Stereoelectronic effect at nitrogen in 2,6-di-*tert*-butyl-4-(*N*,*N*-disubstituted aminomethyl)phenoxyl radicals

Martin Jäger and Hartmut B. Stegmann*

Institut für Organische Chemie der Universität, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

A variety of 2,6-di-*tert*-butyl-4-(*N*,*N*-disubstituted aminomethyl)phenoxyl radicals have been studied with respect to the *para* substituents' and *meta* protons' coupling constants observed in EPR and ENDOR experiments. For all molecules considered, restricted rotation dominates the spectroscopic features of the β-nuclei, and this plays a key role throughout the investigation. Based on the well-known McConnell–Heller equation, an empirical formula is proposed for analyzing the conformation at the α-carbon atom relative to the aroxyl plane. The results obtained reveal a strong stereoelectronic interaction between the β-nitrogen atom and the aromatic π-system. Hence, sterically unfavorable orientations are found to be preferred. The stereoelectronic interdependence is finally interpreted in terms of the generalized anomeric effect.

Introduction

Among organic free radicals, aroxyls have attracted the attention of many EPR spectroscopists from the 1950s[1,2] until now.[3–5] In order to understand the observed splitting constants these radicals have been subject to thorough investigation in both experiment[6–8] and theory.[9–11] The dependence of the spin density distribution and the dihedral angles of β-coupling constants upon solvent and temperature have been examined.[12–14]

While systems with either fixed or freely rotating substituents have proved to be readily understandable, aroxyls with $CR^1R^2R^3$-substituents exhibiting restricted rotation with the removal of a threefold barrier need further analysis.[15–17]

In this study, we take a close look at a variety of 2,6-di-*tert*-butyl-4-(aminomethyl)aroxyls where the β-nitrogen is primary, secondary, tertiary or quaternary. To our knowledge, no attempt has yet been made to collect and analyze the data available with respect to the conformation of such substituents in aroxyl radicals, nor has any theoretical point of view successfully been established describing the situation found in these systems.

Experimental

2,6-Di-*tert*-butyl-4-(*N*,*N*-dimethylaminomethyl)phenol **1** is commercially available. The synthesis of 2,6-di-*tert*-butyl-4-(aminomethyl)phenol **2** is described in ref 18. Radical generation was achieved by oxidizing the corresponding phenols with lead dioxide. Deoxygenation was carried out by bubbling argon through the samples. The EPR spectra were recorded on a Bruker ESP 300 E spectrometer.

Results

Normal resolved EPR spectra of all described 2,6-di-*tert*-butyl-4-(*N*-alkylaminomethyl)phenoxyls reveal the β-protons splitting ($a_{H_β}$), the *meta* protons splitting (a_{H_m}) and the nitrogen coupling (a_N), while the γ-splittings provide values within the linewidth. While the *meta* protons as α-substituents are described[19] by eqn. (1), the β-substituents follow the well known McConnell–Heller equation[20] which will be used in the simple form, eqn. (2), where ρ_{C_m} and ρ_{C_p} are the corresponding spin densities.

$$a_H = -Q^{H}_{C\text{–}H}\,\rho_{C_m} \qquad (1)$$

$$a_X = B^{X}_{C_p\text{–}CH_2X}\,\rho_{C_p}\langle\cos^2\Theta\rangle \qquad (2)$$

Values of 2.4 and 5.6 mT have been used for Q^H and $B^{X}_{C_p\text{–}CH_2X}$.[12] $\langle\cos^2\Theta\rangle$ is the quantum mechanical average over the dihedral angles Θ between the substituent X and the plane normal of the aroxyl. When the *para* substituent is free rotating, $B^{H}_{C_p\text{–}CH_3}\,\rho_{C_p}$ can be calculated. For 2,6-di-*tert*-butyl-4-methylphenoxyl (TBMP) a value of 2.220 mT is obtained in toluene, the *meta* protons coupling constant being 0.166 mT.

