Acid–Base Equilibria of Co-ordinated Ligands. Part 1. The Effect of Basicity of Co-ordinated Nitrogen Donors upon the Acidity of Chelating 8-Aminoquinoline in some Dicationic Platinum(II) Complexes†

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Cationic complexes of the type $[Pt(8NH_2\text{-quin})L_2][ClO_4]_2$ and $[Pt(8NH_2\text{-quin})(L\text{–}L)][ClO_4]_2$ ($8NH_2$-quin = 8-aminoquinoline), where L and L–L are mono- and bi-dentate nitrogen donors respectively, have been prepared. In aqueous solution, they undergo reversible deprotonation of the amino group of the quinoline ligand. The corresponding ionization constants (K_a^c) have been determined by UV/VIS spectrophotometry at 25 °C and $I = 0.1$ mol dm^{-3}. The linear free-energy relationship $pK_a^c = \alpha + \beta pK_a^L$ is verified for the *para*-substituted pyridines, pK_a^L referring to the basicity of L in water at 25 °C.

The ability of a transition-metal ion to transmit electronic effects among ligands has been studied for a long time in connection with both kinetic and ground-state properties of co-ordination compounds. The extent to which an observable property of a ligand is sensitive to the nature of the others can be used as a measure of this effect.

As far as planar four-co-ordinate complexes are concerned, investigations have often been aimed to relate possible observed changes by measurement of relative metal–ligand bond strengths. For instance, Chatt *et al.*[1] considered the N–H stretching frequency in complexes of the type *trans*-$[Pt(NHR_2)(L)Cl_2]$ (R = alkyl or aryl) as an indirect measure of the relative strength of Pt–N bond, and hence of the *trans*-influence of L.

The dependence of the ionization constant of an acidic group present in one of the ligands upon the nature of the other ligands can also provide a thermodynamic measure of the transmission of electronic effects. Acidity data for square-planar complexes in the literature are scanty and do not provide enough examples to allow any proper comparison as such studies require substrates of the same metal and charge and containing the same deprotonable species. We decided to use the chelating species 8-aminoquinoline ($8NH_2$-quin) as the probe ligand, and synthesized a number of dicationic platinum(II) complexes of the type $[Pt(8NH_2\text{-quin})L_2][ClO_4]_2$ and $[Pt(8NH_2\text{-quin})(L\text{–}L)][ClO_4]_2$, where L and L–L are neutral mono- and bi-dentate nitrogen donors respectively. These new species behave as acids in aqueous solution. Their dissociation equilibrium constants have been determined and are reported and commented on in this paper. Complexes of transition metals, including platinum, with 8-aminoquinoline are known,[2,3] but no examples of acid–base behaviour are reported.

Experimental

Materials.—Dipotassium tetrachloroplatinate(II) was prepared from metallic platinum according to the reported procedure.[4] Commercial pyridines were purified by distillation over KOH. The other organic bases, inorganic salts and solvents were of reagent grade.

Preparation of the Complexes.—*cis*-Diamminedichloroplatinum(II) was prepared by the reported procedure.[5] The other compounds *cis*-$[PtL_2Cl_2]$ [L = 4-methylpyridine (4Me-py), 4-chloropyridine (4Cl-py), 4-dimethylaminopyridine ($4NMe_2$-py), 4-aminopyridine ($4NH_2$-py), pyridine (py) and piperidine (pip)] were prepared according to the standard method[6] by adding the required amount of the appropriate amine to an aqueous solution of $K_2[PtCl_4]$. In the case of $4NMe_2$-py, preliminary experiments showed that an excess (*ca.* 20%) of the organic base is required in order to avoid the formation of the rather insoluble $[4NMe_2\text{-Hpy}]_2[PtCl_4]$. The compounds $[Pt(L\text{–}L)Cl_2]$ [L–L = 1,2-diaminoethane (en), 1,3-diaminopropane (tn) or *N,N,N′,N′*-tetramethyl-1,2-diaminoethane (tmen)] were prepared by the method of Natile and co-workers.[7]

