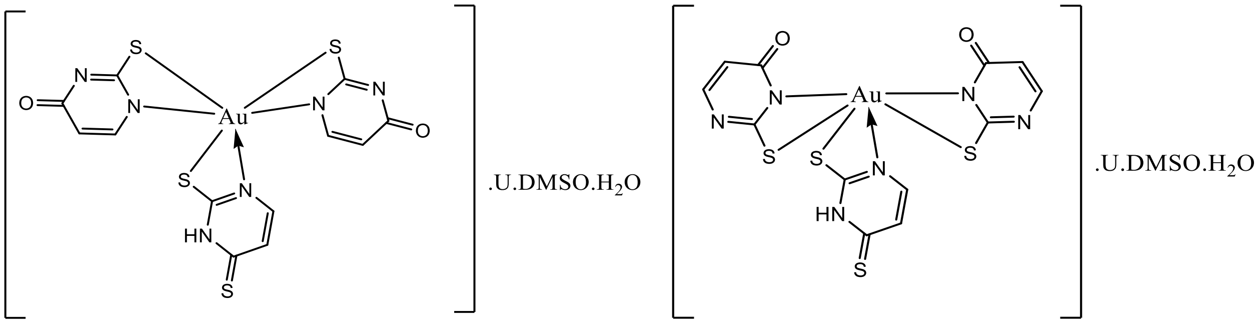
Table 9. ^{1}H NMR data assigned for Au complex [500.13 MHz][a]

Атом	2,4-DTu [b]	2-Tu [b]	U [b]	2,4-DTu.(2-Tu)$_2$.Au [c]
1	12.88, s	12.27, s	10.81, s	14.13, s (2,4-DTu)
2				
3	13.62, s	12.43, s	11.00, s	-
4				
5	6.51, d(6.7 Hz)	5.81, d(7.50 Hz)	5.44, m	7.10, d(6.8 Hz), (2,4-DTu) 7.39, m, (2-Tu) 7.39, m, (2-Tu)
6	7.26, t(6.2 Hz)	7.39, m	7.39, m	7.76, d(6.7 Hz), (2,4-DTu) 8.31, d(4.7 Hz), (2-Tu) 8.31, d(4.7 Hz), (2-Tu)

[a] *In DMSO-d_6 solution. All assignments were in agreement with HSQC data.*

[b] *Corresponding assignments concern the uncoordinated ligands – 2,4-dithiouracil, 2-thiouracil and uracil.*

[c] *Spectral data indicated that the ligands in the inner coordination sphere of Au complex are 2,4-DTu and 2-Tu.*



IXa ***IXb***

Figure 4. Possible structures of Au complex

The signal at 14.13 ppm with an area of 1.00 showed that there is a tautomeric form of 2,4-dithiouracil with one deprotonated nitrogen that is coordinated with Au as 14.13 ppm corresponded to the signal of the NH-3 proton. Additionally, the ^{1}H NMR solution spectrum showed a signal at 2.54 ppm, which was an indication of the presence of DMSO-h_6 in the Au complex as there was also one HSQC correlation (2.54 ppm–40.11 ppm). The presence of DMSO-h_6 in the Au complex was confirmed by the signal at 42.1 ppm in the solid-state CP MAS and CPPI MAS.

Structure elucidation of Cu complex by NMR

There were singlets at 10.80 ppm, 11.00 ppm, 12.26 ppm, and 12.43 ppm, similar to those found in the ^{1}H NMR spectrum of the Au complex for 2-thiouracil and uracil, indicated again that 2,4-dithiouracil underwent desulfurization under the alkaline conditions of the synthesis of the Cu complex due to the used NaOH (Table 10). The found HSQC correlations, (5.45 ppm -

99.78 ppm) and (5.81 ppm – 105.03 ppm), were close to those, observed in HSQC spectrum of Au complex for the protons and carbons (H-5 and C-5) in the uncoordinated uracil and 2-thiouracil, respectively.

Table 10. ^1H NMR data assigned for Cu complex [500.13 MHz][a]

Атом	**2-Tu** [b]	**U** [b]	**2-Tu.U.Cu** [c]
1	12.26, s	10.80, s	
2			
3	12.43, s	11.00, s	
4			
5	5.81, d (7.3 Hz)	5.45, d (8.2 Hz)	7.28, d (5.5 Hz) (U) 7.40 [d], m (2-Tu)
6	7.38 [d], m	7.38 [d], m	8.33, m (U) 8.33, m (2-Tu)

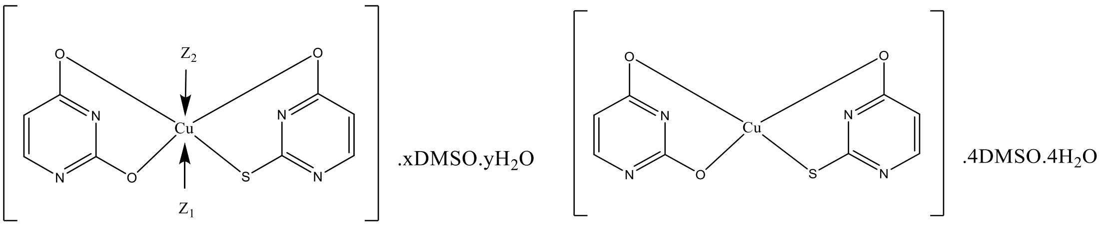
[a] *In DMSO-d_6 solution. All assignments were in agreement with HSQC data.*

[b] *The corresponding assignments concern the uncoordinated ligands –2-thiouracil (2-Tu) and uracil (U).*

[c] *Spectral data suggest that 2-Tu and U are the ligands in the inner coordination sphere of the Cu complex.*

[d] *Assigned from the HSQC spectrum.*

There is a multiplet at 7.39 ppm with area 3.27, consisted of three signals closely located to each other. HSQC spectrum indicated the following correlations: (7.40 ppm–115.27 ppm) and (7.38 ppm–141.85 ppm), where the signals at 7.38 ppm and 141.85 ppm were assigned for the protons and carbons, H-6 and C-6, in the structures of uncoordinated ligands, i.e. uracil and 2-thiouracil. Thus, for the ligands coordinated with Cu, there were one signal at 7.40 ppm, one signal at 7.28 ppm and two signals at 8.33 ppm in *^{1}H NMR spectrum*.



Xa ***Xb***

Figure 5. Possible structures of Cu complex. If $Z_1=H_2O$ or DMSO-h_6, then $Z_2=H_2O$ or DMSO-h_6.

HSQC correlations, (7.40 ppm – 115.27 ppm) and (8.33 ppm – 156.26 ppm) indicate that the 7.40 ppm, 8.33 ppm, 115.27 ppm and 156.26 ppm were for the signals of the protons and carbons (H-5, H-6, C-5 and C-6) in coordinated 2-thiouracil.

Table 11. Assigned Raman and ATR bands for 2,4-dithiouracil, Au and Cu complexes

2,4-DTu		**Au complex**		**Cu complex**	
Raman, cm^{-1}	**ATR, cm^{-1}**	**Raman, cm^{-1}**	**ATR, cm^{-1}**	**Raman, cm^{-1}**	**ATR, cm^{-1}**
3097(ν(C-H)) 3080 (ν(C-H)) 1547 (ν(C=C)) 1254 (ν(C=S))	3168 (ν(NH)) 3096 ((ν(C-H)) 3080 (ν(C-H) 1565 (ν(C=C)) 1252 (ν(C=S))	3066 (ν(C-H)) 1544 (ν(C=C)) 1253 (ν(C=S))	3064 (ν(C-H)) 1539 (ν(C=C)) 1252 (ν(C=S))	3018 (ν(C-H)) 1546 (ν(C=C))	3386 (ν(O-H)) 3078 (ν(C-H)) 1546 (ν(C=C))

The other pair of signals (7.28 ppm and 115.48 ppm) and (8.33 ppm and 156.26 ppm) corresponded to protons and carbons H-5, C-5, H-6 and C-6, respectively in coordinated uracil (Figure 5). The ^{1}H NMR solution spectrum showed a signal at 2.54 ppm, which is also an indication of the presence of DMSO-h_6 in the Cu complex. In addition, there was one HSQC correlation (2.54 ppm–40.06 ppm). The solid-state CP MAS and CPPI MAS showed a signal at 40.5 ppm, confirming the presence of DMSO-h_6 in the Cu complex.

The structure elucidation of Au(III) and Cu(II) complexes with the fully assigned NMR data was published in *Applied Sciences, MDPI* [9].

1.5. Structure verification of dispiroimidazolidines

Dispiroimidizaolidines were synthesized for the first time by the team of Assoc. Prof. Dr. Marin Marinov and coworkers (Agricultural University - Plovdiv).

Structure verification of XI

The suggested structure of compound XI with the atom numbering used only for the spectral assignments (Table 12) is presented on Figure 6.