In order to estimate the dihedral angles Θ_X of a given aroxyl, the following assumptions were made. 1. The influence of the substituent X in CH_2–X upon $B^{H}_{C_p\text{–}CH_2X}$ can be neglected. Thus, the value of 5.6 mT for $B^{H}_{C_p\text{–}CH_2X}$ can be applied for all radicals discussed in this paper, where X is $-NR^1R^2$. 2. A deviation from the average coupling constant from $\bar{a}_{H_β} = \frac{1}{2}B^{H}_{C_p\text{–}CH_3}\,\rho_{C_p} = 1.110$ mT is due to a change of ρ_{C_p} and $\cos^2\Theta$. 3. A change in ρ_{C_p} due to solvent dependence of a radical can be roughly taken into account by comparing its *meta*-protons coupling with those of TBMP as reference. On collecting all data obtainable for TBMP in different solvents,[8] a linear regression ($a_{H_β}$ *vs.* a_{H_m}) shows a reciprocal correlation between both coupling constants. This result together with the assumptions given leads to an extension of eqn. (2) as follows to give eqn. (3).

$$a = B^{TBMP}_{C_p\text{–}CH_3}\,\rho^{TBMP}_{C_p}\,\frac{a^{TBMP}_{H_m}}{a_{H_m}}\langle\cos^2\Theta\rangle \qquad (3)$$

As only an average value of the two β-protons' coupling constants is observed at room temperature, with the exception of **2** in THF, we will assume further that $\bar{a}_{H_β} = \frac{1}{2}(a_{H_{β(1)}} + a_{H_{β(2)}})$ can be approximated by the geometric average of the two dihedral angles the protons would occupy if their position were fixed.

If the sp^3-hybridization at the α-carbon atom is undisturbed, the hyperconjugation angles will be correlated by 120° in each case. Eqn. (3) can then be written as eqn. (4), where K is given by eqn. (5). The solution of eqn. (4) yields the angle $\Theta_{H_β}$, from

$$\frac{\bar{a}_{H_β}}{K} = \tfrac{1}{2}[\cos^2\Theta_{H_β} + \cos^2(\Theta_{H_β} + 120°)] \qquad (4)$$

$$K = B^{TBMP}_{C_α\text{–}C_p}\,\rho^{TBMP}_{C_p}\,\frac{a^{TBMP}_{H_m}}{a_{H_m}} \qquad (5)$$

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* E-mail: stegmann@uni-tuebingen.de

Table 1 Solvent dependence of the hf parameters, calculated dihedral angles and $B^{N}_{C_p\text{–}CN}$ of 2,6-di-*tert*-butyl-4-(*N*,*N*-dimethylaminomethyl)phenoxyl **1**

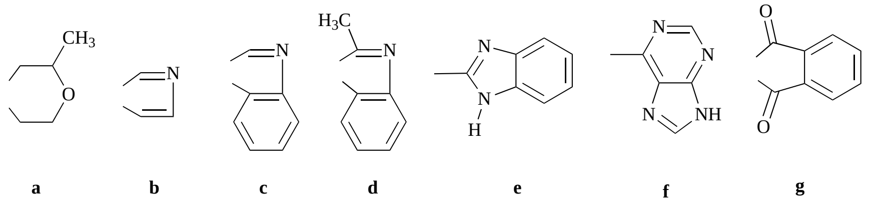
$\bar{a}_{H_\beta}$/mT	a_{H_m}/mT	a_N/mT	$\Theta_{H_{\beta(1)}}$/°	Θ_N/°	ρ_{C_p}	$B^{N}_{C_p\text{–}CN}$/mT	Solvent
1.066	0.188	0.195	10	130	0.350	1.35	*n*-hexane
1.070	0.180	0.195	12	132	0.366	1.19	cyclohexane
1.082	0.176	0.199	13	133	0.374	1.14	dioxane
1.098	0.188	0.188	8	128	0.350	1.42	toluene
1.090	0.176	0.194	12	132	0.374	1.16	ethyl acetate
1.094	0.176	0.199	12	132	0.374	1.19	THF
1.094	0.172	0.199	13	132	0.383	1.16	pyridine
1.082	0.176	0.203	13	133	0.374	1.17	acetone
1.031	0.172	0.215	17	137	0.383	1.05	dichloromethane
0.977	0.172	0.223	20	140	0.383	0.99	chloroform
0.930	0.176	0.238	21	141	0.374	1.05	ethanol

Table 2 Solvent dependence of the hf parameters, calculated dihedral angles and $B^{N}_{C_p\text{–}CN}$ of 2,6-di-*tert*-butyl-4-(aminomethyl)phenoxyl **2**

$\bar{a}_{H_\beta}$/mT	a_{H_m}/mT	a_N/mT	$\Theta_{H_{\beta(2)}}$/°	Θ_N/°	ρ_{C_p}	$B^{N}_{C_p\text{–}CN}$/mT	Solvent
1.094	0.176	0.160	12	132	0.374	0.96	*n*-hexane
1.090	0.172	0.164	15	135	0.383	0.86	cyclohexane
1.094	0.168	0.129	15	135	0.392	0.66	dioxane
1.148	0.168	0.148	12	132	0.392	0.84	toluene
1.137	0.168	0.133	13	133	0.392	0.73	ethyl acetate
1.207, 1.148	0.168	0.188	11	131	0.392	1.12	THF
1.148	0.161	0.132	15	135	0.409	0.65	pyridine
1.059	0.168	0.148	17	137	0.392	0.71	dichloromethane
1.008	0.168	0.156	20	140	0.392	0.68	chloroform