$[Pt(8NH_2\text{-quin})(py)_2][ClO_4]_2$. The complex was prepared by the following procedure: a solution of $Ag[ClO_4]$ (146.8 mg, 0.708 mmol) in water (5 cm^3) was added with stirring to a suspension of *cis*-$[Pt(py)_2Cl_2]$ (0.15 g, 0.354 mmol) in water (50 cm^3), and the mixture was stirred overnight in the dark at 60 °C. The mixture was then treated at room temperature with an aqueous solution (20 cm^3) of $8NH_2$-quin (0.354 mmol) and perchloric acid (0.708 mmol). After stirring for *ca.* 30 min, the precipitated AgCl was filtered off and the solution concentrated to 20 cm^3 on a rotary evaporator. A standard NaOH solution (0.1 mol dm^{-3}) was slowly added, with stirring, until the pH was nearly 5 and stirring was continued for a further 30 min. Concentration of the mixture in a rotary evaporator (*ca.* 5 cm^3) led to precipitation of the crude product which was filtered off, washed twice with diluted $HClO_4$ (2 cm^3, 0.1 mol dm^{-3}) and air dried. The complex was recrystallized from a filtered nitromethane solution by careful addition of diethyl ether, washed twice with diethyl ether and dried *in vacuo* over P_2O_5.

The cationic complexes $[Pt(8NH_2\text{-quin})L_2][ClO_4]_2$ (L = NH_3, pip, 4Cl-py, 4Me-py, $4NMe_2$-py or $4NH_2$-py) and $[Pt(8NH_2\text{-quin})(L\text{–}L)][ClO_4]_2$ (L = en, tn or tmen) were prepared by the same procedure. Analytical data and yields are reported in Table 1.

$[Pt(8NH\text{-quin})(4Me\text{-py})_2][ClO_4]$. To a solution of $[Pt(8NH_2\text{-quin})(4Me\text{-py})_2][ClO_4]_2$ (50 mg, 0.07 mmol) in water (1.5 cm^3), an aqueous solution (0.7 cm^3) of sodium hydroxide (0.07 mmol) was added with stirring; a purple precipitate formed immediately. The mixture was cooled in an ice-bath and stirred for a further 5 min. The resulting precipitate was collected by filtration, washed with a few drops of cold water and dried *in vacuo* over $CaCl_2$. It was recrystallized from a

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† *Supplementary data available* (No. SUP 56986, 6 pp.): measured absorbance values. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical data and yields for the cationic complexes

Complex	Yield (%)	Analysis* (%) C	H	N	Cl
$[Pt(8NH_2\text{-quin})(4Cl\text{-py})_2][ClO_4]_2$	54	29.3 (29.8)	2.05 (2.10)	7.15 (7.30)	17.6 (18.5)
$[Pt(8NH_2\text{-quin})(py)_2][ClO_4]_2$	72	32.4 (32.8)	2.50 (2.60)	7.95 (8.05)	10.1 (10.2)
$[Pt(8NH_2\text{-quin})(4Me\text{-py})_2][ClO_4]_2$	60	34.1 (34.8)	3.10 (3.05)	7.80 (7.75)	9.75 (9.80)
$[Pt(8NH_2\text{-quin})(4NH_2\text{-py})_2][ClO_4]_2$	68	29.2 (31.4)	2.65 (2.75)	10.3 (11.6)	9.20 (9.75)
$[Pt(8NH_2\text{-quin})(4NMe_2\text{-py})_2][ClO_4]_2$	64	34.0 (35.3)	3.45 (3.60)	10.3 (10.7)	8.95 (9.05)
$[Pt(8NH_2\text{-quin})(NH_3)_2][ClO_4]_2$	75	18.6 (18.9)	2.35 (2.45)	9.80 (9.80)	12.1 (12.4)
$[Pt(8NH_2\text{-quin})(pip)_2][ClO_4]_2$	55	32.0 (32.2)	4.20 (4.25)	7.85 (7.90)	10.5 (10.0)
$[Pt(8NH_2\text{-quin})(en)][ClO_4]_2$	72	21.9 (22.1)	2.60 (2.70)	9.20 (9.35)	11.8 (11.9)
$[Pt(8NH_2\text{-quin})(tn)][ClO_4]_2$	76	23.4 (23.5)	2.90 (2.95)	9.10 (9.15)	11.4 (11.6)
$[Pt(8NH_2\text{-quin})(tmen)][ClO_4]_2$	65	27.1 (27.4)	3.95 (4.00)	8.60 (8.55)	10.9 (10.8)

