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Authors: Marija Baranac-Stojanović

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FULL PAPER

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Can Variations of ^{1}H NMR Chemical Shifts in Benzene Substituted with an Electron-Accepting (NO_2)/Donating (NH_2) Group be Explained in Terms of Resonance Effects of Substituents?

Marija Baranac-Stojanović*[a]

Abstract: The classical textbook explanation of variations of ^{1}H NMR chemical shifts in benzene substituted with an electron-donating (NH_2) and electron-withdrawing (NO_2) group in terms of substituent resonance effects was examined by an analysis of molecular orbital contributions to the total shielding. It was found that the π-electronic system shows a more pronounced shielding effect on all ring hydrogen atoms, relative to benzene, irrespective of substituent $+R/-R$ effects. For the latter, this is in contrast to the traditional explanations of downfield shift of nitrobenzene proton resonances, which are found to be determined by the σ-electronic system and oxygen in-plane lone pairs. In aniline, $+R$ effect of NH_2 group can be used to explain fully the upfield position of *meta*-H signals and partly the upfield position of *para*-H signal, the latter also being influenced by the σ-system. The position of the lowest frequency signal of *ortho*-Hs is fully determined by σ-electrons.

Introduction

The π-electron delocalization is an important concept in chemistry which accounts for the greater stability of conjugated versus nonconjugated systems, planarity, small bond length alternation and special chemical reactivity.[1-4] If it is cyclic, it is referred to as aromaticity which presents another significant chemistry concept, exemplified by benzene.[5,6] Benzene's planar structure, equal CC bond lengths, higher stability relative to acyclic conjugated reference molecules and peculiar reactivity (substitution rather than addition reactions) are all ascribed to the propensity of π-electrons to delocalize and stability of thus formed delocalized π-electronic system. Aromatic compounds are easily recognized by ^{1}H NMR spectroscopy because they show characteristic low-field signals classically associated with deshielding effects of the π-electron ring current, created by magnetic field acting perpendicularly to the ring plane.[7-9] Recent theoretical studies, however, have questioned some traditional explanations based on π-orbitals and brought to light the significance of the often neglected σ-electronic system. For example, benzene's symmetric structure was shown to result from delocalizing force of σ-electrons, while π-electrons tend to localize double bonds.[10] In NMR spectroscopy, benzene protons are, in fact, shielded by π-electrons and deshielded by σ-orbitals,[11] and the familiar anisotropy cone is determined by the σ molecular framework.[12] The π electronic system deshields

benzene protons only when an external magnetic field acts at right angles to the ring plane, while even in this orientation they are shielded by all orbitals.[13-15]

The π- and σ-electron density in benzene ring is influenced by electronic properties of substituents, which are usually classified as activating and deactivating toward electrophilic substitution reactions.[1-3] The former, as for example NH_2, increase the π-electron density in the ring thereby increasing the rate of a reaction, while the latter, as for example NO_2, decrease the π-electron density and reduces benzene ring's reactivity. As is shown in Figure 1, an activating substituent increases π-electron density particularly in *ortho*- and *para*-positions by its positive resonance effect ($+R$), while a deactivating substituent decreases the π-electron density at the same positions by its negative resonance effect ($-R$). Accordingly, activating groups are *ortho*- and *para*-directing, whereas deactivating groups are *meta*-directing.[1-3] Inductive effect, which affects the σ-electronic system, is electron-withdrawing for both groups ($-I$), but is more pronounced for NO_2 because of the combined withdrawing properties of nitrogen and oxygen atoms.[16] Recent computational studies, based on density functional theory (DFT), confirmed these classical arguments.[17,18]
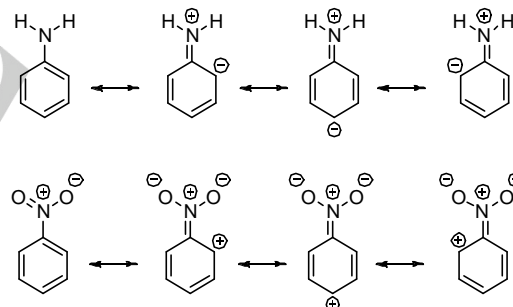

Figure 1. Resonance structures of aniline and nitrobenzene.