Table 3 Hf parameters, calculated dihedral angles and $B^{N}_{C_p\text{–}CN}$ of a series of 2,6-di-*tert*-butyl-4-(*N*,*N*-substituted aminomethyl)phenoxyls

Compound	R^1	R^2	$\bar{a}_{H_\beta}$/mT	a_{H_m}/mT	a_N/mT	$\Theta_{H_{\beta(1)}}$	Θ_N/°	ρ_{C_p}	$B^{N}_{C_p\text{–}CN}$/mT	Solvent	Ref.
3	$-CH_3$	$-C(CH_3)_3$	1.157	0.173	0.173	10	130	0.380	1.10	toluene	27
4	$-CH_3$	$-CH_2(C_6H_5)$	1.099	0.180	0.180	11	131	0.366	1.14	toluene	27
5	$-CH(CH_3)_2$	$-CH_2(C_6H_5)$	1.165	0.173	0.173	10	130	0.380	1.10	toluene	27
6	$-C_2H_5$	$-CH_2(C_6H_5)$	1.099	0.180	0.180	11	131	0.366	1.14	toluene	27
7	**a**	**a**	1.105	0.184	0.184	9	129	0.358	1.30	toluene	27
8	**b**	**b**	1.150	0.190	0.130	4	124	0.346	1.20	benzene	31
9	**c**	**c**	1.170	0.190	0.133	2	122	0.346	1.37	benzene	31
10	**d**	**d**	1.220	0.190	0.110	0	120	0.346	1.27	benzene	31
11	$-C_2H_5$	$-(C_6H_4)CH_3$	1.310	0.165	0.085	5	125	0.399	0.65	toluene	27
12	$-C_2H_5$	$-(C_6H_5)$	1.340	0.170	0.075	1	121	0.387	0.73	toluene	27
13	$-H$	**e**	1.180	0.184	0.125	5	125	0.358	1.06	dichloromethane	26
14	$-H$	$-(C_6H_5)$	1.200	0.161	0.161	12	132	0.409	0.88	toluene	27
15	$-H$	$-C(CH_3)_3$	1.185	0.183	0.183	5	125	0.360	1.54	toluene	27
16	$-H$	**f**	0.918	0.188	0.215	19	139	0.350	1.08	toluene	26
17	**g**	**g**	0.754	0.187	0.234	29	149	0.352	0.91	chloroform	32
18	$-(CH_3)_3$	+	0.970	0.175	0.220	19	139	0.376	1.03	chloroform	27



Structure of β-nitrogen substituents, R^1 and R^2, Table 3

which the position of the nitrogen atom can easily be derived. Notice these angles do not refer to fixed conformations because the radicals exhibit restricted rotation. Therefore the values obtained are approximations which will give only relative information.

Table 1 presents the hf parameters of **1** in different solvents. It can be seen that the nitrogen coupling constant depends strongly on the solvent. With the increasing of its value the methylene proton splitting decreases. A hyperconjugation angle for the nitrogen can then be estimated to vary between 128 and 141° (see Fig. 1). Table 2 illustrates the solvent dependence of **2**. Here, the nitrogen occupies a position $131 \leqslant \Theta_N \leqslant 140°$. In Table 3, data for a variety of 2,6-di-*tert*-butyl-4-(*N*,*N*-disubstituted aminomethyl)phenoxyls are collected. For secondary and tertiary amines, the nitrogen angle is found to have values between 120 and 149°. The only quaternary amine (**18**) reveals a Θ_N of 139°.

With ρ_{C_p} calculated from eqn. (4), $B^{N}_{C_p\text{–}CN}$ can be estimated by eqn. (6) and will be discussed below.

$$a_N = B^{N}_{C_p\text{–}CN}\,\rho_{C_p}\cos^2\Theta_N \qquad (6)$$

Discussion

1. The spin density distribution of the aroxyls investigated may be modified by solvent interactions[21,22] and variation of the *N*-substituents.[23,24]