* Required values are given in parentheses.

filtered acetonitrile solution by addition of diethyl ether, washed twice with diethyl ether and dried *in vacuo* over calcium chloride. Yield 71% (Found: C, 39.3; H, 3.30; N, 8.75. $C_{21}H_{21}ClN_4O_4Pt$ requires C, 40.4; H, 3.40; N, 9.00%); $\tilde{\nu}_{max}/cm^{-1}$ 3340 (NH) and 1085 (ClO_4^-).

Equilibrium Measurements.—The position of the acid-dissociation equilibrium of the cationic complexes in water, as a function of pH, was determined spectrophotometrically as follows. Aliquots (10 cm^3) of a freshly prepared solution of the complex (10^{-4} mol dm^{-3}) in water were brought to 25 °C in a thermostat and then mixed with 1 cm^3 of the appropriate buffer solution. A fraction of the resulting mixture was transferred into a thermostatted (25 °C), 1 cm quartz spectrophotometer cell and the UV/VIS spectrum recorded; the pH was measured on the remainder of the solution with a glass electrode. Buffer solutions of sodium dihydrogen phosphate–disodium hydrogen phosphate and sodium borate–boric acid were used for pH values in the range 5.7–8 and 7.7–9.5 respectively; ionic strength was kept constant with sodium sulfate. The solutions used to record the spectra of the undissociated and dissociated form of the complex were prepared by mixing the 10 cm^3 aliquots with 1 mol dm^{-3} sulfuric acid (1 cm^3) or 1 mol dm^{-3} sodium hydroxide, respectively. The equilibrium constants, K_a^c, were calculated using the method described by Albert and Serjeant[8] and are reported in Table 2 as pK_a^c. Primary data for the values of absorbance of the complexes at various pH values in water at 25 °C are provided as supplementary material (SUP 56986).

Apparatus.—UV/VIS spectra were obtained with a Perkin-Elmer Lambda 5 recording spectrophotometer. pH Measurements were made with a Gibertini DP-100NE digital pH meter using commercial standard buffer solutions (pH 4 and 7) as reference points. Infrared spectra of Nujol mulls between NaCl plates were recorded with a Perkin-Elmer 683 spectrophotometer.

Results and Discussion

The cationic complexes of the type $[Pt(8NH_2\text{-quin})L_2]^{2+}$ described here behave as acids as can be observed in their synthesis (see Experimental section), the success of which depends chiefly upon the pH. A slightly acidic reaction medium is in fact required to avoid deprotonation of the co-ordinated quinoline ligand (see below) as well as the formation of unreactive hydroxo species.