Substituent effects can be traced by significant changes in ^{13}C and ^{1}H NMR chemical shifts of substituted relative to unsubstituted benzene ring, which are believed to be determined by substituent resonance effects.[8,9] According to the classical explanation, an increased π-electron density in the ring shields all protons more than those in benzene, but *ortho*- and *para*-positions are the most affected. Thus, while benzene's ^{1}H NMR chemical shift is found at 7.31 ppm,[19] *ortho*- and *para*-hydrogens in aniline show signals at 6.68 ppm and 6.76 ppm, respectively.[20] On the contrary, a decreased π-electron density in the ring deshields all hydrogen atoms with respect to those in benzene, and the effect is again the most prominent at *ortho*- and *para*-positions. As an example, the signals of *ortho*- and *para*-hydrogens in nitrobenzene are found at 8.16 ppm and 7.68 ppm, respectively.[20] Hydrogen atoms at *meta*-positions are less affected, 7.15 ppm and 7.52 ppm for NH_2 and NO_2 substituents,

[a]   Prof.Dr. M. Baranac-Stojanović
       University of Belgrade – Faculty of Chemistry
       Studentski trg 12-16
       11000 Belgrade, Serbia
       E-mail: mbaranac@chem.bg.ac.rs

respectively,[20] and this is in accordance with resonance effects shown in Figure 1. Changes of ^{13}C NMR chemical shifts of *ortho*- and *para*-carbon atoms follow the same trend, except that the *ortho*-carbons in nitrobenzene are shielded due to the substituent proximity. Carbon nuclei at *meta*-positions are little affected by substituents and this is, again, in agreement with the substituent resonance effects.[8,9]

Recently, the results of a computational DFT study of Viesser et al.[21] have inverted the roles of π- and σ-orbitals in (de)shielding mechanism on carbon nuclei in substituted benzenes. It was found that π-electron effects, in terms of familiar resonance structures (Figure 1), do not explain the π-electron donating and withdrawing substituent influences, which are, in fact, confined only to the few σ-orbitals which are nearest to the carbon nucleus in question. Though, an indirect relationship between two kinds of orbitals can be derived.[21]

The current literature does not provide information of a possible role of σ-electrons in the shielding mechanism of aromatic protons in substituted benzenes. Thus, the purpose of this study is to analyze contributions from both π- and σ-electronic systems. Quantum-chemical calculations were performed on benzene, aniline and nitrobenzene. The (de)shielding effects were analyzed in terms of the familiar orbitals representing individual bonds, lone pairs and inner-shell electrons.

Computational Details

All calculations were performed by using the Gaussian 09.[22] Molecular structures were optimized by using the density functional BPW91[23-25] and 6-311++G(d,p) basis set.[26] Solvent effects were included by using the integral equation formalism polarizable continuum model (IEFPCM, solvent = chloroform).[27] Frequency calculations, which were done at the same level of theory, confirmed each structure as energy minimum. Aniline was studied with its C_s symmetry having slightly pyramidalized nitrogen atom.[2] Magnetic shielding values (σ) were computed by using the GIAO method[28,29] at the BPW91/6-311G(d,p) level. Analysis of individual orbital contributions to the total magnetic shielding was based on natural chemical shielding (NCS) analysis[30] and natural localized molecular orbitals (NLMOs) created by the NBO 6.0 program.[31-33] Chemical shift is referenced to tetramethysilane (TMS), and was calculated as following: $\delta_i = \sigma_{TMS} - \sigma_i$. The discussion is based on isotropic shielding values (σ_{iso}), which represent an average of the three tensor components, σ_{xx}, σ_{yy} and σ_{zz}, each corresponding to a particular orientation of a molecule with respect to magnetic field direction. The σ_{iso} is closely related to the information that we obtain in a real NMR experiment, where molecular tumbling in solution averages tensor components. Complete results of NCS/NLMO analysis are given in Table S2, in ESI. Decomposition of total shielding into its paramagnetic and diamagnetic parts has been done by using the NBO 3.1 version, included in Gaussian 09.