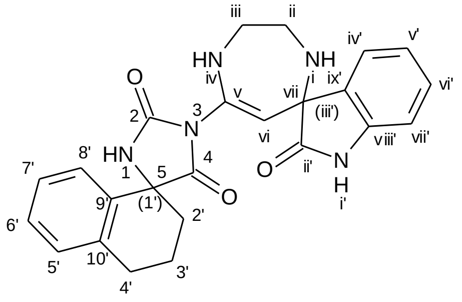


Figure 6. Suggested structure for XI

Table 12. ^{1}H and ^{13}C NMR data assigned for XI [^{1}H [500.13 MHz] and ^{13}C [125.76 MHz]]^a

Atom	δ (^{13}C), ppm	DEPT^b	δ (^{1}H), ppm	Multiplicity (J, Hz)	^{1}H-^{1}H COSY ^{b}	HMBC^b
2(C=O)	154.23	C				
4(C=O)	174.47	C				
1(NH)			11.78	br. s		
(1’)	66.25	C				
2’	29.75	CH_2	2.12(H_a)^c 2.48(H_b)^c	m dd(12.9, 3.9)	2’(H_b), 3’(H_c), 3’(H_d); 2’(H_a), 3’(H_c)^d,3’(H_d)^d	4’^{f} (1‘), 3‘,4‘,4
3’	19.38	CH_2	1.88(H_c)^c 2.18 (H_d)^c	m	2’(H_a),2’(H_b)^d,3’(H_d),4’; 2’(H_a)^d 2’(H_b)^d,3’(H_c), 4’	(1‘)^f 2‘^{f}, 4’^{f}
4’	28.47	CH_2	2.76	dd(7.6;4.5)	3’(H_c), 3’(H_d)	2’,3’,5’, 9’,10’
9’	132.51	C				
10’	138.46	C				
8’	124.03	CH	7.03^d	m	7‘	(1‘), 6‘, 10’
7‘	126.56	CH	7.12^d	m	6‘,8‘	5‘
6‘	127.50	CH	7.16^d	m	5‘,7‘	8‘, 10‘
5‘	129.26	CH	7.15^d	m	6‘	4‘^{e}
ii’(C=O)	177.93	C				
v	167.79	C				
iv (NH)			11.78	br. s		
iii	33.52	CH_2	2.06 (H_e)^c 1.90 (H_f)^c	m	ii(H_g), ii(H_h), iii(H_f); ii(H_g), ii(H_h), iii(H_e)	
ii	18.41	CH_2	1.80(H_g)^c 2.09(H_h)^c	m	ii(H_h), iii(H_e), iii(H_f) ii(H_g),iii(H_e), iii(H_f)	(iii’)^e, iv’^{f}
i(NH)			10.81	s		
(iii’)	63.08	C				
i’(NH)			8.51	s		(iii’), ii’, viii’
viii’	156.47	C				
ix’	137.72	C				
iv’	126.52	CH	7.07^d	m	v’	(iii’)^e
v’	126.61	CH	7.20^c	m	iv’,vi’	
vi’	134.37	CH	7.17	m	v’, vii’	
vii’	127.94	CH	7.21^c	m	vi’	ix’
vi	25.93	CH	2.42	s		v

[a] *In DMSO-d_6 solution. All spectral assignments were in agreement with HSQC, HMBC and COSY spectra.*

[b] *Abbreviations: DEPT, Distortionless Enhancement by Polarization Transfer spectrum; ^{1}H-^{1}H COSY – proton-proton homonuclear correlation spectrum; HSQC, Heteronuclear Single Quantum Correlation experiment; HMBC, Long range ^{1}H-^{13}C Heteronuclear Multiple Bond Correlation experiment.*

[c] *Assigned from the HSQC spectrum.*

[d] *Assigned from the HMBC spectrum.*

[e] *Weak correlations.*

[f] *Extremely weak correlations.*

Molecular formula of XI is $C_{24}H_{23}N_5O_3$. Both signals at 174.47 ppm and 177.93 ppm correspond to the carbonyl carbons, respectively C^4=O and $C^{ii'}$=O, whereas the signal at 154.23 ppm was assigned to C^2=O. The signals at 63.08 ppm and 66.25 ppm correspond to the two spirocarbons - $C^{(iii')}$ and $C^{(1')}$. The singlet at 8.51 ppm with area 0.52 was assigned to the NH-i' proton in the isatine fragment. The HMBC correlations – (8.51 ppm – 63.08 ppm), (8.51 ppm – 177.93 ppm) and (8.51 ppm – 156.47 ppm), confirmed the assignment of the signals at 177.93 ppm and 156.47 ppm, respectively to the carbons, C-ii 'and C-viii'. The widened singlet at 11.78 ppm with area 1.01 included the signals of NH-1 and NH-iv protons, as the singlet at 10.81 ppm with area 0.53 was for NH-i proton.

Vibrational data assigned for XI

ATR, cm^{-1}: 3212 (v(N-H)), 3108 v(C-H), 3034 (v(C-H)), 2948 ($v_{as}(CH_2)$), 1758 v(C=O), 1707 v(C=O), 1679 v(C=O), 1497 (v(C=C)), 1449 (v(C=C)), 1435 (v(C=C))

Structure verification of XII

The suggested structure for XII is shown on Figure 7 with the atom numbering used only for the spectral assignments.

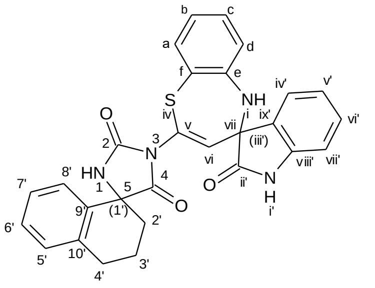


Figure 7. Suggested structure for XII

Molecular formula of XII is $C_{28}H_{22}SN_4O_3$. There is a ^{1}H singlet at 7.25 ppm with area 1.04, for which the following HMBC correlations were found – (7.25 ppm – 74.31 ppm), (7.25 ppm – 108.42 ppm), (7.25 ppm – 124.11 ppm), (7.25 ppm – 147.20 ppm), (7.25 ppm – 176.17 ppm). The weak HMBC correlation (7.25 ppm – 108.42 ppm) indicate the interaction of NH-i proton with the closest carbon from the benzene ring of the benzothiazepine fragment – C-d. Based on the strong meta HMBC correlations – (7.03 ppm – 125.70 ppm), (7.03 ppm – 147.20 ppm), (6.63 ppm – 124.11 ppm), (6.63 ppm – 108.42 ppm), (6.91 ppm – 121.09 ppm), (6.91 ppm – 147.20 ppm), (6.55 ppm – 118.65 ppm) and (6.55 ppm – 124.11 ppm), it can be concluded that 7.03 ppm, 6.63 ppm, 6.91 ppm and 6.55 ppm were for the signals of the protons, H-a, H-b, H-c, H-d (Table 13). The following HMBC correlations were found for the singlet at 10.36 ppm, assigned for NH-i' proton – (10.36 ppm – 141.31 ppm), (10.36 ppm – 129.79 ppm), (10.36 ppm – 176.17 ppm), (10.36 ppm – 74.31 ppm), indicating its interaction with carbons, C-viii', C-ix', C-ii', and C-iii'. The singlet at 11.83 ppm was for the NH-1 proton, supported by the available extremely weak HMBC correlations, (11.83 ppm – 66.25 ppm) and (11.83 ppm – 154.13 ppm), indicating the interaction of NH-1 proton with the spirocarbons, C-1' and carbonyl carbon, C-2.

Vibrational data assigned for XII

ATR, cm^{-1}: 3313 (v(N-H)), 3191 v(N-H), 3084 (v(C-H)), 3071 (v(C-H)), 3037 (v(C-H)), 1754 (v(C=O)), 1706 (v(C=O)), 1680 (v(C=O)), 1619 (v(C=C)), 1604 (v(C=C)), 1578 (v(C=C)), 1498 (v(C=C)), 1473 ($\delta_s(CH_2)$), 1463 (v(C=C))

Table 13. ^{1}H and ^{13}C NMR data assigned for XII. [^{1}H [500.13 MHz] and ^{13}C [125.76 MHz]][a]

Atom	*δ (^{13}C), ppm*	*DEPT*[b]	*δ (^{1}H), ppm*	*Multiplicity (J, Hz)*	*^{1}H-^{1}H COSY* [b]	*HMBC*[b]
2(C=O)	*154.13*	*C*				
4(C=O)	*174.36*	*C*				
1(NH)			*11.83*	*s*		*(1')[f],2[f]*
(1')	*66.25*					
2'	*29.74*	*CH$_2$*[g]	*2.12(H$_a$)*[c,g] *2.48(H$_b$)*[c,g]	*dt(13.3, 3.9)* *dd(12.9, 3.8)*	*2'(H$_b$), 3'(H$_c$), 3'(H$_d$);* *2'(H$_a$), 3'(H$_c$)[e],3'(H$_d$)[e]*	*4'[f]* *(1'), 3',4',4*
3'	*19.37*	*CH$_2$*[g]	*1.88(H$_c$)*[c,g] *2.18 (H$_d$)*[c,g]	*m*	*2'(H$_a$),2'(H$_b$)[e],3'(H$_d$),4';* *2'(H$_a$)[e] 2'(H$_b$)[e],3'(H$_c$), 4'*	*(1')[f]*
4'	*28.46*	*CH$_2$*	*2.76*	*dd(7.9;4.3)*	*3'(H$_c$), 3'(H$_d$)*	*2',3',5', 9',10'*
9'	*132.47*	*C*				
10'	*138.46*	*C*				
8'	*124.03*	*CH*	*7.04*[d]	*m*	*7'*	*(1'), 10'*
7'	*126.56*	*CH*	*7.13*[d]	*m*	*6',8'*	*5'*
6'	*127.51*	*CH*	*7.16*[d]	*m*	*5',7'*	*8', 10'*
5'	*129.26*	*CH*	*7.17*[d]	*m*	*6'*	*4'[f], 9'*
ii'(C=O)	*176.17*	*C*				
v	*167.79*	*C*				
i(NH)			*7.25*	*s*		*(iii'),d[f],f,e,ii'[e]*
(iii')	*74.31*	*C*				
i'(NH)			*10.36*	*s*		*(iii'), ii'[e], viii',ix'*
viii'	*141.31*	*C*				
ix'	*129.79*	*C*				
iv'	*125.61*	*CH*	*7.55*	*d(7.1)*	*v', vi'[f], vii'[f]*	*(iii'),vi', vii'[e], viii'*
v'	*122.46*	*CH*	*7.05*[d]	*m*	*iv',vi', vii'[e]*	*vii',ix'*
vi'	*130.48*	*CH*	*7.29*	*td(7.7, 1.2)*	*iv'[f], v', vii'*	*iv', vii', viii'*
vii'	*110.04*	*CH*	*6.85*	*d(7.8)*	*iv'[f], vi', v'[e]*	*(iii')[e], v',ix'*
vi	*25.93*	*CH*	*2.42*	*s*		*v*
a	*121.09*	*CH*	*7.03*[g]	*m*	*b, c[e], d[f]*	*c,e*
b	*118.65*	*CH*	*6.63*[g]	*td(7.5, 1.0)*	*a, c, d[e]*	*d,f,e[e]*
c	*125.70*	*CH*	*6.91*[g]	*td(7.7, 1.2)*	*a[e], b, d*	*a, d[e], e*
d	*108.42*	*CH*	*6.54*[g]	*d(7.8)*	*a[f], b[e], c*	*b,f*
e	*147.20*	*C*				
f	*124.11*	*C*				

[a] *In DMSO-d$_6$ solution. All spectral assignments were in agreement with HSQC, HMBC and COSY spectra.*

[b] *Abbreviations: DEPT, Distortionless Enhancement by Polarization Transfer spectrum; ^{1}H-^{1}H COSY – proton-proton homonuclear correlation spectrum; HSQC, Heteronuclear Single Quantum Correlation experiment; HMBC, Long range ^{1}H-^{13}C Heteronuclear Multiple Bond Correlation experiment.*

[c] *Assigned from the HSQC spectrum.*

[d] *Assigned from the HMBC spectrum.*

[e] *Weak correlations.*

[f] *Extremely weak correlations.*

[g] *Chemically inequivalent protons in CH$_2$ groups are marked with a capital letter H and lower subscript from a to d, in comparison with the benzene protons which are marked in the text in the following way H-a, H-b, H-c, H-d.*

Structure verification of XIII

The suggested structure of XIII with the atom numbering used only for the spectral assignments is shown on Figure 8.