Table 2 Dissociation equilibrium constants, pK_a^c, of the complexes $[Pt(8NH_2\text{-quin})L_2][ClO_4]_2$ and $[Pt(8NH_2\text{-quin})(L\text{–}L)][ClO_4]_2$ in water at 25 °C and I = 0.1 mol dm^{-3}

L or L–L	pK_a^c	pK_a^L*	$pK_a^L + \log(n/s)$
4Cl-py	7.03 ± 0.03	3.79	3.79
py	7.40 ± 0.02	5.25	5.25
4Me-py	7.52 ± 0.02	6.03	6.03
$4NH_2$-py	8.01 ± 0.04	9.11	9.11
$4NMe_2$-py	8.28 ± 0.05	9.57	9.57
NH_3	8.57 ± 0.02	9.25	9.85
pip	7.44 ± 0.03	11.12	11.4
en	8.64 ± 0.06	9.93	10.1
tn	8.41 ± 0.02	10.3	10.5
tmen	6.92 ± 0.01	9.14	8.84

* Data at 25 °C from ref. 16.

These complexes are all pale pink crystalline solids, soluble in most polar solvents. In water they are rather inert towards attack by common anionic nucleophiles; even in the presence of 0.1 mol dm^{-3} thiocyanate ion the electronic spectra of the complexes remain unchanged over several hours. Considerable spectral changes can be observed on changing the pH of the solution. In the presence of acid (pH < 3) the spectra of all complexes do not show absorption bands above 390 nm. However, on adding sodium hydroxide a band appears in the visible region with a maximum between 470 and 490 nm, depending on the nature of the complex. This spectral change is complete within the time of mixing and fully reversed by acidification. At pH > 10 a slow decomposition process takes place. It does not interfere with the proton exchange reaction and was not further investigated.

Slow colour changes occurring in solutions of 8-aminoquinoline[2] and 8-amino-2-methylquinoline[9] metal complexes have been reported in the literature, the changes being accelerated in the presence of hydrogen peroxide. In very basic solutions, the complexes described here possibly undergo a similar oxidation process.

A typical set of spectra, as a function of pH, is shown in Fig. 1

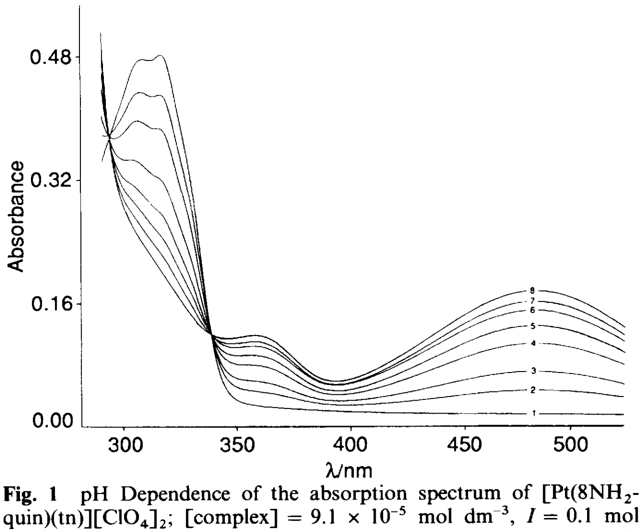
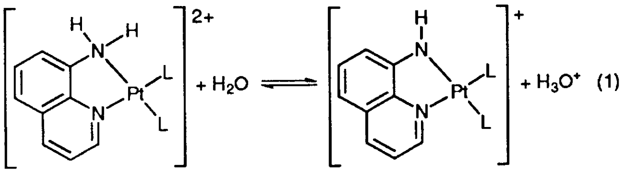


Fig. 1 pH Dependence of the absorption spectrum of $[Pt(8NH_2\text{-quin})(tn)][ClO_4]_2$; [complex] = 9.1 × 10^{-5} mol dm^{-3}, I = 0.1 mol dm^{-3} at 25 °C. Curves 1–8 show, respectively, spectra at pH 1.00, 7.80, 8.12, 8.54, 8.83, 9.11, 9.41 and 11.0

for the complex $[Pt(8NH_2\text{-quin})(tn)]^{2+}$. In all the cases the presence of isosbestic points suggests that only two absorbing species are involved in the process. In the case of L = 4-methylpyridine the conjugate amido species $[Pt(8NH\text{-quin})(4Me\text{-py})_2[ClO_4]$ has been isolated and characterized. As the spectral changes are qualitatively very similar for any L or L–L ligand, the above reported observations allow us to attribute the experimental measurements in all cases to equilibria of the type shown in equation (1).



