ОРГАНІЧНА ХІМІЯ / ORGANIC CHEMISTRY

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^{1}H NMR SPECTRA OF N-METHYL-4-TOLYL-1-(4-BROMONAPHTHYL)-AMINE AND N-PHENYL-1-(4-BROMONAPHTHYL)-AMINE: A COMBINED EXPERIMENTAL AND THEORETICAL STUDY

Theoretical investigations of the conformational properties and ^{1}H NMR chemical shifts for *N*-methyl-4-tolyl-1-(4-bromonaphthyl)amine and *N*-phenyl-1-(4-bromonaphthyl)amine are reported. The calculations were performed at the DFT level (PBE1PBE functional) using magnetically consistent 6-31G$^{\#\#}$ and STO$^{\#\#}$-3G$_{mag}$ basis sets. Conformational properties of the amines were studied using potential energy surface scanning. Chemical shifts were calculated using the GIAO and CSGT methods and averaged in proportion to the population of the corresponding conformations. Solvent effects ($CDCl_3$) were accounted via PCM method. The obtained results allowed to assign the ^{1}H NMR signals for the naphthalene moiety, which could not be done based on the experimental data alone.

Keywords: N-methyl-4-tolyl-1-(4-bromonaphthyl)amine; N-phenyl-1-(4-bromonaphthyl)amine; NMR; DFT; basis set.

Introduction. N-Aryl-naphthylamines and their derivatives are prospective compounds for investigation of reactivity in electrophilic substitution reactions since they include several reaction centers. Number of authors have been studied reactions of nitration, bromination and formylation of amines [1-2], but obtained results were rather fragmented. Therefore we have performed comprehensive study of the reactivity of amines (**1-3**). Obtained therein results concerning regioselectivity of phosphorylation, formylation, bromination, nitration and azocoupling reactions are collected in reviews [3-8]. In particular, it has been shown that in the case of N-phenyl-1-naphthylamine (**3**),bromination, formylation and reactions proceed at position 4 of naphthalene fragment (**13-15**), methyl group at Nitrogen atom (amine **2**) changes the direction of electrophilic substitution which results in formation of 4-phenyl derivatives (**8-12**). Such changes in regiochemistry could be determined by conformational changes of source molecule. To confirm this assumption, we introduce methyl group to position 4 of benzene fragment which, as expected, leads to decreasing of N-mephyl-4-tolyl-1-naphthylamine (**1**) if compare to amines (**2, 3**) [5].

For identification of obtained compounds and determination of reactions regiochemistry one is one of the most commanding methods is nuclear magnetic resonance (NMR) spectroscopy, but in some cases it is very difficult or even impossible to make signal assignments, based on experimental NMR spectra alone. In these cases, quantum-chemical calculations can provide valuable assistance, since direct comparison of experimental and accurately predicted theoretical spectra allows one almost

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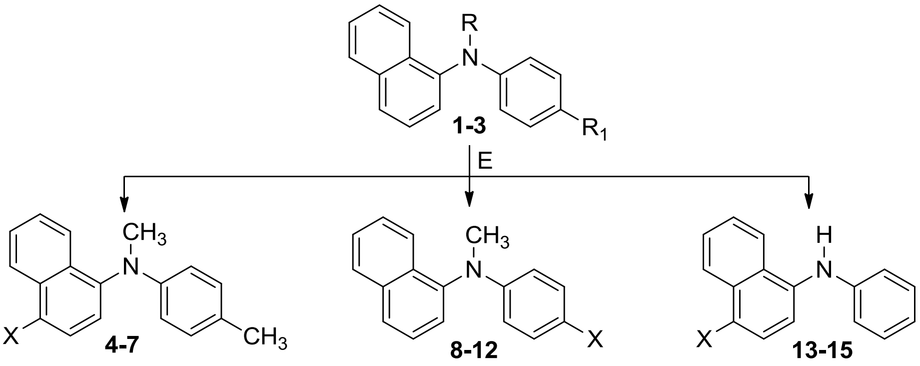
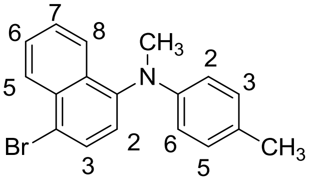
unambiguously to accept or decline suggested structure. Such a “complex NMR study” has been applied for investigation of stereoisomeric tetrahydroindene diepoxides [9]**.**



R = R_1 = CH_3 (**1**);
R = CH_3; R_1 = H (**2**);
R = R_1 = H (**3**);

X = CHO (**4**, **11**, **14**); X = Br (**5**, **9**, **13**);
X = PBr_2 (**8**); X = NO_2 (**6**, **10**)
X = *n*-N=N–$C_6H_4NO_2$ (**7**, **12**, **15**)

Here we present the results of quantum-chemical investigation of conformational properties and ^{1}H NMR properties of amines (**5** and **13)**.