In order to account for the contribution of these factors

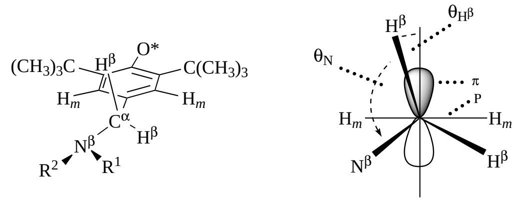


Fig. 1 Perspective view of 2,6-di-*tert*-butyl-4-(*N*,*N*-disubstituted aminomethyl)phenoxyl and definition of the hyperconjugation angles used ($\Theta_{H_β}$: angle of the β-proton; Θ_N: angle of the nitrogen; P: aromatic plane; π aromatic π-system)

to the change in spin density, we introduced the quotient $a_{H_m}^{TBMP}/a_{H_m}$ into eqn. (2), choosing TBMP as a reference with experimentally accessible spin densities. Hence, $B_{C_p–CH_2X}\ \rho_{C_p}$ = 2.220 mT is reduced to 1.938 mT at maximum, or $\rho_{C_p}^{TBMP} = 0.396$ is lowered to $\rho_{C_p} = 0.346$ if *B* is taken as constant.

2. (*a*) On considering the cosine term for the β-coupling constants, spectroscopic equivalence of the methylene protons in CH$_2$–X substituted aroxyls is known to be caused either by free rotation, a symmetric isomerization,[15,16,25] or by a fixed conformation. Temperature dependent measurements[17,26] have revealed the slowing of the restricted rotation at lower temperatures, and hence allow the application of the 'two-jump' model for the molecules discussed. Nonetheless, we are well aware that the assumptions leading to eqn. (4) represent a simple approach.

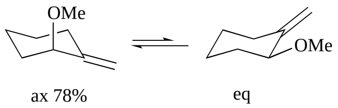
2. (*b*) In all the aroxyls discussed (one exception being where $\Theta_N = 149°$), the nitrogen atom occupies a position between 120 and 141°. Given this range, it is clear that the position of the nitrogen cannot be explained by solely steric interactions, which would favour $\Theta_N = 180°$. The lack of interacting π- or non-bonding electron pairs in 2,6-di-*tert*-butyl-4-ethylphenoxyl means its conformation is governed exclusively by steric interactions and thus it has a perpendicular arrangement. In contrast, for many amines considered in this work, the application of eqn. (4) yields an orientation of the nitrogen atom as would be expected from $\mathrm{d}a_N/\mathrm{d}T \geqslant 0$ for dihedral angles $120 \leqslant \Theta_N \leqslant 135°$. These temperature gradients have been observed (see refs. 17, 26 and 27).

In discarding mere steric interactions as driving forces, it is not surprising that a general trend, $\Theta_{N(prim)} \leqslant \Theta_{N(sec)} \leqslant \Theta_{N(tert)} \leqslant \Theta_{N(quart)}$ does not exist, when comparing the nitrogen hyperconjugation angle Θ_N in the series of primary, secondary, tertiary and quaternary amines.

3. The solvent dependent measurements of **1** (*cf.* Table 1 and Fig. 1) present the increasing of the nitrogen coupling constant with the increasing of Θ_N in line with eqn. (6). However, the corresponding primary amine (**2**) does not show a similar uniform behavior, which might be due to the interaction of the solvent with the primary nitrogen. On considering the variety of tertiary amines, the general trend that a larger nitrogen coupling constant refers to a more perpendicular orientation, is found within a certain deviation as well. Thereby, with aliphatic substituents, the nitrogen presents a larger coupling constant than with aromatic substituents. This is also true for secondary amines. The nitrogen splitting increases in the quaternary amine (**18**). This phenomenon can be interpreted in terms of the nitrogen atom exposed to two kinds of influences, the steric effect directing it to a perpendicular position and the electronic effect driving it to a coplanar orientation. The substituents with delocalized electrons, *i.e.* aromatic systems, which increase the electron density at the nitrogen, favour the electronic interaction with the aroxyl (*cf.* **12** to **6**). Thus, the nitrogen is found closer to the phenoxyl plane. Consequently, the more the substituents are electron withdrawing or less electron donating, the closer the dihedral angle approaches the perpendicular position (*cf.* **3** to **15**). Hence, the quaternary amine exhibits an orientation farther from the aroxyl plane than that seen in **1** due to the lack of the non-bonding electron pair. Within the phthalimido aroxyl (**17**, R^1, R^2 = **g**), the nitrogen is likely to have a partial positive charge due to the two strong electron withdrawing substitutents (C=O), thus leading to a larger coupling constant (*cf.* **17** to **7**).