(1)

The increase of acidity of an amino group upon co-ordination is known and expected as a consequence of electron withdrawal by the metal ion. In the case of platinum(II) complexes, the few reported acidity data concern +2 cations.[10,11] Although the dicationic nature of the complex seems to be important, charge considerations alone are not sufficient in predicting acidity; for instance $[Pt(NH_3)_4]^{2+}$ cannot be significantly deprotonated in aqueous solution whereas $[Pt(NH_3)_3(Me_2SO)]^{2+}$ possesses an acidic amino group (pK_a = 8.18).[11] In the present case the change of hybridization of the nitrogen atom from sp^3 (amino) to sp^2 (amido), in the deprotonated species, can promote pseudo-aromaticity in the Pt–quinoline chelate ring and this fact, while accounting for the spectral behaviour of the complexes, may well be an additional driving force for deprotonation.

The distinct spectral changes, associated with reaction (1), allowed us to measure the acid-dissociation equilibrium constants of the various dicationic complexes by UV/VIS spectrophotometry under the same experimental conditions (25 °C, I = 0.1 mol dm^{-3}) (details on the procedure are given in the Experimental section). Quantitative evaluation of the data was carried out by a plot of pH *vs.* $\log[(A - A_0)/(A - A_\infty)]$, where A is the absorbance, at a given wavelength, of the solution at a given pH, and A_0 and A_∞ the absorbances measured in the presence of a sufficient excess of acid or base to force all the substrate into the acid or basic form, respectively. In keeping with the relationship $pH = pK_a^c + \log[(A - A_0)/(A_\infty - A)]$, the plot was in all cases a straight line. The experimentally determined values (reported as pK_a^c in Table 2) proved to be dependent upon the nature of the co-ordinated amine. For the isosteric pyridine derivatives a linear free energy relationship [equation (2)] was obeyed, the value of pK_a^c responding

$$pK_a^c = \alpha + \beta pK_a^L \qquad (2)$$

linearly, within the limit of experimental error, to the basicity of the ligand as measured by its pK_a^L value according to equilibrium (3). A weighted linear regression analysis gave $\alpha = 6.4 \pm 0.1$ and $\beta = 0.19 \pm 0.02$.

$$HL^+ + H_2O \rightleftharpoons L + H_3O^+ \qquad (3)$$

The value of the constant β represents the response of the dissociation of the co-ordinated amino group to the electron-donating capacity of amine L and therefore is a measure of the effectiveness of the platinum atom to transmit electronic effects from the nitrogen atom of L to that of the acidic group. The effect is likely to be largely inductive since in all these species steric factors will prevent the pyridine rings to lie coplanar to the 8-aminoquinolinate moiety in the co-ordination plane.

The effect of *para*-substituents upon the acidity constants of a class of compounds is usually correlated with the Hammet equation (4) in which the constant σ_X for each substituent was

$$pK_a(X) = pK_a(H) - \rho\sigma_X \qquad (4)$$

defined as $\sigma_X = pK_a(H) - pK_a(X)$ for *p*-substituted benzoic acids as standard substrates (ρ = 1).[12] In the present case the same equation can be applied. The resulting plot is linear and a weighted linear regression analysis gave $pK_a^c(H) = 7.35 \pm 0.03$ and $\rho = 1.09 \pm 0.09$ (correlation coefficient = 0.995). We may assume, as a first approximation, that the effect of the *para*-substituent is independent of the location of the ligand in the complex (either *cis* or *trans* to the acidic group, $-NH_2$). Under this hypothesis the numerical value of ρ may be corrected to 1.09/2 = 0.55, the effect being due to the additive effects of both ligands. This value can be compared with those found for the dissociation (in water at 25 °C) of $p\text{-}XC_6H_4CH_2CO_2H$ (0.49),[13] $p\text{-}XC_6H_4(CH_2)_2CO_2H$ (0.21)[13] and $p\text{-}C_6H_4CH_2NH_3^+$ (1.06).[14]