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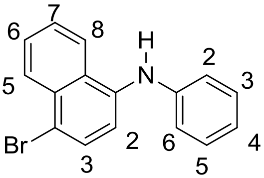

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Computational Details. Optimization of geometry has been performed at DFT level (functional PBE1PBE) using magnetically corrected 6-31G$^{\#\#}$ and STO$^{\#\#}$-3G$_{mag}$ basis sets constructed by augmentation of standard 6-31G and STO-3G basis sets by the additional functions which determined from the analytical expressions for the first-order correction (response) functions to the unperturbed basis AO’s. The response functions have been obtained by solution of the inhomogeneous Schrödinger equation for the model problem “an one electron atom in an external uniform field” using of the closed analytical representation of the Green’s function that enabled us not only to account the contributions of both discrete and continuous spectra, but it allows us to improve the wave function in those regions of the perturbed space which give the main contribution to the calculated property [10; 11]. The efficiency of this approach has been confirmed earlier for construction of basis sets for calculations of nuclear magnetic shielding [12–15], spin-spin coupling constants [16], magnetic susceptibility [13; 17; 20], polarizability [13; 18] and vibrational frequencies [19].

For calculations of nuclear magnetic shielding 6-31G$^{\#\#}$and STO$^{\#\#}$-3G$_{mag}$ basis sets have been applied for “heavy” nuclei and original 6-31G and STO-3G basis sets for nuclei of interest (protons). Such combination of basis sets is based on the property of first-order correction functions which in the case of external magnetic field equals zero at the point of origin ($R_{x,y,z} = 0$).

Chemical shifts were obtained by subtracting the calculated magnetic shielding for the ^{1}H nuclei of interest from the reference compound (for tetramethylsilane TMS), shielding (see Table 1). CSGT (continuous set of gauge transformations) [20] and GIAO (gauge independent atomic orbitals) [21–22] formulations at the CHF level as implemented in the Gaussian 09 program [23] have been used therein.

Table 1

Calculated ^{1}H magnetic shieldings (ppm) for the reference compound TMS

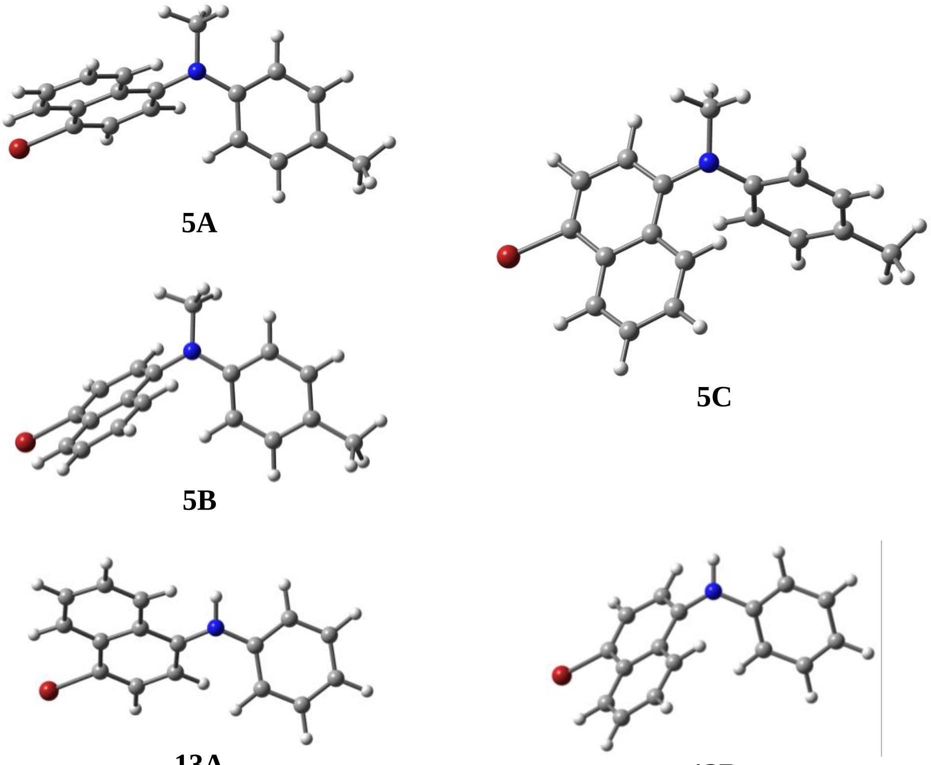
Basis set	GIAO	CSGT
6-31G$^{\#\#}$/6-31G	32.19	31.10
STO$^{\#\#}$-3G$_{mag}$/ STO-3G	31.52	30.43

