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Ab Initio Calculations of Effect of (Thio)xanthenyl and Dibenzosuberenyl Substituents on Dehydrogenation of *N*-Benzylanilines

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Abstract—Higher values of the energies of the highest occupied molecular orbitals for *N*-benzyl-4-[9-(thio)-xanthenyl]aniline, *N*-benzyl-4-(5-dibenzosuberenyl)aniline molecules and their zwitterions and the electron density increase on the reaction center (carbon atom in the CH_2-group) for the latter were obtained in the quantum-chemical calculations by RHF/6-31G(d) method. This explains the possibility and the ease of dehydrogenation of *N*-benzyl-4-[9-(thio)xanthenyl]aniline with imines in trifluoroacetic acid due to effect of the substituents. The calculated data suggest the same possibility for *N*-benzyl-4-(5-dibenzosuberenyl)aniline: it is dehydrogenated already in the synthesis from *N*-benzylaniline and dibenzosuberenol in acetic acid.

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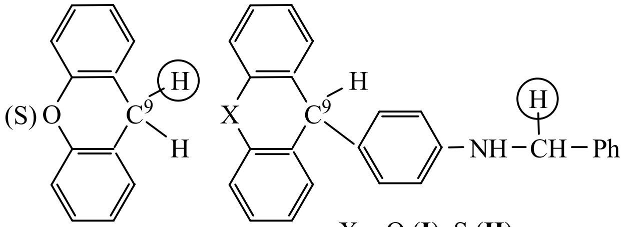
Previously [1] to explain partial recovery of a number of heterocyclic *N*-nucleophiles in the reaction with the tritylium cation (*N*-methylacridane > thioxanthene > 1,3-benzodithiol > xanthene) or protonated imines (*N*-methylacridane > xanthene > thioxanthene > 1,3-benzodithiol) a mechanism of the dehydrogenation of imines, including the intermediate formation of ylides isomeric to the heterocycles has been suggested. Based on the results of quantum-chemical calculations performed by RHF/6-31G(d) method, the energies of the highest occupied molecular orbitals (E_{HOMO}) and the electron density on the reaction center C^9 for ylides are significantly higher than the corresponding values for these heterocycles. In combination with the kinetic data this fact confirms the proposed reaction mechanism. The tentative threshold value of the energy gap $|\Delta E|$ between E_{HOMO} of heterocycle ylide and E_{LUMO} of the protonated imine is 2.737 eV for the reactions with the "ylide" mechanism. Below this value the interaction of imines with heterocyclic H-nucleophiles by this mechanism is possible and above it, impossible.

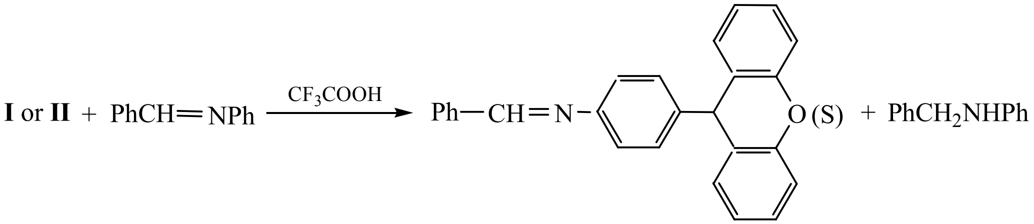
In continuation of these studies, in this work we evaluated the effect of xanthenyl, thioxanthenyl, and dibenzosuberenyl substituents on the process of dehydrogenation of CH_2–NH group of *N*-arylmethylanilines by the quantum-chemical calculations using the RHF/6-31G(d) method. This is due to that the reaction of imines with dibenzopyran (xanthene) [2] or dibenzothiopyran (thioxanthene) [3] leads to dehydrogenation of heterocyclic group C^9H, while using in the same reaction the heterocycle substituted at the carbon atom C^9, e. g., *N*-phenyl-methyl-4-[9-(thio)xanthenyl]aniline **I** or **II** the CH_2–NH group is subjected to dehydro-genation instead of C^9H moiety.



X = O (**I**), S (**II**).

The aim of this work is to clarify the reasons for changing the reaction center from C^9H moiety to CH_2–NH group and to substantiate the unusual ease of dehydrogenation of (thio)xanthenyl-containing amines **I** and **II**. The secondary aromatic amines are known to be dehydrogenated under rigid conditions. For example, *N*-benzylaniline is dehydrogenated to *N*-

Scheme 1.