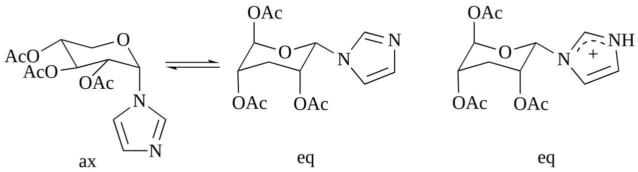
While for the primary amine in different solvents, a $B_{C_p–CN}^{N}$ of (0.799 ± 0.158) mT as well as (1.170 ± 0.124) mT for **1** can be estimated, which is found to be in good agreement with that reported in the literature,[27,†] a value of $B_{C_p–CN}^{N}$ (1.094 ± 0.229) mT is obtained for the secondary, tertiary and the quaternary amines (*cf.* Table 3). Nevertheless, the two phenyl substituted tertiary (**11** and **12**) and the *tert*-butyl substituted secondary (**15**) amines do not fit this estimation well.

The generalized anomeric effect is known as the interaction of two electronegative atoms—one of them can be replaced by a π-system—through a central carbon atom. In appropriate cyclic systems, one of the atoms then prefers an axial position (see Scheme 1), whereas steric interactions alone as driving forces would favour an equatorial orientation.[28] Almost all molecules investigated in this paper exhibit a dihedral angle of the nitrogen atom between 120 and 141°, *i.e.* its orientation with respect to the aromatic plane which corresponds to the axial position in Scheme 1 is dominant. The bulkiness of the substituent is therefore less critical to its conformation than its electronic nature. A phenyl substituent at the nitrogen atom of secondary and tertiary amines strengthens the anomeric effect, which is found to be true for phenyl ethers as well. The nitrogen coupling constant depends on the solvent, as can be seen from the data in Table 2.



Scheme 1 Anomeric effect at oxygen towards a double bond. Axial (ax) conformation is favored (78% in CCl$_4$).

A striking example summarizing our results is given in Scheme 2 according to ref. 28. In apolar media an equilibrium between axial (ax) and equatorial (eq) conformations exists as a compromise between steric and anomeric effect. Protonation at the imidazole moiety lowers the electron density at the nitrogen, reduces the ability of electronic interactions and decreases the percentage of axial conformer present in the equilibrium mixture. The electronic effects are known to lead to a restricted rotation around the barrier of a single bond. The isomerization process, described by the 'two-jump' mechanism, also involves a restricted rotation.



Scheme 2 Anomeric effect at nitrogen. Equilibrium between axial (ax) and equatorial (eq) orientation depends on the polarity of the solvent; conformation with imidazole group equatorial is favored in protonating solvent.

The basics of the anomeric effect at oxygen related to a C–X double bond are considered as an overlap of the $n_π$-orbital (or p_z for a canonical basis set) with the π*-orbital of the C–X bond and an additional interaction between $n_σ$- and the $σ^*_{C–X}$-orbital. Aroxyls have been reported to interact with oxygen by an anomeric effect.[29] The nitrogen can only establish one of the two types of overlap. Assuming a benzene type orbital symmetry of the aroxyl, the non-bonding electron pair of the nitrogen and

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[†] The value of $B_{C_p–CN}^{N} \approx 1.0$ mT has been obtained by temperature variation analyzed by a plot of $\mathrm{d}a_N/\mathrm{dT} \sim \mathrm{d}\bar{a}_H/\mathrm{d}T$.

the aromatic π-system (most likely a n_N–π^*_{aroxyl} interaction) are likely to have maximum overlap when the nitrogen occupies a position close to the phenoxyl plane.

The preference of sterically unfavorable conformations due to more dominant stereoelectronic effects is obviously a general quality of π-radicals.[30] It should be considered when dealing with systems of appropriate substituents exhibiting restricted rotation.

Conclusions

A variety of 2,6-di-*tert*-butyl-4-(*N*,*N*-substituted aminomethyl)-phenoxyl radicals has been investigated with respect to the conformation of the α-carbon atom. A simple method based upon the McConnell–Heller equation is proposed to estimate the positions of the methylene protons and the nitrogen atom relative to the aroxyl plane. The modifications of the principal equation are compared thoroughly to observations and theoretical considerations given in the literature. The effects on spin distribution and the existence of a fast 'two-jump' isomerization process are briefly discussed.

Despite the simplicity of the method applied, the results are surprisingly consistent. A conformation with the nitrogen in vicinity of the aromatic plane is favoured, while a decrease in electron density leads to a preference for the perpendicular arrangement. Comparing these results to those for similar oxygen systems, we interpret this stereoelectronic-based effect as the existence of an anomeric effect at nitrogen in phenoxyl radicals.

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