The calculations have been performed taking into account the effect of solvent ($CDCl_3$) via PCM method [24].

Results and Discussion. Since for conformationally flexible molecules NMR spectra usually show averaged values of chemical shifts, first we investigated conformational properties of amines. Analysis of potential energy surface shows that amine (**5**) exists in 3 univocal conformations (**A** – **C**). Due to symmetry of benzene ring for each of those conformers energetically degenerate structure could be obtained by rotation around corresponding N-C bond on 180° which results in averaging of *ortho*- and *para*- protons of benzene fragment.

As could be seen from Figure 1 and Table 2, in the most stable conformer (**5A**) benzene ring is oriented close to the plane of N-C_{Met} bond while naphthalene fragment approaching plane perpendicular to N-C_{Met} bond. Conformers (**5B**, **5C**) where both benzene and naphthalene fragments distorted from the plane of N-C_{Met} bond are in 2,53 and 4.46 kJ/mole less stable if compare to conformer (**5A**) correspondingly. Population of each conformer, calculated according to Eq. 1, is shown in Table 2.

$$n_i = \frac{\exp(-\Delta G_i / RT)}{\sum_i \exp(-\Delta G_i / RT)} \qquad (1)$$



5A

5C

5B

13A

13B

Fig. 1. Conformations of amines (5, 13)

Table 2

Absolute and relative values of Gibbs free energy and population of conformations for amines (5, 13), calculated at PBE1PBE/6-31G$^{\#\#}$ level of theory

Conformer	$\angle C_2'C_1'NC(H)$	$\angle C_2C_1NC(H)$	ΔG, a.u.	ΔG_{rel}, kJ/mol	Population (n_i), %
5					
A	-1.95	101.47	-3322.473270	0.00	65.35
B	15.28	56.80	-3322.472307	2.53	23.72
C	57.54	24.76	-3322.471570	4.46	10.93
13					
A	-13.59	139.32	-3243.940369	0.00	82.86
B	31.00	32.92	-3243.938872	3.93	17.14

^{1}H NMR spectrum of N-methyl-4-tolyl-1-(4-bromonaphthyl)-amine (**5**) is characterized by two signals of methyl groups [singlets at 2,23 ppm (3H, CH_3-Ar) and 3.39 ppm (3H, CH_3-N)] (Table 3). There are two doublets of *para*-disubstituted benzene ring (at 6.53 and 6.93 ppm) in the region of aromatic protons, signals of naphthalene ring protons appear as four doublets at 7.17, 7.76, 7.92 and 8.26 ppm, and two triplets at 7.44 and 7.57 ppm. While signals of methyl groups and benzene ring could be unambiguously assigned to the corresponding nuclei, it is not a case for signals of naphthalene fragment.

Table 3

Observed and calculated values of chemical shifts of aromatic protons for amines (5, 13)in $CDCl_3$ solution relative to TMS (ppm) and Parameters of the Linear Regression Equation $\delta_{expt}=A*\delta_{calc} + B$