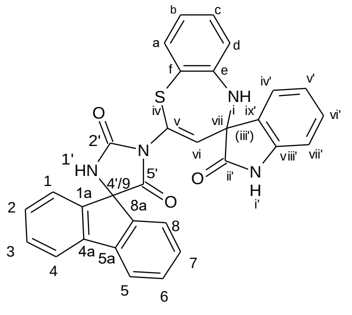


Figure 8. Suggested structure for XIII

Table 14. ^{1}H and ^{13}C NMR data assigned for XIII. [^{1}H [500.13 MHz] and ^{13}C [125.76 MHz]]^{a}

Atom	*δ (^{13}C), ppm*	*DEPT^{b}*	*δ (^{1}H), ppm*	*Multiplicity (J, Hz)*	*^{1}H-^{1}H COSY ^{b}*	*HMBC^{b}*
2‘(C=O)	154.19	C				
5‘(C=O)	170.74	C				
1‘(NH)			12.24	s		
4’/9	74.14					
1/8	122.37	CH	7.54^{c}	d(7.6)	2/7, 3/6^{d}, 4/5^{e}	4’/9, 3,4a
2/7	127.95	CH	7.30^{c}	td(7.5, 0.9)	1/8, 3/6, 4/5^{d}	(4’/9)^{d}, 4,1a
3/6	129.37	CH	7.45^{c}	td(7.5;0.9)	1/8^{d}, 2/7, 4/5	1,2,4a
4/5	120.71	CH	7.88^{c}	d(7.5)	1/8^{e}, 2/7^{d}, 3/6	1^{d},3,1a
1a/8a	141.36	C				
4a/5a	140.95	C				
ii’(C=O)	176.17	C				
v	166.90	C				
i(NH)			7.27	s		(iii’),ii’^{d},d^{d},e,f
(iii’)	74.32	C				
i’(NH)			10.36	s		(iii’), ii’^{d}, viii’,ix’
viii’	141.31	C				
ix’	129.80	C				
iv’	125.60	CH	7.55^{c}	d(6.9)	v’, vi’^{e}, vii’^{e}	vii’^{d},vi’
v’	122.47	CH	7.05^{c}	td(7.6, 1.4)	iv’,vi’,vii’^{d}	vii’,ix’
vi’	130.49	CH	7.29^{c}	td(7.7, 1.3)	iv’^{e}, v’, vii’	iv’
vii’	110.06	CH	6.84	d(7.7)	iv’^{e}, v’^{d}, vi’	v’,ix’
vi	25.24	CH	2.40	s		v
a	121.10	CH	7.03^{c}	dd(7.5, 0.5)	b, c^{d}, d^{e}	c,e
b	118.65	CH	6.64	td(7.5, 1.0)	a, c, d^{d}	d,f,e^{d}
c	125.71	CH	6.90	td(7.7, 1.2)	a^{d}, b, d	a, d^{d}, e
d	108.43	CH	6.54	dd(7.8, 0.6)	a^{e}, b^{d}, c	b,f
e	147.20	C				
f	124.11	C				

[a] In DMSO-d$_6$ solution. All spectral assignments were in agreement with HSQC, HMBC and COSY spectra

[b] Abbreviations: DEPT, Distortionless Enhancement by Polarization Transfer spectrum; ^{1}H-^{1}H COSY – proton-proton homonuclear correlation spectrum; HSQC, Heteronuclear Single Quantum Correlation experiment; HMBC, Long range ^{1}H-^{13}C Heteronuclear Multiple Bond Correlation experiment.

[c] Assigned from the HSQC spectrum.

[d] Weak correlations.

[e] Extremely weak correlations.

The molecular formula is $C_{31}H_{20}SN_4O_3$. Protons and carbons in both benzene rings of the fluorene fragment are chemically equivalent due to which their signals in ^{1}H, ^{13}C, DEPT 135, HSQC and HMBC spectra were the most intensive (Table 14).

The strong HMBC correlation (7.54 ppm – 74.14 ppm) indicate that 7.54 ppm was for the signal of H-1/8, located only three bonds away from the spirocarbon, C-4’/9 (74.14 ppm). For each of the doublets at 7.88 ppm and 7.54 ppm, three COSY correlations were found - (7.88 ppm – 7.54 ppm), (7.88 ppm – 7.30 ppm), (7.54 ppm – 7.45 ppm), (7.88 ppm - 7.45 ppm), (7.54 ppm – 7.30 ppm). Thus, 7.88 ppm, 7.45 ppm and 7.30 ppm were assigned correspondingly for the H-4/5, H-3/6 and H-2/7 protons. The weak HMBC correlation (7.30 ppm – 74.14 ppm) indicates additionally the interaction of H-2/7 proton with spirocarbon, C-4’/9 (74.14 ppm). As result from the strong HMBC correlations - (7.54 ppm – 140.95 ppm), (7.45 ppm – 140.95 ppm), (7.30 ppm – 141.36 ppm) and (7.88 ppm – 141.36 ppm), 140.95 ppm and 141.36 ppm were assigned to the signals of the nonprotonated carbons, C-4a/5a and C-1a/8a.

Vibrational data assigned for XIII

ATR, cm^{-1}: 3313 (ν(N-H)), 3183 ν(N-H), 3071 (ν(C-H)), 3037 (ν(C-H)), 1757 (ν(C=O)), 1705 (ν(C=O)), 1690 (ν(C=O)), 1619 (ν(C=C)), 1604 (ν(C=C)), 1578 (ν(C=C)), 1462 (ν(C=C)), 1452(ν(C=C))

Structure verification of XIV

The tautomeric structures (XIVa and XIVb) that are in equilibrium are shown on Figure 9 with the atom numbering used only for the spectral assignments.

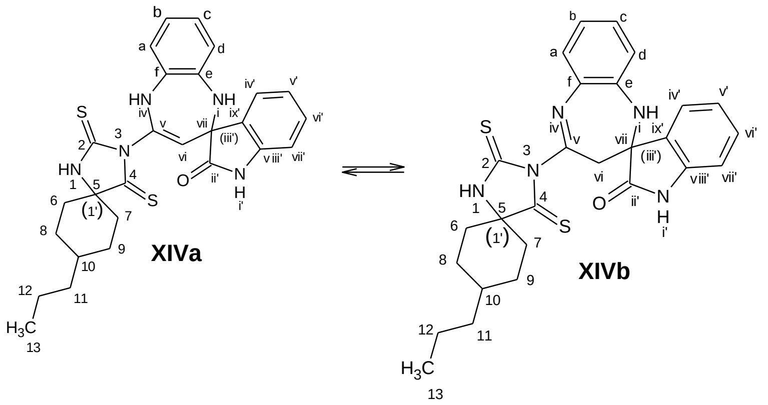


Figure 9. Suggested structures for XIVa and XIVb

The molecular formula of compound XIVa and its tautomer XIVb is $C_{27}H_{29}N_5S_2O$. The reason for presenting the tautomer of compound XIVa was the missing signal of NH-iv proton in the ^{1}H NMR spectrum.

Table 15. ^{1}H and ^{13}C NMR data assignment for compounds XIVa and XIVb. [^{1}H [500.13 MHz] and ^{13}C [125.76 MHz]]^a

Atom	δ (^{13}C), ppm	DEPT^b	δ (^{1}H), ppm	Multiplicity (J, Hz)	^{1}H-^{1}H COSY ^{b}	HMBC^b
2(C=S)	180.25	C				
4(C=S)	208.63	C				
1(NH)			13.91	s		
(1′)	79.79	C				
6/7	30.77	CH_2	2.66^c(H_a)^f 1.80^c (H_b)^f	td(13.4, 4.7) m	H_b, H_c, H_d H_a, H_c, H_d	(1′), 8/9, 4
8/9	21.13	CH_2	2.20^c (H_c)^f 1.59^c (H_d)^f	qd(13.2, 4.0) m	H_d, H_a, H_b,10 H_c, H_a, H_b,10	6/7^d, 10^e
10	45.05	CH	1.06^c	m	H_c, H_d	
11	20.31	CH_2	2.17^c (H_e)^f 1.55^c (H_f)^f	qd(13.2, 4.0) m	H_f, 10, H_g,H_h H_e,10, H_h,H_g	
12	35.05	CH_2	1.86^c (H_g)^f 1.63^c (H_h)^f	m m	H_e, H_f, H_h H_e, H_f, H_g	
13	27.38	CH_3	0.86^c	s		10
ii′(C=O)	176.15	C				
v	171.30	C				
i(NH)			7.26	s		
(iii′)	74.30	C				
iv(NH)						
i′(NH)			10.34	s		(iii′), viii′,ix′
viii′	141.30	C				
ix′	129.78	C				
iv′	125.59	CH	7.55	d(7.4)	v′,vi′^{e}	(iii′), viii′,vi′
v′	122.44	CH	7.07^c	td(7.6, 0.9)	iv′,vi′,vii′^{e}	vii′,ix′
vi′	130.46	CH	7.29	td(7.7, 1.2)	v′, vii′,iv′^{e}	iv′,viii′
vii′	110.03	CH	6.84	d(7.8)	v′^{e},vi′	v′,ix′
vi	29.17/32.14	CH/CH_2	2.72	s		v
a	121.07	CH	7.04^{c,f}	dd(7.5,0.8)	b,c^e	c,e
b	118.63	CH	6.63^f	td(7.5, 1.0)	a,c,d^e	d,f
c	125.68	CH	6.90^f	td(7.7, 1.2)	a^e,b,d	a, e
d	108.41	CH	6.53^f	dd(7.8, 0.8)	b^e, c	b,f
e	147.19	C				
f	124.10	C				