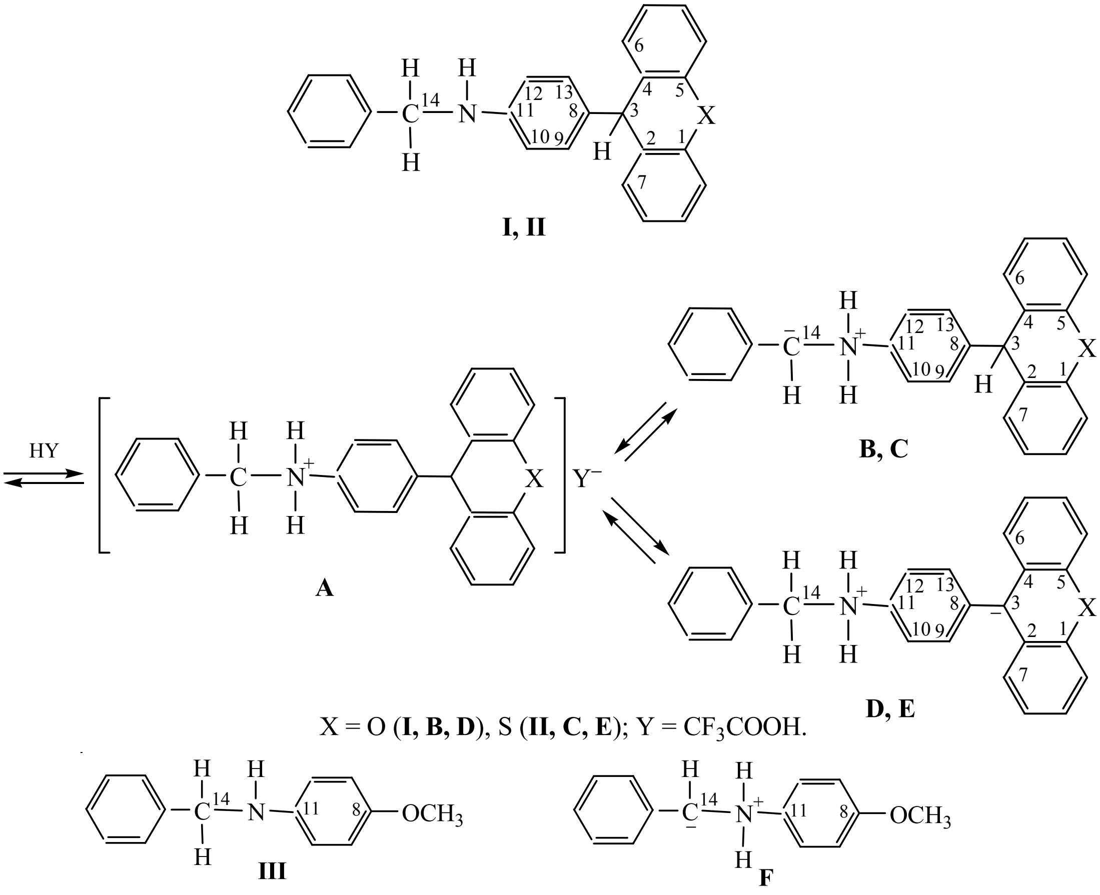
benzylideneaniline with use of industrial vanadium catalyst B-3 at 300°C [3].

The products of reaction of imines with xanthene [2] or thioxanthene [3], for example, *N*-phenylmethyl-4-[9-(thio)xanthenyl]anilines, are readily converted to the corresponding *N*-phenylmethylene-4-[9-(thio)xanthenyl]anilines on heating with *N*-benzylideneanilines in trifluoroacetic acid (Scheme 1).

It is presumable that the heterocyclic substituents in these molecules are strong electron-donors and thus contribute to the process of dehydrogenation of the CH_2–NH group of the secondary amines. However, the control experiment showed that under these conditions *N*-benzyl-4-methoxyaniline containing *p*-electron-donor methoxy group is not dehydrogenated with *N*-benzylideneaniline. Moreover, this reaction is pH-dependent, since it occurs only in trifluoroacetic acid, but not in ethanol or benzene. Probably, the role of trifluoroacetic acid is the formation of an amine complex **A** (or $\mathbf{A}^1$) with the acid and the conversion of the latter into a more reactive intermediate, zwitterion (Scheme 2, 3).

