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**FULL ASSIGNMENT OF ¹H AND ¹³C NMR SPECTRA
OF (9H-FLUOREN-9-YL) UREA**

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Abstract: The purpose of this paper is to fully assign the ¹H and ¹³C NMR spectra of (9H-fluoren-9-yl)urea. The assignment was assisted by data obtained from ¹H-¹H COSY, DEPT-135, HMQC spectrum and confirmed by HMBC spectrum. The experimental data was compared to data obtained with quantum chemistry. The calculations were performed for two geometrical structures of TMS with the eclipsed one showing closer approximation to the experimental data. Hartree-Fock exchange correlation functional was employed and the 6-311+g(2d,p) basis set. The difference between calculated and experimental ¹H NMR chemical shifts have standard deviation of 0.60 ppm with a maximum deviation 0.97 ppm and the difference between calculated and experimental ¹³C NMR chemical shifts have standard deviation of 6.49 ppm with a maximum deviation 11.17 ppm.

Keywords: (9H-fluoren-9-yl)urea, ¹H NMR spectra, ¹³C NMR spectra, Quantum chemistry

INTRODUCTION

Some spirohydantoinins are known to have biological activity (Marinova et al., 2014), and citations therein). Considering the aromatic character of fluorene moiety in (9'-fluorene)-spiro-5-hydantoin /spiro-(fluorene-9,4'-imidazolidine)-2',5'-dione/ most of the chemical reactions are expected to break the hydantoin ring as it is reported in (Popova, J., 1997) and (Todorov, P., et al., 2008) giving either an alpha amino acid (as in the first cited paper) or a urea derivative. In our case (9H-Fluoren-9-yl)urea was obtained via alkaline hydrolysis with Ba(OH)₂·8H₂O of spiro(fluoren-9,4'-imidazolidine)-2',5'-dione as it is described in (Todorov, P., et al., 2008). Additionally, the full assignment of ¹H- and ¹³C-NMR signals is given with the aid of 1D and 2D NMR spectra which coincides with partially assigned NMR spectra reported in the above cited paper.

RESULTS AND DISCUSSIONS

(9H-Fluoren-9-yl)urea, 1, has the molecular formula C₁₄H₁₂N₂O (Fig.1). Since the compound itself was identified by comparison of 1D NMR spectra signals, the 2D NMR spectra confirmed the assignment of ¹H and ¹³C signals. This was used as a starting point in the spectral analysis allowing the assignment of signals in the fluorene segment and the following identification of urea. The ¹³C NMR (DMSO) spectrum showed eight signals, six of which with

considerably higher intensity belonging to the magnetically equivalent C atoms of the two aromatic rings. Four of them appear in the DEPT-135 (DMSO) spectrum together with the only methine group in the compound – C-9' (δ_C 55.02). ^1H NMR (DMSO) spectrum showed seven signals four of which, in the interval between δ_H 7.83-7.32, can be identified as aromatic. The ^1H - ^1H COSY spectrum additionally shows the adjacency of the aromatic H-atoms confirming the relations of the ^1H NMR peaks. The cross peaks belonging to signals at 7.54 (d, $J=7.4$ Hz, 2H), δ_H 7.32 (t, $J=7.4$ Hz, 2H), δ_H 7.40 (t, $J=7.4$ Hz, 2H) and δ_H 7.83 (d, $J=7.5$ Hz, 2H) are attributed to the couplings between H-1'-H-2', H-2'-H-3' and H-3'-H-4'. The signal at δ_H 7.54 (H-1') has a weak COSY correlation to δ_H 5.79 H-9' (d, $J=8.7$ Hz, 2H). Thus the assignment of the three remaining aromatic signals in the ^1H NMR is determined from ^1H - ^1H COSY spectrum. The signal at δ_H 5.64 (s, 2H) clearly belongs to H-3 and the one at δ_H 6.52 (d, $J=8.7$ Hz, 1H) to H-1. This is confirmed by the cross peaks by signals at δ_H 5.79 and δ_H 6.52 in the ^1H - ^1H COSY spectrum.