[a] *In DMSO-d_6 solution. All spectral assignments were in agreement with HSQC, HMBC and COSY spectra.*

[b] *Abbreviations: DEPT, Distortionless Enhancement by Polarization Transfer spectrum; ^{1}H-^{1}H COSY – proton-proton homonuclear correlation spectrum; HSQC, Heteronuclear Single Quantum Correlation experiment; HMBC, Long range ^{1}H-^{13}C Heteronuclear Multiple Bond Correlation experiment.*

[c] *Assigned from HSQC spectrum.*

[d] *Weak correlations.*

[e] *Extremely weak correlations.*

[f] *H-a, H-b, H-c and H-d are the benzene protons whereas the chemically inequivalent methylene protons were marked with capital letter H and with the corresponding letter from a to h as a lower subscript.*

However, the ^{1}H singlet at 2.72 ppm, with an area of 1.81, indicated the transfer of the NH-iv proton to the C-vi carbon, forming the CH_2 group in the structure of tautomer XIVb. Moreover, the HSQC spectrum showed two correlations involving the signal at 2.72 ppm–(2.72–28.90 ppm) and (2.72–32.09 ppm). The former HSQC correlation was positive, indicating the presence of the H-vi proton and C-vi carbon in the CH group in compound XIVa. The latter HSQC correlation was negative, including the chemical shifts of the signals of the methylene protons and carbon in the CH_2-vi group that is present in compound XIVb. Thus, the ^{1}H singlet at 2.72 ppm was assigned to both protons in CH_2-vi in tautomer XIVb. Also, instead of observing 25 signals in the ^{13}C spectrum, there were 26 signals, where those at 29.17 ppm and 32.14 ppm, as already suggested by the HSQC spectrum, corresponded to the carbon C-vi in the tautomers XIVa and XIVb. Meanwhile, the DEPT 135 spectrum showed a positive ^{13}C signal at 29.17 ppm as there was not any signal at 32.14 ppm. Consequently, the ^{1}H NMR spectrum showed the resonances specifically for compound XIVb while the ^{13}C NMR and HSQC spectra showed some resonances for both tautomers. The DEPT 135 spectrum included the CH and C^6H_2, C^7H_2, C^8H_2, C^9H_2, $C^{11}H_2$, and $C^{12}H_2$ signals only for tautomer XIVa. Evidently, the NMR data indicated the mutual presence of both tautomers XIVa and XIVb in the reaction mixture, as the mobile NH-iv proton participated in the tautomeric interconversion. For this reason, there was no NH-iv signal detected in the ^{1}H NMR spectrum (Table 15).

Vibrational data assigned for XIVa and XIVb

ATR, cm^{-1}: 3313 (ν(N-H)), 3136 ν(C-H), 3085 (ν(C-H)), 3070 (ν(C-H)), 3060 (ν(C-H)), 2953 ($\nu_{as}(CH_3)$), 2937 ($\nu_{as}(CH_2)$), 1705 ν(C=O), 1619 (ν(C=C)), 1603 (ν(C=C)), 1577 (ν(C=C)), 1493 (ν(C=C)), 1473 $\delta_s(CH_2)$, 1462 (ν(C=C)), 1257ν (C=S)

1.6. Structure verification of some benzamide derivatives

Benzamide derivatives were synthesized by the team of Assoc. Prof. Dr. Jan Petrov and coworkers (Faculty of Chemistry, University of Plovdiv ”Paisii Hilendarski”) [13]. All ^{13}C NMR assignments for the benzamide structures were supported by HOSE predictions included in Section 3 of the dissertation - “Results from Spectral Assignments”.

Structure verification of XV

Some partially assigned NMR and vibrational data can be found for XV (Figure 10), supported by quantum chemical calculations [13][12], but fully assigned NMR data does not exist for this compound.

The molecular formula of XV is $C_9H_7N_2Cl_3O_2$. There are two doublets at 7.96 ppm and 8.43 ppm, as well as two triplets at 7.31 ppm and 7.64 ppm (Table 16). The ^{1}H signal of H-2’ proton has only strong COSY correlation which is with the signal of its neighbor, H-3’ – (7.96 ppm – 7.31 ppm). Both strong COSY correlations, (7.64 ppm – 7.31 ppm) and (7.64 ppm – 8.43 ppm), together with the ^{1}H multiplicity of the signals at 7.64 ppm and 8.43 ppm indicated that 7.64 ppm and 8.43 ppm were for the protons, H-4’ and H-5’.

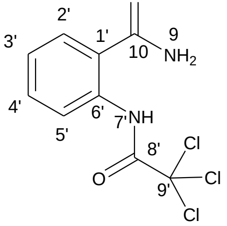


Figure 10. Suggested structure for XV

Table 16 ^{1}H and ^{13}C NMR data assigned for XV. [^{1}H [600.13 MHz] and ^{13}C [150.90 MHz]]^{a}

Atom	***δ (^{13}C), ppm***	***DEPT^{b}***	***δ (^{1}H), ppm***	***Multiplicity (J, Hz)***	***^{1}H-^{1}H COSY ^{b}***	***HMBC^{b}***
1’	*119.91*	*C*				
2’	*128.93*	*CH*	*7.96*	*d(7.1)*	*3’, 4’^{d}*	*4’,6’,10*
3’	*124.50*	*CH*	*7.31*	*t(7.6)*	*2’,4’,5’^{d}*	*1’, 2’^{d}*
4’	*133.02*	*CH*	*7.64*	*t(7.5)*	*2’^{d}, 3’, 5’*	*1’^{c}, 2’, 6’*
5‘	*119.86*	*CH*	*8.43*	*d(8.3)*	*3’^{d},4’*	*1’, 3’*
6‘	*138.17*	*C*				
7’(NH)			*13.72*	*s*		*5’,8’*
8’(C=O)	*159.33*	*C*				
9’	*92.92*	*C*				
9(NH_2)			*8.01-H_a*	*s*		*1’*
			8.55-H_b	*s*		*1’^{c},10^{d}*
10(C=O)	*170.64*	*C*				

[a] *In DMSO-d_6 solution. All spectral assignments were in agreement with HMQC, HMBC and COSY spectra.*

[b] *Abbreviations: DEPT, Distortionless Enhancement by Polarization Transfer spectrum; ^{1}H-^{1}H COSY – proton-proton homonuclear correlation spectrum; HMQC, Heteronuclear Multiple Quantum Correlation experiment; HMBC, Long range ^{1}H-^{13}C Heteronuclear Multiple Bond Correlation experiment.*

[c] *Weak correlations.*

[d] *Extremely weak correlations.*

Based on the strong meta HMBC correlations – (7.31 ppm – 119.91 ppm), (8.43 ppm – 119.91 ppm), (7.96 ppm – 138.17 ppm) and (7.64 ppm – 138.17 ppm), 138.17 ppm and 119.91 ppm were assigned for the signals of the carbons, C-6’ and C-1’. HMBC correlations (8.01 – 119.91 ppm), (8.55 ppm – 119.91 ppm) and (8.55 ppm – 170.64 ppm) indicated that the singlets at 8.01 and 8.55 ppm were for the NH_2 protons.

Vibrational data assigned for XV

IR, cm^{-1}: 3395 ($v_{as}(NH_2)$), 3302 ($v_s(NH_2)$), 3224 (v(NH), 3106 (v(Csp^{2}-H)), 3084 (v(Csp^{2}-H)), 3067 (v(Csp^{2}-H)), 3028 (v(Csp^{2}-H)), 1698 (v(C=O)), 1657(v(C=O)), 1593(v(C=C)), 1518(v(C=C)), 1459(v(C=C)), 1308 (v(C=C)), 1048 (v(C=C)), 763 (ϒ(C-H))

Raman, cm^{-1}: 3074(v(Csp^{2}-H)), 3028(v(Csp^{2}-H)), 1697 v(C=O), 1657 v(C=O), 1584 (v(C=C)), 1520 (v(C=C)), 1462 (v(C=C)), 1307 (v(C=C)), 1049(v(C=C)), 761 (ϒ(C-H))

Structure verification of XVI

There is NMR data presented in the DSc thesis of Prof. DSc Plamen Penchev [1] (Faculty of Chemistry, University of Plovdiv „Paisii Hilendarski“) for structure XVI (Figure 11) assigned from one- and two-dimensional NMR spectra.

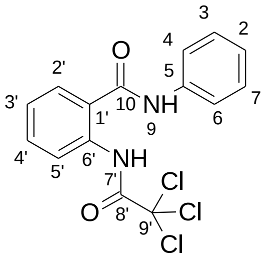


Figure 11. Suggested structure for XVI

Table 17 presents independently and fully assigned NMR data for XVI, as the novelty in this case is the simulation of ^{1}H spectrum of the AA’MM’X system in benzene ring, bonded with NH-9 group, with the aim to find its coupling constants. The molecular formula of XVI is $C_{15}H_{11}N_2Cl_3O_2$.