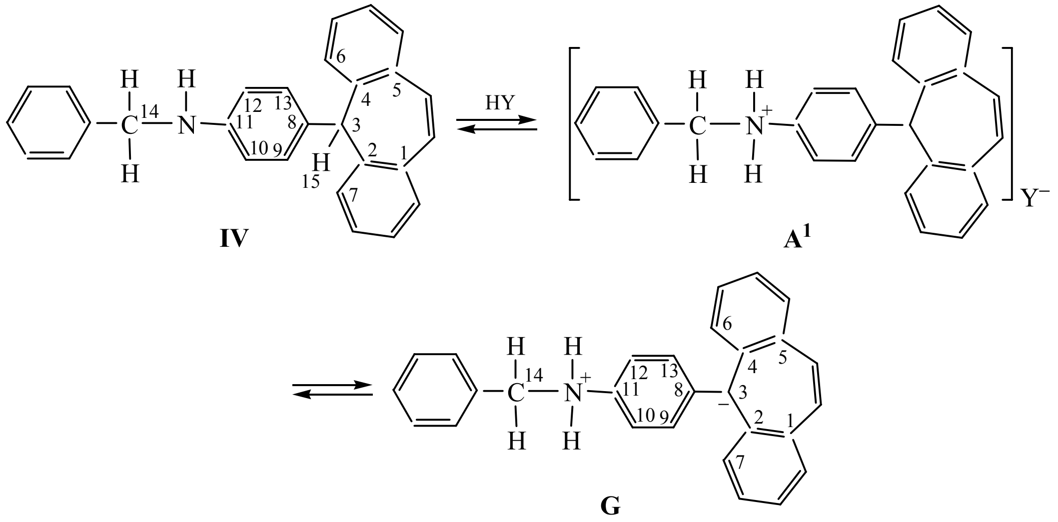
Based on this assumption, we performed the quantum-chemical calculation at the RHF/6-31G(d) level using Gaussian 03W program [4] of *N*-benzyl-4-(9-

Scheme 2.



X = O (**I, B, D**), S (**II, C, E**); Y = CF_3COOH.

Scheme 3.



Y = CF_3COO.

xanthenyl)aniline **I** and *N*-benzyl-4-(9-thioxanthenyl)-aniline **II** molecules as well as the corresponding two types of most likely zwitterions: (a) **B** and **C**, in which the negative charge is formally located on the carbon atom of the C–N group, and (b) **D** and **E**, in which the negative charge is located on the heterocycle. For comparison, the quantum-chemical calculations were performed also for the secondary amine *N*-benzyl-4-methoxyaniline **III**, containing the *p*-electron-donor methoxy group in the *para*-position of aniline ring instead of the heterocycle, and for the corresponding zwitterion **F**. Furthermore, the molecules of *N*-benzyl-4-(5-dibenzosuberenyl)aniline **IV**, containing the structurally analogous dibenzosuberenyl substituent, and the corresponding zwitterion **G** were calculated. The zwitterions formation is described in Schemes 2 and 3.

The calculated data are shown in Tables 1 and 2. The E_{HOMO} values (Table 1) and charges on the carbon atoms of the C–N group in the zwitterions **B**, **C** and **F** (Table 2) are comparable. Therefore, it can be assumed that these zwitterions are not capable to be dehydrogenated, since *N*-benzyl-4-methoxyaniline **III** is not dehydrogenated under the above conditions. The E_{HOMO} values of the zwitterions **D**, **E**, and **G** are higher than that for **B**, **C**, and **F** and significantly higher than for the structures **I**–**IV**.

The calculated values of the energy gaps $|\Delta E|$ (Table 1) for the reaction of zwitterions **D**, **E**, and **G** with the protonated *N*-benzylideneaniline $[PhCH{=}NHPh]^+$ **V** indicate a significant convergence of the HOMO energy level of these zwitterions and LUMO of the molecule of **V** compared to the energy difference of the frontier orbitals of amines **I**, **II**, **IV** and the molecule **V**. The obtained values of the energy gaps are significantly lower than the previously found threshold value $|\Delta E|$ for the reaction of the protonated imine with ylides of *N*-methylacridane, xanthene and thioxanthene [1], which indirectly confirms the high reactivity of zwitterions **D**, **E**, and **G** corresponding to amines **I**, **II** and **IV**.