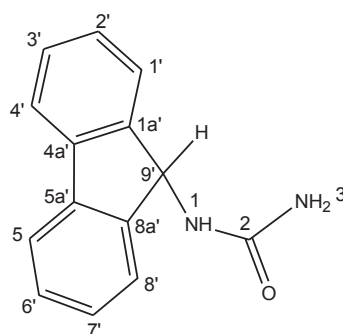


Fig. 1. Structure of (9H-fluoren-9-yl)urea, 1. The numbering of the atoms is only for spectral assignment

Table 1. ^1H NMR and ^{13}C NMR spectral data and ^1H - ^1H COSY and HMBC correlations for (9H-fluoren-9-yl)urea

Position	$\delta^{13}\text{C}$, ppm	DEPT-135	$\delta^1\text{H}$, ppm	multiplicity, (J , Hz)	^1H - ^1H COSY	HMBC
1	-		6.52	d (8.7)	9'	
2	159.25	C	-			1,9'
3	-		5.64	s		
1' / 8'	124.90	CH	7.54	d (7.4)	2', 3' ^c , 4' ^c , 9' ^b	2' ^c , 3', 4' ^b , 9' ^c
2' / 7'	127.59	CH	7.32	t (7.4)	1', 3', 4' ^c	3' ^c , 4'
3' / 6'	128.27	CH	7.40	t (7.4)	1' ^c , 2', 4'	1', 2' ^c
4' / 5'	120.11	CH	7.83	d (7.5)	1' ^c , 2', 3'	1' ^c , 2', 3' ^b
9'	55.16	CH	5.79	d (8.6)	1, 1' ^b	1, 1'
1a' / 8a'	145.88	C	-			2', 3' ^b , 4', 9'
4a' / 5a'	139.75	C	-			1', 2' ^b , 3', 4', 9' ^b

^aDMSO- d_6 solvent, ^1H 600.13 MHz, δ_{ref} 2.50 ppm; ^{13}C 150.9 MHz, δ_{ref} 39.51 ppm; All these assignments were in agreement with COSY, HMQC and HMBC spectra; ^b These correlations are weak; ^c These correlations are very weak.

The signals in HMQC help assign ^{13}C NMR peaks at δ_C 124.90, δ_C 127.59, δ_C 128.27 and δ_C 120.11 to the corresponding atoms C-1', C-2', C-3' and C-4'. The ^{13}C NMR peak at δ_C 159.25 is characteristic for the NC=O group (Pretsch et al., 2000). The assignment of the two remaining signals at δ_C 145.88 and δ_C 138.75 can be revealed by the HMBC spectrum, which also confirms the assignment of all ^1H NMR and ^{13}C NMR peaks. Table 1 contains the fully assigned spectral data.

Table 2 shows the comparison between the experimental spectral data and the predicted chemical shifts made by quantum chemistry. For this purpose the program Gaussian 98W was

used (Frisch M. J., et al., 1998). The geometry of the molecule was optimized with B3LYP (Becke three-parameter Lee–Yang–Parr) exchange-correlation functional on 6-31g (d) basis and the NMR data obtained with HF (Hartree–Fock) exchange-correlation functional on 6-311+g(2d,p) basis. When the data was processed better result were achieved for simulation with the eclipsed form of TMS for which the ¹³C NMR chemical shifts have standard deviation between calculated and experimental chemical shifts of 6.49 ppm with a maximum deviation of 11.17 for C-9'. The ¹H NMR shifts for H-1 and H-3 cannot be predicted accurately by this model and are therefore excluded from the calculation of standard deviation between calculated and experimental chemical shifts for ¹H which is 0.60 ppm with a maximum deviation of 0.97 ppm for H-9'.

Table 2. Comparison of experimental ¹H NMR and ¹³C NMR spectral data and data obtained with Quantum chemistry

Position	exp. $\delta^{13}\text{C}$	QC $\delta^{13}\text{C}$	exp. $\delta^1\text{H}$	QC $\delta^1\text{H}$
1	-	-	6.52	2.04
2	159.25	155.53	-	-
3	-	-	5.64	2.31
1' / 8'	124.90	134.39	7.54	8.20
2' / 7'	127.59	132.06	7.32	7.62
3' / 6'	128.27	135.59	7.40	7.81
4' / 5'	120.11	123.19	7.83	8.20
9'	55.16	43.99	5.79	4.82
1a' / 8a'	145.88	150.80	-	-
4a' / 5a'	139.75	140.58	-	-

CONCLUSIONS

Full assignment of the ¹H and ¹³C NMR spectra of (9H-fluoren-9-yl)urea was made. The assignment was assisted by data obtained from ¹H-¹H COSY, DEPT-135, HMQC spectrum and confirmed by HMBC spectrum. A comparison between experimental and data obtained with Quantum chemistry showed standard deviation between calculated and experimental chemical shifts for ¹H NMR and ¹³C NMR of 0.60 ppm and 6.49 ppm respectively.

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