Table 17. ^1H and ^{13}C NMR data assigned for XVI. [^1H [600.13 MHz] and ^{13}C [150.90 MHz]][a]

Atom	*δ (^{13}C), ppm*	*DEPT*[b]	*δ (^1H), ppm*	*Multiplicity (J, Hz)*	*^1H-^1H COSY*[b]	*HMBC*[b]
1’	*123.17*	*C*				
2’	*129.27*	*CH*	*8.02*	*dd(7.9, 1.3)*	*3’,4’*[d]	*1’*[d]*,5’*[d]*,4’,6’,10*
3’	*125.02*	*CH*	*7.42*[c]	*td(7.6, 1.0)*	*2’,4’,5‘*[e]	*1’,4’*[d]*,5‘*
4’	*132.74*	*CH*	*7.69*[c]	*td(7.9, 1.5)*	*2’*[d]*, 3’, 5’*	*2’,6’*
5‘	*121.05*	*CH*	*8.29*	*dd(8.3, 0.8)*	*3‘*[e]*, 4’*	*1’,3’, 6’, 10*[d]
6‘	*136.87*	*C*				
7’(NH)			*12.43*	*s*		*1’,5’,8’*
8’(C=O)	*159.39*	*C*				
9’	*92.72*	*C*				
2	*124.57*	*CH*	*7.16*	*tt(7.4, 1.2)*	*3/7, 4/6*[d]	*4/6, 3/7, 5*[d]
3/7	*128.76*	*CH*	*7.39*[c]	*m*	*2, 4/6*	*3/7, 5*
4/6	*121.33*	*CH*	*7.71*[c]	*m*	*2*[d]*, 3/7*	*2, 4/6,5*
5	*138.19*	*C*				
9(NH)			*10.65*	*s*		*4/6,10*
10(C=O)	*166.91*	*C*				

[a] *In DMSO-d_6 solution. All spectral assignments were in agreement with HSQC, HMBC and COSY spectra.*

[b] *Abbreviations: DEPT, Distortionless Enhancement by Polarization Transfer spectrum; ^1H-^1H COSY – proton-proton homonuclear correlation spectrum; HSQC, Heteronuclear Single Quantum Correlation experiment; HMBC, Long range ^1H-^{13}C Heteronuclear Multiple Bond Correlation experiment.*

[c] *Assigned from the HSQC spectrum.*

[d] *Weak correlations.*

[e] *Extremely weak correlations.*

^{13}C signals of the chemically equivalent carbons, C-3/7 and C-4/6, respectively at 128.76 ppm and at 121.33 ppm, were with the highest intensity. COSY correlations (7.39 ppm - 7.16 ppm) and (7.71 ppm - 7.39 ppm), indicate that 7.39 ppm was assigned for the signals of protons, H-3/7 and these at 7.71 ppm and 7.16 ppm – for the signals of the protons, H-4/6 and H-2. The weak HMBC correlation (7.16 ppm – 138.19 ppm) indicated the interaction between the proton, H-2, and the carbon, C-5. The strong HMBC correlations, (7.39 ppm – 138.19 ppm) and (7.71 ppm – 138.19 ppm), indicate for the closer interactions of the protons, H-3/7 and H-4/6, with C-5. Strong HMBC correlations were found for the signal of NH-9 proton with the signals of carbons, C-4/6, (10.65 ppm – 121.33 ppm). ^1H spectrum of AA’MM’X system was simulated by using the option *Spin Simulation* and the following parameters. - (δ_H 7.71 ppm for H-4/6 (AA’ part); δ_H 7.39 ppm for H-3/7 (MM’ part); δ_H 7.16 (X part)); $J^3_{MX}=J^3_{M'X}$= 7.4 Hz, $J^4_{AX}=J^4_{A'X}$=1.3 Hz, $J^4_{AA'}$ = 1.5 Hz, $J^4_{MM'}$ = 2.0 Hz, J^3_{AM}= $J^3_{A'M'}$ = 8.2 Hz, $J^5_{AM'}=J^5_{A'M}$= 0.3 Hz).

Vibrational data assigned for XVI

IR, cm^{-1}: 3427 (ν(NH)), 3286 (ν(NH), 3109 (ν(Csp^2-H)), 3063 (ν(Csp^2-H)), 1772 (ν(C=O)), 1588 (ν(C=C)), 1509 (ν(C=C)), 1495 (ν(C=C)), 1447 (ν(C=C)), 757 (ϒ(C-H).

Raman, cm^{-1}: 3064 (ν(Csp^2-H)), 1725 ν(C=O), 1588 (ν(C=C)), 1494 (ν(C=C)), 1449 (ν(C=C))

Structure verification of XVII

The structure of XVII is presented on Figure 12 with atom numbering used only for the spectral assignments (Table 18).

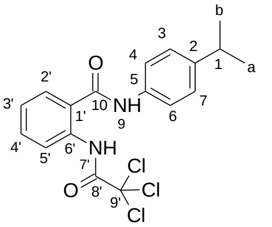


Figure 12. Suggested structure for XVII

The molecular formula of XVII is $C_{18}H_{17}N_2Cl_3O_2$. Protons H-3, H-7, H-4 and H-6 form AA’XX’ system.

Table 18. ^{1}H and ^{13}C NMR data for XVII. [^{1}H [600.13 MHz] and ^{13}C [150.90 MHz]][a]

Atom	δ (^{13}C), ppm	DEPT[b]	δ (^{1}H), ppm	Multiplicity (J, Hz)	^{1}H-^{1}H COSY [b]	HMBC[b]
1’	122.90	C				
2’	129.20	CH	8.01	d(7.4)	3’, 4’[d]	4’,6’,10
3’	124.97	CH	7.41	t(7.6)	2’,4’, 5’[d]	1’,2’[c],5‘
4’	132.74	CH	7.68	t(7.8)	2’[d],3’, 5’	2’, 5’[d],6’
5‘	120.86	CH	8.31	d(8.3)	3’[d], 4’	1’, 3’
6‘	136.95	C				
7’(NH)			12.53	s		5’[c],8’[c]
8’(C=O)	159.37	C				
9’	92.72	C				
1	33.02	CH	2.87	sept(6.9)	a/b	2,3/7,a/b
2	144.82	C				
3/7	126.50	CH	7.25	m	4/6	1, 3/7, 4/6[c], 5
4/6	121.52	CH	7.59	m	3/7, 9[d]	2, 4/6, 5[c]
5	135.84	C				
a/b	23.98	CH_3	1.20	d(6.9)	1	a/b,1,2
9(NH)			10.60	s	4/6[d]	4/6,10
10(C=O)	166.80	C				

[a] *In DMSO-d_6 solution. All spectral assignments were in agreement with HMQC, HMBC and COSY spectra.*

[b] *Abbreviations: DEPT, Distortionless Enhancement by Polarization Transfer spectrum; ^{1}H-^{1}H COSY – proton-proton homonuclear correlation spectrum; HMQC, Heteronuclear Multiple Quantum Correlation experiment; HMBC, Long range ^{1}H-^{13}C Heteronuclear Multiple Bond Correlation experiment.*

[c] *Weak correlations.*

[d] *Extremely weak correlations.*

The *Spin Simulation* option was used to simulate the spectra of the AA’ and XX’ parts with the following set of parameters - δ_H 7.25 ppm for H-3/7 (AA’ part), δ_H 7.59 ppm for H-4/6 (XX’ part), $J^4_{AA'}$ = 2.0 Hz, $J^4_{XX'}$ = 1.5 Hz, J^3_{AX}= $J^3_{A'X'}$ = 6.0 Hz, $J^5_{AX'}$=$J^5_{A'X}$= 0.3 Hz. The most intensive ^{13}C signals at 126.50 ppm and 121.52 ppm correspond to carbons, C-3/7 and C-4/6. ^{1}H doublet at 1.20 ppm with area of 6.07 correspond to the protons in both -CH_3 groups a and b, supported by the strong COSY correlation between the signals of -CH_3 protons and H-1 proton – (1.20 ppm – 2.87 ppm). The strong HMBC correlation, (7.25 ppm – 33.02 ppm), indicated the interaction between the protons H-3/7 and carbon, C-1. The HMBC correlations (7.59 ppm – 144.82 ppm), (2.87 ppm – 144.82 ppm) and (1.20 ppm – 144.82 ppm) corresponded to the interaction of protons H-4/6, H-1 and H-a/b with the nonprotonated carbon, C-2.

Vibrational data assigned for XVII

IR, cm^{-1}: 3431 (v(NH)), 3273 (v(NH)), 3063 (v(Csp^2-H)), 3047(v(Csp^2-H)), 2966 (v_{as}(CH_3)), 2867 (v_s(CH_3)), 1725 (v(C=O)), 1600 v(C=C), 1449 (v(C=C)), 755 (ϒ(C-H)

Raman, cm^{-1}: 3063 (v(Csp^2-H)), 3047(v(Csp^2-H)), 2969 (v_{as}(CH_3)), 2867 v_s(CH_3), 1725 (v(C=O)), 1612 (v(C=C)), 1596 v(C=C), 1589 (v(C=C)), 1448 (v(C=C)), 763 (ϒ(C-H)

Structure verification of XVIII

The structure of XVIII is presented on Figure 13 with the atom numbering used only for the spectral assignments (Table 19).