Proton	6-31G$^{\#\#}$/6-31G				STO$^{\#\#}$-3G$_{mag}$/ STO-3G				Experiment [7]
	Averaged[1]		Corrected[2]		Averaged[1]		Corrected[2]		
	CSGT	GIAO	CSGT	GIAO	CSGT	GIAO	CSGT	GIAO	
5									
H2	6.68	7.49	7.17	7.25	6.07	7.14	7.18	7.24	7.17
H3	7.07	7.83	7.52	7.59	6.40	7.48	7.45	7.54	7.76
H5	7.83	8.56	8.20	8.30	7.53	8.25	8.39	8.23	8.26
H6	7.18	7.93	7.62	7.69	6.44	7.63	7.49	7.67	7.57
H7	7.07	7.81	7.52	7.57	6.34	7.51	7.40	7.57	7.44
H8	7.67	8.01	8.06	7.76	7.02	7.83	7.96	7.85	7.92
H2′, H6′	6.00	6.79	6.56	6.58	5.43	6.25	6.64	6.44	6.53
H3′, H5′	6.43	7.06	6.95	6.84	5.94	6.92	7.07	7.04	6.93
R	0.979	0.976			0.964	0.975			
A	0.90	0.97			0.83	0.90			
B	1.18	-0.03			2.11	0.84			
13									
H2	6.86	7.74	7.38	7.41	6.20	7.21	7.35	7.30	7.20
H3	6.96	7.84	7.48	7.51	6.32	7.39	7.44	7.48	7.65
H5	7.78	8.62	8.24	8.24	7.50	8.22	8.37	8.29	8.25
H6	7.17	8.00	7.67	7.66	6.44	7.63	7.54	7.71	7.61
H7	7.05	7.86	7.56	7.52	6.32	7.50	7.45	7.59	7.51
H8	7.48	8.33	7.97	7.97	6.89	7.75	7.90	7.83	8.02
H2′, H6′	6.42	7.25	6.97	6.95	5.97	6.89	7.17	7.00	6.98
H3′, H5′	6.73	7.59	7.26	7.27	6.13	7.21	7.30	7.31	7.25
H4′	6.34	7.18	6.89	6.88	5.62	6.78	6.90	6.88	6.94
R	0.977	0.976			0.954	0.968			
A	0.94	0.94			0.79	0.98			
B	0.91	0.15			2.47	0.25			

[1] Avarged proportionally to population of conformations.

[2] Corrected using parameters of linear regression equation.

Based on comparison of experimental ^{1}H NMR spectra for the series of N-phenyl-1-naphtylamines (**4-7**) signals at 7.17 , 7.76, 7.92 and 8.26 ppm have been assigned to H^2,

H^8, H^5 and H^3 nuclei correspondingly [7]. Analysis of calculated values of chemical shifts has shown incorrectness of such assignment since all theoretical approaches used predict smaller value of chemical shift for H^3 nucleus if compare to H^8 and H^5 protons. Triplets at 7.44 and 7.57 ppm could be assigned to H^7 and H^6 nuclei, correspondingly. Such assignment does not contradict with results obtained in ref. [25; 26]. In the case of N-methyl-4-tolyl-1-(4-bromonaphthyl)-amine (**5**), as well as for 1-bromo-naphthalene [26], signal of the proton at *peri*-position to bromine atom is shifted to weak field on 0.59 ppm due to anisotropic influence of C–Br bond.

Assignment of signals in ^1H NMR spectrum of N-phenyl-1-(4-bromonaphthyl)-amine (**13**) coincides with assignment in N-methyl-4-tolyl-1-(4-bromonaphthyl)-amine (**5**). There is a small deviation of chemical shifts for nuclei in naphthalene fragment (+0.11 ppm for H^3 and -0.10 ppm for H^8) while signals of *ortho*- and *para*- protons of phenyl ring in (**13**) are shifted to weak field on 0.45 ppm and 0.32 ppm if compare to signals in toluene fragment in amine (**5**).

Comparison of the performance of basis sets and approaches used for calculations of chemical shifts values shows slight superiority of 6-31G$^{\#\#}$/6-31G scheme over STO$^{\#\#}$-3G$_{mag}$/ STO-3G and GIAO approach over CSGT.