The charges on the carbon atoms of C^{14}–N group for zwitterions **D**, **E**, and **G** increase compared with

Table 1. Energies of the highest occupied molecular orbitals (E_{HOMO}) of structures **I**–**IV** and energy gaps $|\Delta E| = E_{\mathrm{HOMO}}$ (**I**–**IV**, **B**–**G**) – E_{LUMO} (**V**)[a]

Structure	E_{HOMO}, eV	$\lvert\Delta E\rvert$, eV
I	–7.594	4.664
B	–5.930	3.001
D	–4.455	1.526
II	–7.551	4.622
C	–5.908	2.979
E	–4.627	1.698
III	–7.320	4.391
F	–5.896	2.967
IV	–7.469	4.540
G	–4.530	1.601

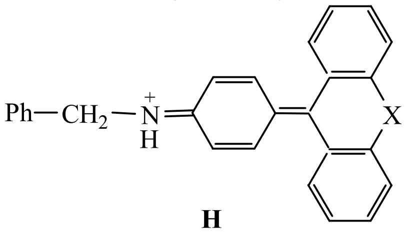
[a] E_{LUMO} $[PhCH{=}NHPh]^+$ (**V**) = –2.929 eV [1].

Table 2. Charges on atoms (q) in structures **I**–**IV** and **B**–**G**

Structure	q, e													
	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}	C^{13}	C^{14}
I	0.390	–0.032	–0.202	–0.033	0.390	–0.194	–0.195	0.035	–0.189	–0.254	0.346	–0.265	–0.221	–0.138
B	0.393	–0.031	–0.222	–0.033	0.391	–0.197	–0.197	0.079	–0.203	–0.225	0.185	–0.180	–0.244	–0.254
D	0.373	–0.013	–0.123	–0.013	0.372	–0.240	–0.241	0.102	–0.282	–0.179	0.028	–0.169	–0.295	–0.199
II	–0.205	0.071	–0.293	0.068	–0.207	–0.198	–0.200	0.050	–0.205	–0.255	0.347	–0.264	–0.219	–0.138
C	–0.204	0.066	–0.298	0.062	–0.207	–0.198	–0.200	0.085	–0.216	–0.225	0.186	–0.180	–0.242	–0.254
E	–0.215	0.070	–0.203	0.070	–0.215	–0.223	–0.224	0.106	–0.283	–0.178	0.028	–0.166	–0.295	–0.199
III								0.409			0.319			–0.141
F								0.447			0.171			–0.255
IV	0.028	0.003	–0.216	0.033	0.028	–0.230	–0.230	–0.013	–0.212	–0.257	0.344	–0.263	–0.207	–0.136
G	0.007	0.009	–0.191	0.007	0.007	–0.215	–0.213	0.110	–0.297	–0.163	0.016	–0.173	–0.285	–0.196

the charges for the molecules **I**–**IV** (Table 2). This explains the easy dehydrogenation of the secondary aromatic amines **I** and **II** containing heterocyclic moiety. The partial negative charges on the carbon atom C^3 of the structures **D**, **E**, and **G** are significantly lower than that for the same carbon atom in the structures **I**–**III** (Table 2). This explains the deactivation of C^3H group and also the transfer of the reaction center from this group to the CH_2–NH fragment.

The electron density on the carbon atoms C^9, C^{13}, and C^{11} in zwitterions **D**, **E**, and **G** increases as compared with those atoms in the structures **I**–**III**. Apparently, such redistribution of the electron density in the zwitterions demonstrates the significant contribution of quinoid structure **H**, thereby increasing the electron density on the carbon atom C^{14} and explains the easy dehydrogenation of the secondary aromatic amines **I** and **II** containing heterocyclic moiety.



H

X = O, S.