Results and Discussion

The theory level used in this study gave good agreement between calculated and experimental chemical shift values[19,20] (Figure 2 and Table S1 in ESI), which deviate from each other by less than 4% and the experimentally observed trend is well reproduced by calculations. Therefore, the chosen level of theory allows a meaningful analysis.
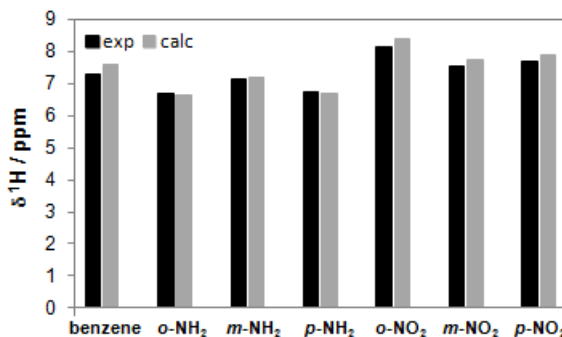

Figure 2. Calculated and experimental[19,20] proton chemical shift values for benzene, aniline and nitrobenzene.

First of all, only the π-orbitals' contributions to the total shielding values (σ) of *ortho*-, *meta*- and *para*-protons in aniline and nitrobenzene were analyzed and are shown in Figure 3, relative to benzene. In benzene, the π-eletronic system is composed of the three NLMOs each representing the π-component of the three CC double bonds. In aniline, four orbitals are involved. Three of them represent the π-component of the three CC double bonds and the fourth involves the nitrogen lone pair (LP_N). In nitrobenzene, the π-system comprises five orbitals. Three of them are, again, associated with the CC double bonds, while the remaining two represent the π-component of the NO double bond and the p-type oxygen lone pair (LP_O), which is in parallel orientation with the rest of the π-system. The π-orbitals' contribution to the total shielding of protons is given as the sum of individual orbital contributions, $\pi = \pi_{CC} + \pi_{CC} + \pi_{CC}$ for benzene, $\pi = \pi_{CC} + \pi_{CC} + \pi_{CC} + LP_N$ for aniline and $\pi = \pi_{CC} + \pi_{CC} + \pi_{CC} + \pi_{NO} + LP_O$ for nitrobenzene.
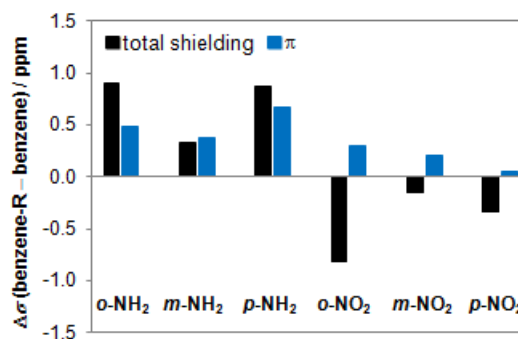
Figure 3. Sum of all NLMO contributions (total shielding, black) and only the orbitals constituting π-electronic system (π, blue) to the isotropic shielding of protons *ortho*-, *meta*- and *para*-related to the substituent (abbreviated as *o*-R, *m*-R and *p*-R; R = NH$_2$, NO$_2$) in aniline and nitrobenzene, relative to benzene.

Data in Figure 3 show that all protons in aniline are, indeed, shielded more than those in benzene by the π-electronic system. Furthermore, protons at *ortho*- and *para*-positions are shielded more than protons in *meta*-position. This is in accordance with resonance effect of NH$_2$ group, shown in Figure 1, and with the classical explanation of the influence of electron-donating substituents on chemical shift values in substituted benzenes. However, while the slightly lower chemical shift of *meta*-H relative to benzene ($\Delta\delta_{calc}$ = 0.33 ppm) can be fully rationalized in terms of +R effect of substituent, π-orbitals contribute 77% of total higher shielding of *para*-H and only 54% of total higher shielding of *ortho*-Hs in aniline.

The peculiar results are observed for nitrobenzene. As can be seen from Figure 3, the π-electronic system do not contribute, at all, to the smaller shielding of protons in benzene ring. On the contrary, it shields them more than they are shielded in benzene. This is not compatible with the classical explanation based on −R effect of NO$_2$ substituent. Thus, a carefull analysis of other orbital contributions is needed.[34]

Table S2 lists contributions from all NLMOs to the total magnetic shielding of protons in the three studied molecules. Only those which are the most important for the discussion are shown in Figure 4. In the figure, the contributions from the π-system are the same as in Figure 3, those for the C−C molecular framework represent the sum for all six σ bonds in the ring, contributions from substituent, denoted as R, are the sum of contributions from the C$_{ipso}$−N bond, two σ bonds (N−H for NH$_2$ and N−O for NO$_2$) and four in-plane lone pairs of NO$_2$ group, while the C1−H is the contribution from the C−H bond in which the proton in question is involved.