Conclusions. The conformational properties and ^1H NMR spectra of N-phenyl-1-(4-bromonaphthyl)-amine (**5**) and N-methyl-4-tolyl-1-(4-bromonaphthyl)-amine have been studied (**13**). There are three local minima on the potential energy surface of amine (**5**) which correspond to stable conformers **5A-5C**. Two of them (**5A, 5B**) are characterized by rather planar orientation of benzene ring relatively to N-C bond and differ on orientation of naphthalene fragment while in conformer (**5C**) both aromatic rings are twisted in relation to N-C bond. For amine (**13**) two tautomers have been located – (**13A**) where benzene ring oriented close to N-H bond and naphthalene ring is twisted and (**13B**) where both rings slightly derived from plane. Values of ^1H NMR chemical shifts calculated by PBE1PBE functional using magnetically corrected 6-31G$^{\#\#}$ and STO$^{\#\#}$-3G$_{mag}$ basis sets are in good correspondence with experimental data. GIAO/PBE1PBE/6-31G$^{\#\#}$ shows the best agreement among theoretical levels used herein. The results of our calculations allowed to solve a problem of the signal assignments for both of amines under study, especially for protons of naphthalene ring where using of previously established empirical rules gives incorrect assignment.

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ИДЕНТИФИКАЦИЯ N-МЕТИЛ-4-ТОЛИЛ-1-(4-БРОМНАФТИЛ)-АМИНА И N-ФЕНИЛ-1-(4-БРОМНАФТИЛ)-АМИНА ПО ДАННЫМ СПЕКТРОВ ^{1}H ЯМР: КОМПЛЕКСНОЕ ЭКСПЕРИМЕНТАЛЬНОЕ И ТЕОРЕТИЧЕСКОЕ ИССЛЕДОВАНИЕ

Представлены результаты теоретического исследования конформационных свойств и химических сдвигов ядер в спектрах ^{1}H ЯМР N-метил-4-толил-1-(4-бромнафтил)-амина и N-фенил-1-(4-бромнафтил)-амина. Расчеты проведены в приближении теории функционала плотности (функционал PBE1PBE) с использованием адаптированных для расчета магнитных свойств наборов базисных функций 6-31G$^{\#\#}$ и STO$^{\#\#}$-3G$_{mag}$. Конформационные свойства аминов рассчитаны путем сканирования поверхности потенциальной энергии. Величины химических сдвигов рассчитаны методами GIAO и CSGT как средние величины, пропорционально заселенности соответствующих конформеров. Влияние растворителя, используемого при записи ЯМР спектров (CDCl$_3$), учитывалось методом PCM. Полученные результаты позволили выполнить отнесение сигналов в спектрах к соответствующим ядрам, в частности, для нафталинового фрагмента, что не представлялось возможным сделать на основании только экспериментальных спектральных данных.

Ключевые слова: N-метил-4-толил-1-(4-бромнафтил)амин; N-фенил-1-(4-бромнафтил)амин; ЯМР; теория функционала плотности; базисные функции.

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ІДЕНТИФІКАЦІЯ N-МЕТИЛ-4-ТОЛІЛ-1-(4-БРОМОНАФТИЛ)-АМІНУ ТА N-ФЕНІЛ-1-(4-БРОМОНАФТИЛ)-АМІНУ ЗА ДАНИМИ СПЕКТРІВ ^{1}H ЯМР: КОМПЛЕКСНЕ ЕКСПЕРИМЕНТАЛЬНЕ ТА ТЕОРЕТИЧНЕ ДОСЛІДЖЕННЯ

Наведені результати теоретичного дослідження конформаційних властивостей та хімічних зсувів ядер в спектрах ^{1}H ЯМР N-метил-4-толіл-1-(4-бромонафтил)-аміну та N-феніл-1-(4-бромонафтил)-аміну. Розрахунки проведені в наближенні теорії функціоналу густини (функціонал PBE1PBE) з використанням адаптованих для розрахунку магнітних властивостей наборів базисних функцій 6-31G$^{\#\#}$ и STO$^{\#\#}$-3G$_{mag}$. Конформаційні властивості амінів розраховані шляхом сканування поверхні потенційної енергії. Значення хімічних зсувів розраховані методами GIAO и CSGT як середні значення, пропорційно заселеності відповідних конформерів. Вплив розчинника який використовувався під час запису спектрів ЯМР (CDCl$_3$) враховувався методом PCM. Отримані результати дозволили виконати віднесення сигналів в спектрах до відповідних ядер, зокрема, для нафталінового фрагменту, що було неможливо зробити лише на основі експериментальних спектральних даних.

Ключові слова: N-метил-4-толіл-1-(4-бромонафтил)амін; N-феніл-1-(4-бромонафтил)амін; ЯМР; теорія функціоналу густини; базисні функції.

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