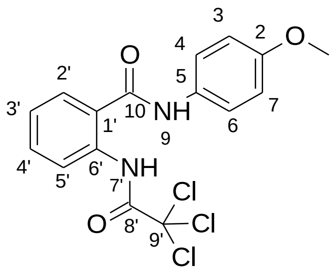


Figure 13. Suggested structure for XVIII

Table 19. ^{1}H and ^{13}C NMR data assigned for XVIII. [^{1}H [600.13 MHz] and ^{13}C [150.90 MHz]]^{a}

Atom	*δ (^{13}C), ppm*	*DEPT^{b}*	*δ (^{1}H), ppm*	*Multiplicity (J, Hz)*	*^{1}H-^{1}H COSY ^{b}*	*HMBC^{b}*
1’	*122.71*	*C*				
2’	*129.09*	*CH*	*8.02*	*dd(7.9, 1.2)*	*3’, 4’^{d}*	*4’,6’,10*
3’	*124.91*	*CH*	*7.40*	*t(7.6)*	*2’,4’, 5’^{d}*	*1’,2’^{c},5‘,6’^{d}*
4’	*132.67*	*CH*	*7.68*	*m*	*2’^{d},3’, 5’*	*2’,6’*
5‘	*120.76*	*CH*	*8.32*	*d(8.3)*	*3’^{d},4’*	*1’, 3’,6’^{d}*
6‘	*137.00*	*C*				
7’(NH)			*12.62*	*s*		*5’^{c},8’^{c}*
8’(C=O)	*159.34*	*C*				
9’	*92.73*	*C*				
2	*156.24*	*C*				
3/7	*113.88*	*CH*	*6.96*	*m*	*4/6*	*2,3/7,5*
4/6	*123.04*	*CH*	*7.60*	*m*	*3/7, 9^{d}*	*2, 4/6, 5*
5	*131.02*	*C*				
-OCH$_3$	*55.25*	*CH$_3$*	*3.75*	*s*		*2*
9(NH)			*10.55*	*s*	*4/6^{d}*	*4/6,10*
10(C=O)	*166.56*	*C*				

^{a}In DMSO-d$_6$ solution. All spectral assignments were in agreement with HMQC, HMBC and COSY spectra.

^{b}Abbreviations: DEPT, Distortionless Enhancement by Polarization Transfer spectrum; ^{1}H-^{1}H COSY – proton-proton homonuclear correlation spectrum; HMQC, Heteronuclear Multiple Quantum Correlation experiment; HMBC, Long range ^{1}H-^{13}C Heteronuclear Multiple Bond Correlation experiment.

^{c} Weak correlations.

^{d}Extremely weak correlations.

The molecular formula of XVIII is $C_{16}H_{13}N_2Cl_3O_3$. Protons, H-3/7 and H-4/6, form AA‘XX’spin system that produced complex ^{1}H multiplets at 7.60 ppm and 6.96 ppm. It was easy to observe the most intensive ^{13}C signals at 113.88 ppm and 123.04 ppm corresponding to the chemically equivalent pair of carbons, C-3/7 and C-4/6. *Spin Simulation* was used to simulate the spectrum of the AA’XX’ spin system with the following set of parameters - δ_H 6.96 ppm for H-3/7 (AA’ part); δ_H 7.60 ppm for H-4/6 (XX’ part), $J^4_{AA'}$ = 3.0 Hz, $J^4_{XX'}$ = 2.2 Hz, J^3_{AX}= $J^3_{A'X'}$ = 7.8 Hz, $J^5_{AX'}$=$J^5_{A'X}$= 0.45 Hz. The signals at 55.25 ppm and 3.75 ppm were assigned respectively to the carbon and protons in the –OCH_3 group.

Vibrational data assigned for XVIII

IR, cm^{-1}: 3431 (v(NH)), 3295 (v(NH)), 3118 (v(Csp^{2}-H)), 3058 (v(Csp^{2}-H)), 2977 (v$_{as}$(CH$_3$)), 2841 (v(O-CH$_3$)), 1682(v(C=O)), 1603 (v(C=C), 1591 (v(C=C)), 1512 v(C=C), 1474 (v(C=C)), 761(ϒ(C-H)

Raman, cm^{-1}: 3085 (v(Csp^{2}-H)), 3059 (v(Csp^{2}-H)), 3006 (v(Csp^{2}-H)), 2977 (v$_{as}$(CH$_3$)), 2920, 2841 (v(O-CH$_3$)), 1724 (v(C=O)), 1600 v(C=C), 1591 (v(C=C)), 1512 v(C=C), 1448 (v(C=C))

Structure verification of XIX

The suggested structure for XIX is presented on Figure 14 with the atom numbering used only for the spectral assignments (Table 20).

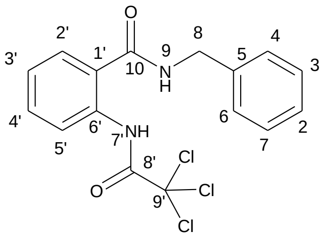


Figure 14. Suggested structure for XIX

Table 20. ^{1}H and ^{13}C NMR data assigned for XIX. [^{1}H [600.13 MHz] and ^{13}C [150.90 MHz]][a]

Atom	*δ (^{13}C), ppm*	*DEPT*[b]	*δ (^{1}H), ppm*	*Multiplicity (J, Hz)*	*^{1}H-^{1}H COSY*[b]	*HMBC*[b]
1’	*120.97*	*C*				
2’	*128.45*	*CH*	*7.97*	*dd(8.0, 1.4)*	*3’,4’*[c]	*1’*[c]*, 4’,6’,10*
3’	*124.77*	*CH*	*7.35*[e]	*td(7.5, 1.0)*	*2’,4’,5’*[c]	*1’, 4’*[c]
4’	*132.83*	*CH*	*7.65*	*m*	*2’*[c]*, 3’, 5’*	*5’*[c]*, 2’, 6’*
5‘	*120.22*	*CH*	*8.39*	*dd(8.4, 1.0)*	*3’*[c]*, 4’*	*1’, 3’,6’*[c]*,10*[d]
6‘	*137.50*	*C*				
7’(NH)			*13.19*	*s*		*5’,8’*
8’(C=O)	*159.35*	*C*				
9’	*92.82*	*C*				
2	*127.02*	*CH*	*7.25*	*dt(8.6,4.4)*	*3/7, 4/6*[c]	*3/7*[c]
3/7	*128.44*	*CH*	*7.34*[e]	*m*	*2, 4/6*	*3/7, 4/6, 5*
4/6	*127.29*	*CH*	*7.33*[e]	*m*	*2*[c]*, 3/7*	*3/7, 4/6, 2, 8*
5	*138.75*	*C*				
8	*42.67*	*CH_2*	*4.52*	*d(6.0)*	*9*	*4/6,5,10*
9(NH)			*9.58*	*t(6.0)*	*8*	*10*
10(C=O)	*168.14*	*C*				

[a] *In DMSO-d_6 solution. All spectral assignments were in agreement with HMQC, HMBC and COSY spectra.*

[b] *Abreviations: DEPT, Distortionless Enhancement by Polarization Transfer spectrum; ^{1}H-^{1}H COSY – proton-proton homonuclear correlation spectrum; HMQC, Heteronuclear Multiple Quantum Correlation experiment; HMBC, Long range ^{1}H-^{13}C Heteronuclear Multiple Bond Correlation experiment.*

[c] *Weak correlations.*

[d] *Extremely weak correlations.*

[e] *Assigned from HMBC spectrum.*

The molecular formula is $C_{16}H_{13}N_2Cl_3O_2$. Protons, H-3/7 and H-4/6, form *AA’BB’X* spin system, producing ^{1}H multiplet at 7.34 ppm with an area of 5.17, including the signals of the protons H-3/7, H-4/6 and H-3’. The differentiation of their signals was based on the strong HMBC correlations, (4.52 ppm – 127.29 ppm) and (7.33 – 42.67 ppm), indicating the interactions of -CH_2 protons with the carbons, C-4/6, as well as the interaction of H-4/6 protons with the carbon, C-8. Simulation of the *AA’BB’X* spectrum was based on the following set of parameters - (δ_H 7.33 ppm for H-4/6 (AA’ part); δ_H 7.34 ppm for H-3/7 (BB’ part); δ_H 7.25 (X part)); $J^3_{BX}=J^3_{B'X}$= 6.5 Hz, $J^4_{AX}=J^4_{A'X}$=3.9 Hz, $J^4_{AA'}$ = 1.2 Hz, $J^4_{BB'}$ = 4.0 Hz, J^3_{AB}= $J^3_{A'B'}$ = 8.5 Hz, $J^5_{AB'}=J^5_{A'B}$= 0.8 Hz). The HMBC correlation, (7.34 ppm – 138.75 ppm), indicated for the strong interaction between the protons H-3/7 and nonprotonated carbon, C-5. The weak HMBC correlation (7.35 ppm – 132.83 ppm) indicate that 7.35 ppm was for the signal of H-3’ proton that interacted weakly with the cabon, C-4’. The another weak HMBC correlation, indicating the interaction between the proton, H-2, and carbons, C-3/7, is (7.25 ppm – 128.44 ppm).

Vibrational data assigned for XIX

IR, cm^{-1} : 3388 (v(NH), 3088 (v(Csp^{2}-H)), 3067(v(Csp^{2}-H)), 3029 (v(Csp^{2}-H)), 2942 ($v_{as}(CH_2)$)), 1722 (v(C=O)), 1599 (v(C=C)), 1588 (v(C=C)), 1523 (v(C=C)), 1495 (v(C=C)), 1452 (v(C=C)), 1435 (v(C=C)), 762 (ϒ(C-H)

Raman, cm^{-1} : 3068 (v(Csp^{2}-H)), 3046 (v(Csp^{2}-H)), 2946 ($v_{as}(CH_2)$)), 1718 (v(C=O)), 1603 (v(C=C)), 1586 (v(C=C)), 1519 (v(C=C)), 1453 (v(C=C)), 1436 (v(C=C)), 763 (ϒ(C-H)

Structure verification of XX

The structure of XX is shown on Figure 15 with the atom numbering used for the spectral assignments (Table 21).