As has already been stated above, substituent resonance effect can account fully for the lower chemical shift of *meta*-H in aniline (contributions from other orbitals cancel each other, as can be inferred from Table S2) and for the major part of increased shielding of *para*-H in aniline relative to benzene. The minor part (23%) comes from the σ-electronic system involving both the C−C and C−H bonds. In particular, the increased shielding with respect to benzene arises almost equally from the increased total shielding effect from the five C−H bonds and reduced deshielding effect from the C−C bonds (data in Table S2, not shown in Figure 4). The effects from the σ-system are compatible with a decreased σ-electron density at the *para*-carbon atom which is due to the increased π-electron density at the same position[17,21,35] and substituent −I effect.

Even though the substituent resonance effect contributes half of increased shielding of *ortho*-Hs in aniline, its effect is fully canceled by the substituent deshielding effect (Figure 4). Thus, the π-system is not responsible for the increased *ortho*-Hs shielding in aniline. Instead, the lower chemical shift of these protons is completely accounted for by the reduced deshielding effect from the C−C molecular framework, which is dominated by the two nearest bonds (Table S2). This finding can be

rationalized by a decreased σ-electron density near the C$_{ortho}$ atom, which is, again, due to the increased π-electron density[17,21,35] and substituent −I effect, more intense at the *ortho*-position. As a result, the *ortho*−Hs are less deshielded by the σ bonds which, in turn, increases the overall shielding of these protons and shifts their NMR signal to the lower δ value.
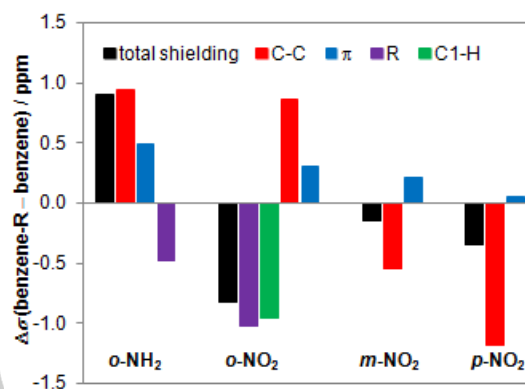

Figure 4. Sum of all NLMO contributions (total shielding, black), all C−C orbitals (C−C, red), all orbitals constituting π-electronic system (π, blue), all orbitals belonging to the substituent without those of the π-kind (R, violet) and contribution from the C−H bond involving proton in question (C1−H, green) to the isotropic shielding of protons *ortho*-, *meta*- and *para*-related to the substituent (abbreviated as *o*-R, *m*-R and *p*-R; R = NH$_2$, NO$_2$) in aniline and nitrobenzene, relative to benzene.

In the case of the substituent with −R effect, such as NO$_2$, the variations in proton chemical shifts can not be explained by the resonance effect. The results of the work show that the π-electronic system shields all ring protons more than in benzene itself and that the strength of this shielding effect decreases with an increased distance from the substituent. The data in Figure 4 show that the strong deshielding of the *ortho*-Hs comes from two sources, the substituent and the C−H bond in which the hydrogen is involved. The overall substituent deshielding of *ortho*-Hs is caused by the deshielding effect of the in-plane oriented oxygen lone pairs (Table S2). The C−H bond shields the hydrogen by ~1 ppm less than in benzene. This should be ascribed to the reduced σ-electron density near the H which is mainly caused by the electric field effect of the spatially close N$^{\delta+}$−O$^{\delta-}$ bond dipole which polarizes the C−H bond in the opposite direction, toward the carbon atom. The effect of the C−C molecular framework on the total shielding of *ortho*-Hs in nitrobenzene is the same as in aniline (less deshieding) and comes mostly from the C$_{ortho}$−C$_{ipso}$ bond which is highly polarized toward the substituent, because of its pronounced −I effect.