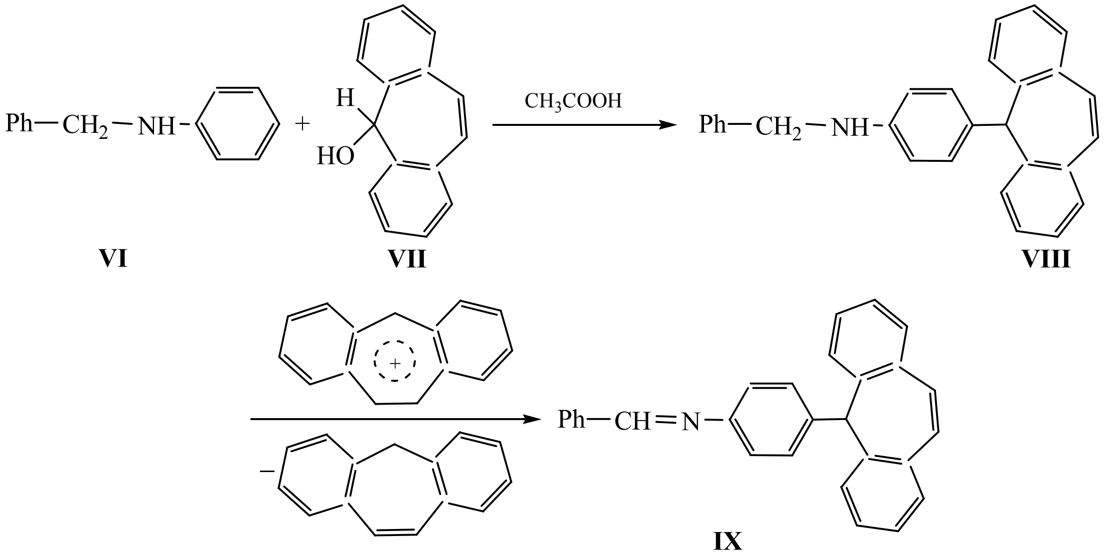
The partial negative charges on the carbon atoms C^6 and C^7 of the heterocyclic moiety in the structures **D** and **E** increase as compared with the charges on the same atoms in the structures **I** and **II**. Apparently, this resulted from the partial delocalization of the charge of the atom C^3. The electron density on the carbon atoms C^1 and C^5 and the oxygen atoms in the zwitterion and amine **I** varies slightly. The charges on the atoms C^{10} and C^{12} (q –0.179, –0.169 e) in the zwitterion are lower as compared with the respective charges in the amine **I** (q –0.254, –0.265 e). Apparently, such charges redistribution is due to an increase in the electron density on the atom C^{11} in the zwitterion.

Thus, on the basis of the calculations performed it is possible to predict the ability of *N*-benzyl-4-(5-dibenzosuberenyl)aniline **IV** to the dehydrogenation. This conclusion is indirectly supported by the experimental fact that the interaction of *N*-benzylaniline **VI** with dibenzosuberenol **VII** in acetic acid is accompanied by the formation of *N*-phenylmethyl-4-(5-dibenzo[*a*,*d*]cycloheptatrienyl)aniline **VIII** as a main product and *N*-phenylmethylene-4-(5-dibenzo[*a*,*d*]cycloheptatrienyl)aniline **IX** as a side product. The latter forms due to the dehydrogenation of CH_2–NH group (Scheme 4).

EXPERIMENTAL

The ^1H NMR spectra were registered on a spectrometer Mercury 300 (300 MHz) with internal reference HMDS. The GC-MS spectra were obtained on a Agilent Technologies 6890N/5975V instrument [column HP-5ms (30 × 0.25 mm, 0.25 μm), carrier gas helium, electron impact ionization (70 eV), the temperature of the oven 100°C, evaporator temperatures

Scheme 4.



260, 270°C. Dibenzosuberenol is a commercial product.

***N*-Phenylmethyl-4-(5-dibenzo[*a*,*d*]cycloheptatrienyl)aniline (VIII).** *a*. A mixture of 0.24 g (1.3 mmol) of *N*-benzylaniline **VI**, 0.21 g (1 mmol) of dibenzosuberenol **VII**, and 4 ml of acetic acid was kept at room temperature for 3 h. The reaction mixture was diluted with water. The crystals were separated, washed several times with water, and dried. Yield 0.22 g (61.3%), mp 128–129°C (hexane). ^{1}H NMR (CDCl$_3$), δ, ppm: 3.85 s (1H, NH), 4.18 s (2H, CH$_2$), 5.27 s (1H, C^{5}H), 6.31–7.43 m (19H, ArH + C^{10}H, C^{11}H). Mass spectrum, m/z (I_{rel}, %): 373 $[M]^+$(100); 282(15); 191 (19); 91(43); 77(3).

b. A mixture of 0.09 g (0.5 mmol) of *N*-benzylaniline **VI**, 0.21 g (1 mmol) of dibenzosuberenol **VII,** and 4 ml of acetic acid was kept at room temperature for 4 h. The reaction mixture was diluted with water. The crystals were separated, washed with water, dried, and extracted with diethyl ether. The precipitated compound **IX** was separated. Yield 0.006 g (3.2%), mp 186–187°C (benzene). From ether extract amine **VIII** was isolated in a yield of 59%.

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