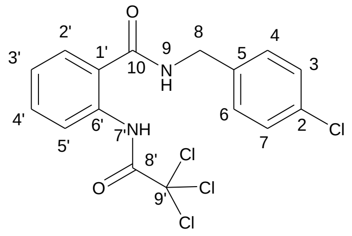


Figure 15. Suggested structure for XX

Table 21. ^{1}H and ^{13}C NMR data assigned for XX. [^{1}H [600.13 MHz] and ^{13}C [150.90 MHz][a]

Atom	δ (^{13}C), ppm	DEPT[b]	δ (^{1}H), ppm	Multiplicity (J, Hz)	^{1}H-^{1}H COSY [b]	HMBC[b]
1’	120.86	C				
2’	128.44	CH	7.96	dd(8.0, 1.3)	3’, 4’[d]	4’,6’,10
3’	124.74	CH	7.35[e]	td(7.6, 1.0)	2’,4’,5‘[d]	1’,5‘
4’	132.86	CH	7.66	m	2’[d], 3’, 5’	2’, 6’
5‘	120.24	CH	8.39	dd(8.3, 0.6)	3’[d], 4’	1’, 3’
6‘	137.50	C				
7’(NH)			13.15	s		5’[c],8’[c]
8’(C=O)	159.32	C				
9’	92.79	C				
2	131.54	C				
3/7	128.35	CH	7.40[e]	m	4/6	3/7, 5
4/6	129.19	CH	7.36[e]	m	3/7	2, 4/6, 8
5	137.79	C				
8	42.04	CH_2	4.50	d(5.9)	9	4/6,5,10
9(NH)			9.59	t(6.1)	8	10
10(C=O)	168.17	C				

[a] *In DMSO-d_6 solution. All spectral assignments were in agreement with HMQC, HMBC and COSY spectra.*

[b] *Abbreviations: DEPT, Distortionless Enhancement by Polarization Transfer spectrum; ^{1}H-^{1}H COSY – proton-proton homonuclear correlation spectrum; HMQC, Heteronuclear Multiple Quantum Correlation experiment; HMBC, Long range ^{1}H-^{13}C Heteronuclear Multiple Bond Correlation experiment.*

[c] *Weak correlations.*

[d] *Extremely weak correlations.*

[e] *Assigned from HMBC spectrum.*

The molecular formula of XX is $C_{16}H_{12}N_2Cl_4O_2$. Protons, H-3/7 and H-4/6, form *AA’BB’* spin system, producing complex multiplets at 7.40 ppm and 7.36 ppm. The ^{13}C sgnals at 128.35 ppm and 129.19 ppm, assigned for the chemically equivalent carbons, C-3/7 and C-4/6, were with the highest intensity. The strong HMBC correlations (7.36 ppm – 42.04 ppm) and (4.50 ppm – 129.19 ppm) indicate the interactions of the H-4/6 and methylene protons, respectively with the cabons, C-8 and C-4/6. The HMBC correlation, (4.50 ppm – 137.79 ppm), indicate the interaction of the methylene protons with the nonprotonated carbon, C-5. The another HMBC correlation, (7.36 ppm – 131.54 ppm), indicated for the interaction of the H-4/6 protons with the cabon, C-2. HMBC correlations, (7.35 ppm – 120.24 ppm) and (7.35 ppm – 120.86 ppm) are result from the meta interactions of the H-3’ proton with the carbons, C-5’ and C-1’. Parameters, used for the simulation of the *AA’BB’ spectrum* with *Spin Simulation* option were: δ_H 7.40 ppm for H-3/7 (AA’ part); δ_H 7.36 ppm for H-4/6 (BB’ part) were: $J^4_{AA'} = J^4_{BB'} = 2.0$ Hz, $J^3_{AB} = J^3_{A'B'} = 8.0$ Hz, $J^5_{AB'} = J^5_{A'B} = 0.2$ Hz.

Vibrational data assigned for XX

IR, cm^{-1}: 3303 (ν(NH), 3196 (ν(NH)), 3115 (ν(Csp^2-H)), 3072 (ν(Csp^2-H)), 2853 (ν$_s$(CH$_2$)), 1716 (ν(C=O)), 1596 (ν(C=C)), 1588 (ν(C=C)), 1522(ν(C=C)), 1493(ν(C=C)), 1449 (ν(C=C)), 762 (ϒ(C-H)

Raman, cm^{-1}: 3070 (v(Csp^2-H)), 2928 (v$_{as}$(CH$_2$)), 2853(v$_s$(CH$_2$)), 1715 (v(C=O)), 1600(v(C=C)), 1586 (v(C=C)), 1520 (v(C=C)), 1449 (v(C=C)), 763 (ϒ(C-H)

Structure verification of XXI

There is NMR data presented in the DSc thesis [1] of Prof. DSc Plamen Penchev (Faculty of Chemistry, University of Plovdiv “Paisii Hilendarski”) for the structure of XXI (Figure 16) which was assigned from one- and two-dimensional NMR spectra. Nevertheless, the spectrum of the *ABX* system, formed by the protons H-4, H-6 and H-7, was not simulated there in order to predict the values of the coupling constants. Moreover, the chemical shifts of the ^{13}C signals of C-4 and C-7 carbons were mistakenly interchanged.

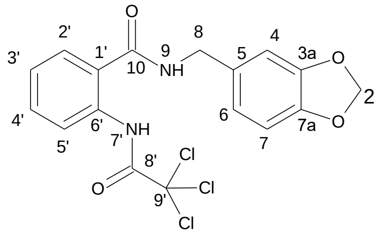


Figure 16. Suggested structure for XXI

The molecular formula is $C_{17}H_{13}N_2Cl_3O_4$. Using the *Spin Simulation* option, the *ABX* spectrum was simulated with the following set of parameters - δ_H 6.92 ppm for H-4 ($^4J_{HH}$ = 1.3 Hz, $^5J_{HH}$ = 0.1 Hz), as well as δ_H 6.81 ppm and δ_H 6.86 ppm for H-6 ($^4J_{HH}$ = 1.3 Hz, $^3J_{HH}$ =8.0Hz) and H-7 ($^5J_{HH}$ = 0.1Hz, $^3J_{HH}$ =8.0 Hz). A strong COSY correlation (6.81 ppm – 6.86 ppm), indicated that the protons, H-6 and H-7, are neighbors (Table 22).

Table 22. ^{1}H and ^{13}C NMR data assigned for XXI. [^{1}H [600.13 MHz] and ^{13}C [150.90 MHz][a]

Atom	*δ (^{13}C), ppm*	*DEPT*[b]	*δ (^{1}H), ppm*	*Multiplicity (J, Hz)*	*^{1}H-^{1}H COSY* [b]	*HMBC*[b]
1’	121.54	C				
2’	128.67	CH	7.94	dd(7.9, 1.3)	3’,4’[d]	1’[d], 4’,6’,10
3’	125.24	CH	7.33	td(7.7, 1.1)	2’,4’,5’[d]	1’, 5’, 2’[c],4’[d], 6’[d]
4’	133.13	CH	7.65	m	2’[d], 3’, 5’	5’[c], 2’, 6’
5‘	120.64	CH	8.38	dd(8.2, 0.6)	3’[d],4’	1’, 3’,6’[c],10[d]
6‘	137.55	C				
7’(NH)			13.17	s		
8’(C=O)	159.72	C				
9’	93.07	C				
2	101.22	CH_2	5.98	s		3a,7a
3a	147.60	C				
7a	146.55	C				
4	108.37	CH	6.92	m	6[c],7[d],8[c]	6, 8,7a
5	132.92	C				
6	121.05	CH	6.81	m	4[c],7,8[d]	4,7a,8
7	108.45	CH	6.86	m	4[d],6	3a,5
8	42.82	CH_2	4.41	d(6.0)	4[c],6[d],9	4,6,5,10
9(NH)			9.50	t(6.1)	8	8[c], 10
10(C=O)	168.41	C				

[a] *In DMSO-d_6 solution. All spectral assignments were in agreement with HMQC, HMBC and COSY spectra.*

[b] *Abbreviations: DEPT, Distortionless Enhancement by Polarization Transfer spectrum; ^{1}H-^{1}H COSY – proton-proton homonuclear correlation spectrum; HMQC, Heteronuclear Multiple Quantum Correlation experiment; HMBC, Long range ^{1}H-^{13}C Heteronuclear Multiple Bond Correlation experiment.*

[c] *Weak correlations.*

[d] *Extremely weak correlations.*

Other useful HMBC correlations were (6.81 ppm - 42.82 ppm) and (6.86 ppm – 132.92 ppm), indicating for the interactions of H-6 and H-7 protons, respectively with the carbons, C-8 and C-5. The assignment of the signals of nonprotonated carbons, C-3a and C-7a, was based on the strong meta HMBC correlations, in which they participate – (6.92 ppm – 146.55 ppm), (6.81 ppm – 146.55 ppm) and (6.86 ppm – 147.60 ppm). The signals of methylene protons, H-2, appear to have strong HMBC correlations with the carbons, C-3a and C-7a – (5.98 ppm – 147.60 ppm) and (5.98 ppm – 146.55 ppm).

Vibrational data assigned for XXI

IR, cm^{-1}: 3318 (v(NH), 3244 (v(NH)), 3075 (v(Csp^2-H)), 2923 (v$_{as}$(CH$_2$)), 1718 (v(C=O)), 1707 (v(C=O)), 1601 (v(C=C)), 1587 (v(C=C)), 1518 (v(C=C)), 1503 (v(C=C)), 1490 (v(C=C)), 1447 (v(C=C)), 764 (ϒ(C-H)

Raman, cm^{-1}: 3076 (v(Csp^2-H)), 2942 (v$_{as}$(CH$_2$)), 1718 (v(C=O)), 1707 (v(C=O)), 1599 (v(C=C)), 1587 (v(C=C)), 1516 (v(C=C)), 1502 (v(C=C)), 1448 (v(C=C))

1.7. 2-amino-1*H*-benzo[*d*]isoquinoline derivatives

Structure verification of XXII

The next two compounds were synthesized by the team of Assoc. Prof. Dr. Marin Marinov (Agricultural University – Plovdiv) and coworkers. There is NMR data existing for the structure of XXII (Figure 17) presented in previous two publications [6][2], but it is only from 1D NMR spectra (Table 23).

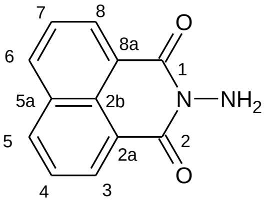


Figure 17. Suggested structure for XXII

Molecular formula of XXII is $C_{12}H_8N_2O_2$. The signals of carbons, C-5a, C-2b and C-2a/8a were assigned according to the strong meta HMBC correlations in the benzene rings – (8.47 ppm – 134.46 ppm), (8.47 ppm – 125.94 ppm), (7.85 ppm – 131.21 ppm), (7.85 ppm – 121.62 ppm) and (8.42 ppm – 125.94 ppm). The only singlet in ^{1}H spectrum at 5.78 ppm was assigned to the signal of the NH_2 protons, for which there were not HMBC correlations.