The C−C molecular framework is the source of higher chemical shifts of *meta*- and *para*-protons (Figure 4). Thus, both hydrogen atoms are more deshielded by the CC σ-system than hydrogen atoms in benzene. The main effect comes from the two nearest bonds in the case of *para*-H (the two C$_{meta}$−C$_{para}$ bonds) and from the C$_{meta}$−C$_{para}$ bond in the case of *meta*-H. The

magnitude of deshielding effect from the C_{meta}–C_{para} bond is the same on both hydrogen atoms (Table S2), which implies little polarization inside it. This deshielding effect is attenuated by the shielding contributions from other orbitals.

An analysis of individual orbital contributions to the total shielding allows us to identify the origin of peculiar and unexpected shielding, relative to benzene, of all ring hydrogen atoms in nitrobenzene by the π-electronic system. As the data in Table S2 show, it is the $π_{N=O}$ orbital from the substituent which gives the overall shielding effect to the π-system in nitrobenzene,[36] and this is in accord with the already observed π-electron shielding, rather than deshielding effect.[11,12]

The proton chemical shift is dominated by diamagnetic component of shielding tensor, as is also shown by decomposition of total shielding into its paramagnetic and diamagnetic parts (Table S3). The latter is positive and represents the main source of chemical shift directions of various protons in aniline and ortho-H in nitrobenzene, while for meta-H and para-H paramagnetic part plays a decisive role. An orbital contribution analysis shows that the C–H bond in which proton is involved is the major contributor to diamagnetic part. The π orbital effects are also related to diamagnetic component, while the rest of the σ system dominates the paramagnetic part of total shielding.

Conclusions

The presented analysis shows that the familiar upfield/downfield shifts of ^{1}H NMR signals in substituted benzenes are not simply related to +R/−R effects of electron-donating and electron-withdrawing substituents (apart from meta-H, when R = NH$_2$). Thus, the ortho-Hs in aniline are less deshielded by the CC molecular framework, which decreases their chemical shift value, while the shielding effect from the π-system is fully canceled by the opposite deshielding effect from the substituent. The π-electron shielding of para-H in aniline accounts for the major part of its smaller chemical shift, relative to benzene, but the σ-framework effects must also be added.

The CC framework effects are responsible for higher chemical shifts of meta- and para-hydrogen atoms in nitrobenzene, relative to benzene, while that of ortho-Hs comes from the combined substituent deshielding effect, coming from the in-plane oxygen lone pairs, and decreased shielding from the C–H bond, which is caused by the electric field effect of the spatially close and parallel NO bond. Contrary to the textbook explanations, the π-electron system shields all ring Hs in nitrobenzene more than those in benzene and the main contribution to this effect comes from the π-component of the NO bond.

Although π orbitals are commonly invoked by chemists to explain various phenomena, this work provides one more example revealing an important role of the σ-electronic system.

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[34] An analysis based on canonical (delocalized) π molecular orbitals has also been performed by using the NBO 6.0 and the results are almost identical to those obtained on the basis of NLMOs. Since σ canonical orbitals are often a mixture of CC, CH, CN, NH and NO σ bonds and in-plane lone pairs, a clear identification of the main source of shielding is not possible. Thus, the discussion in this work is based on NLMOs.

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[36] If this π-orbital was excluded from the π-system, the substituent resonance effect could account for ~90% deshielding of *ortho*-Hs, ~40% deshielding of *meta*-Hs and ~30% deshielding of *para*-H, relative to benzene (in fact, less shielding than in benzene, Table S2). Thus, the σ-framework effects still need to be invoked.

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FULL PAPER

π orbitals, influenced by substituent resonance effects, are commonly invoked to explain downfield/upfield shift of ^1H NMR signals of benzene substituted with an electron-accepting/donating group. Decomposition of total shielding into orbital contributions revealed that π-electronic system shields protons more than in benzene irrespective of resonance properties of substituent and brings to light an important role of σ orbitals.

Δδ ^1H **NMR** (relative to benzene)

shielded by π- and σ-electrons;
dominant shielding by:

σCC H ⬡ H
π H   H
H

shielded by π-electrons;
deshielded by:

NO2
H ⬡ H σCH, LP$_O$
H   H σCC
H
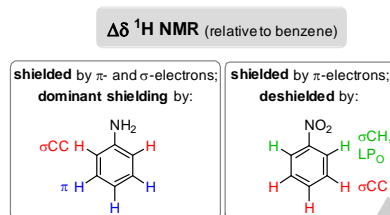
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