Table 23. ^{1}H and ^{13}C NMR data assigned for XXII. [^{1}H [500.13 MHz] and ^{13}C [125.76 MHz]][a]

Atom	*δ (^{13}C), ppm*	*DEPT*[b]	*δ (^{1}H), ppm*	*Multiplicity (J, Hz)*	*^{1}H-^{1}H COSY*[b]	*HMBC*[b]
3/8	*130.75*	*CH*	*8.47*	*dd(7.3, 1.1)*	*4/7, 5/6*	*1/2, 4/7[c], 5/6,2b,2a/8a[c]*
4/7	*127.25*	*CH*	*7.85*	*dd(8.2, 7.3)*	*3/8, 5/6*	*1/2[c],2b[c],5a,2a/8a,3/8[c],5/6[c]*
5/6	*134.46*	*CH*	*8.42*	*dd(8.3, 1.0)*	*3/8, 4/7*	*3/8, 4/7, 2b, 2a/8a[c],5a[c]*
5a	*131.21*	*C*				
2b	*125.94*	*C*				
2a/8a	*121.62*	*C*				
4'(NH$_2$)			*5.78*	*s*		
1/2(C=O)	*160.46*	*C*				

[a] *In DMSO-d$_6$ solution. All spectral assignments were in agreement with HSQC, HMBC and COSY spectra.*

[b] *Abbreviations: DEPT, Distortionless Enhancement by Polarization Transfer spectrum; ^{1}H-^{1}H COSY – proton-proton homonuclear correlation spectrum; HSQC, Heteronuclear Single Quantum Correlation experiment; HMBC, Long range ^{1}H-^{13}C Heteronuclear Multiple Bond Correlation experiment.*

[c] *Weak correlations.*

Partially assigned ^{1}H NMR data was presented for the compound in [6], as the ^{13}C NMR data was not assigned. Meanwhile, NMR data only from 1D NMR spectra was presented in [2], as a part of the^{13}C NMR data presented there was mistakenly assigned. For example, the chemical shifts of the signals assigned for the carbons in [2] were the following – 134.5 ppm (C-3/8), 130.8 ppm (C-5/6), 125.9 ppm (C-5a), 122.4 ppm (C-2b), 130 ppm (C-2a/8a).

Structure verification of XXIII

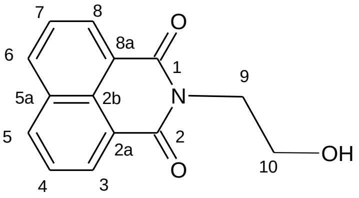


Figure 18. Suggested structure for XXIII

Only partially assigned NMR data was found in the literature for the structure of XXIII [3] (Figure 18), as part of it were in a good agreement with the fully assigned NMR data presented in this dissertation (Table 24).

Table 24. ^{1}H and ^{13}C NMR data assigned for XXIII. [^{1}H [500.13 MHz] and ^{13}C [125.76 MHz]][a]

Atom	δ (^{13}C), ppm	DEPT[b]	δ (^{1}H), ppm	Multiplicity (J, Hz)	^{1}H-^{1}H COSY[b]	HMBC[b]
3/8	130.58	CH	8.44	dd(7.3, 1.0)	4/7, 5/6	1/2, 4/7,5/6,2b,2a/8a[c]
4/7	127.12	CH	7.83	dd (8.1, 7.3)	3/8,5/6	1/2[c],2b[c],5a,2a/8a,3/8[c],5/6[c]
5/6	134.14	CH	8.41	dd(8.3, 0.9)	3/8, 4/7	2a/8a[c], 3/8, 4/7, 2b, 5a[c],1/2[d]
5a	131.21	C				
2b	127.33	C				
2a/8a	122.11	C				
1/2(C=O)	163.47	C				
9	41.79	CH_2	4.14	t(6.6)	10	10,1/2
10	57.78	CH_2	3.62	q(6.4)	9,OH	9
OH			4.81	t(6.0)	10	9,10

[a]In DMSO-d_6 solution. All spectral assignments were in agreement with HSQC, HMBC and COSY spectra.

[b]Abbreviations: DEPT, Distortionless Enhancement by Polarization Transfer spectrum; ^{1}H-^{1}H COSY – proton-proton homonuclear correlation spectrum; HSQC, Heteronuclear Single Quantum Correlation experiment; HMBC, Long range ^{1}H-^{13}C Heteronuclear Multiple Bond Correlation experiment.

[c] Weak correlations.

[d] Extremely weak correlations.

The molecular formula of XXIII is $C_{14}H_{11}NO_3$. HSQC correlations, (4.14 ppm - 41.79 ppm) and (3.62 ppm - 57.78 ppm) (Table 24), together with the multiplicities of the ^{1}H signals at 4.14 ppm (triplet) and 3.62 ppm (quartet) indicate that 4.14 ppm and 41.79 ppm were for the ^{1}H and^{13}C signals of $C^{9}H_2$, while 3.62 ppm and 57.78 ppm – for ^{1}H and ^{13}C signals of $C^{10}H_2$. The conclusions were supported by the COSY correlation, (3.62 ppm – 4.81 ppm), as well as from the strong HMBC correlation, (4.14 ppm – 163.47 ppm).

CONCLUSION

The literature was enriched with fully assigned NMR and partially assigned vibrational data for 23 organic compounds, from which 3-[(4-fluorophenyl)methylidene]-1*H*,3*H*-naphtho-[1,8-*cd*]-pyran-1-one, Au(III) and Cu(II) complexes, dispiroimidazolidines are novel, according to the scientific literature and the structure search in the PubChem database.

The NMRShiftDB database was enriched with the structures of the fluorenylspirohydantoins and naphtopyranones together with the assigned ^{1}H and ^{13}C chemical shifts and ^{1}H signal multiplicities.

Some mistakes in the assigned NMR data, previously published for four of the organic structures, (*5′-oxospiro-(fluorene-9,4′-imidazolidine)-2′-thione*, *2,4-dithiouracil*, *N-[(2H-1,3-benzodioxol-5-yl)methyl]-2-(2,2,2-trichloroacetamido)benzamide*, *2-amino-1H-benzo[d]isoquinoline-1,3(2H)-dione*), included in this dissertation, were corrected.

SCIENTIFIC AND SCIENTIFICALLY APPLICABLE CONTRIBUTIONS

1. Enrichment of scientific literature with fully assigned NMR and partially assigned vibrational data for organic compounds from different classes;
2. Correction of mistakes in previously published and assigned NMR data for four organic structures included in this dissertation;
3. Enrichment of NMRShiftDB database with the structures of fluorenylspirohydantoins and naphtopyranones as well as with a part of the assigned ^{1}H and ^{13}C NMR data.

The connection between the contributions, the dissertation tasks, the place of their description in the dissertation and the corresponding publications on the dissertation topic are shown in Table 25.

Table 25. Contributions, tasks, publications and the place of their description in the dissertation.

Contribution	Tasks	Section from the dissertation	Publications	Conference reports
Contribution 1	1-10	3	1-4	1
Contribution 2	1,3,6,7	3	2, 4	
Contribution 3	1,2,11	3	1,3	

PUBLICATIONS ON THE TOPIC OF DISSERTATION

[1] Marinov.M., Stoitsov, D., Frenkeva, M., Marinova, P., Penchev, P., Stoyanov, N., A complete ^{1}H and ^{13}C NMR data assignment for two substituted fluorenylspirohydantoins, Bulgarian Chemical Communications, Vol. 56, Special Issue D, 2024, pp. 67-72, https://doi.org/10.34049/bcc.56.D.S1P28

[2] Marinova, P., Stoitsov, D., Burdzhiev, N., Tsoneva, S., Blazheva, D, Slavchev, A., Varbanova, E., Penchev, P., Investigation of the Complexation Activity of 2,4-Dithiouracil with Au(III) and Cu(II) and Biological Activity of the Newly Formed Complexes; Applied Sciences, Vol. 14, No. 15, 2024, https://doi.org/10.3390/app14156601

[3] Stoitsov, D., Marinov, M., Penchev, P., Frenkeva, M., Stoyanov, N., A Complete ^{1}H and ^{13}C NMR Data Assignment for Three 3-[Substituted methylidene]-1*H*,3*H*-naphtho-[1,8-

cd]-pyran-1-ones, Crystals, Vol. 14, No. 10, 2024, pp. 871, https://doi.org/10.3390/cryst14100871

[4] Stoitsov, D., Marinov, M., Penchev, P., Marinova, P., Stoyanov, N., 5′-Oxospiro-(fluorene-9,4′-imidazolidine)-2′-thione; Molbank, Vol. 2024, No. 3, 2024, M1864, https://doi.org/10.3390/M1864

PARTICIPATION IN CONFERENCES

[1] Marinov, M., Stoitsov, D., Frenkeva, M., Marinova, P., Penchev, P., Stoyanov, N., A complete ^{1}H and ^{13}C NMR data assignment for two substituted fluorenylspirohydantoins, 12th Chemistry Conference, 13-14 October 2023, Plovdiv

PARTICIPATION IN PROJECTS

[1] „Interdisciplinary applications of NMR spectroscopy – Д23-2-ХФ-013“, Funding source: European Union - NextGenerationEU, through the National Recovery and Resilience Plan of the Republic of Bulgaria, project DUECOS BG-RRP-2.004-0001-C01, Time period: 01.11.2023 г. – 01.11.2025 г.

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- Assoc. Prof. Dr. Jan Petrov for the synthesis of benzamides;
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[18] Stoitsov, D., Marinov, M., Penchev, P., Marinova, P., Stoyanov, N., 5′-Oxospiro-(fluorene-9,4′-imidazolidine)-2′-thione; Molbank, Vol. 2024, No. 3, 2024, M1864, https://doi.org/10.3390/M1864