Therefore if we regard the $p\text{-}XC_5H_4N\text{-}Pt$ moiety as a substituent of $[p\text{-}XC_5H_4N\text{-}Pt\text{-}NH_2]^{2+}$, the attenuation of the inductive effect of X by the $-C_5H_4N\text{-}Pt$ chain on the amino group is much the same as that of the $-C_6H_4CH_2-$ chain on the carboxylic group. However the *trans* and *cis* effects of the ligands are known to differ significantly in platinum(II) complexes and further investigations are required in order to separate the two contributions.

The complexes of the *para*-substituted pyridines form a group of isostructural substrates. In order to extend behavioural comparisons to other nitrogen donors, *i.e.* aliphatic mono- and bi-dentate amines, some preliminary considerations are required.

(*i*) Each pyridine ligand has a single lone pair of electrons for bonding and the corresponding pyridinium ion has a single hydrogen for a proton transfer reaction. This is not necessarily so for aliphatic amines and therefore it is necessary to add to their pK_a^L value a statistical correction[15] $\log(n/s)$, where n is the number of hydrogens attached to nitrogen in the ammonium ion and s the number of equivalent basic sites in the amine. These corrected values, given in Table 2, have been used when plotting the points in Fig. 2. In the case of the diamines, we have chosen as pK_a^L the value corresponding to the dissociation of the monoprotonated species but we are aware that the appropriate value should be somewhat lower since the transmission of positive charge between the nitrogen atoms of the chelated diamine through the carbon chain will certainly decrease to some extent the basicity of the amine with respect to that measured by equilibrium (3). This can be clearly seen for ethylenediamine on comparing the pK_a of the species Hen^+ (9.93), $[Pt(en)(Hen)Cl]^{2+}$ (7.96)[16] and *trans*-$[Pt(Hen)_2Cl_2]^{2+}$

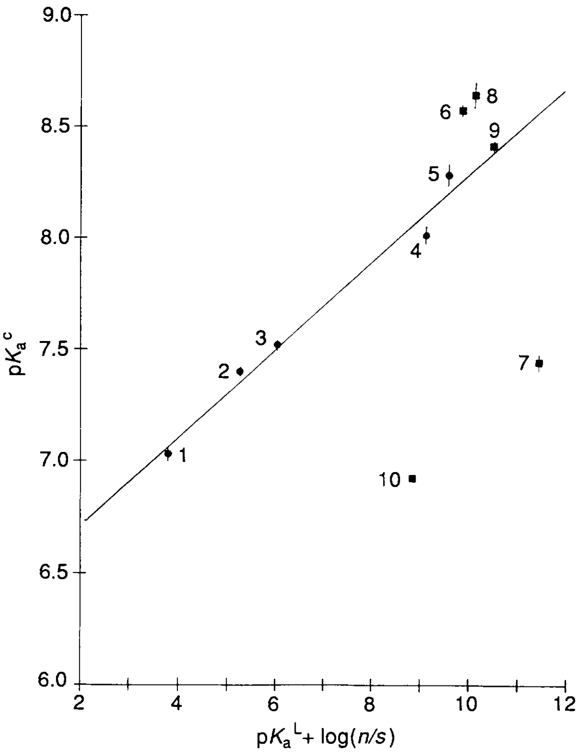


Fig. 2 Correlation of pK_a^c with pK_a^L + log(*n*/*s*) (25 °C, *I* = 0.1 mol dm^{-3}): **1**, 4Cl-py; **2**, py; **3**, 4Me-py; **4**, 4NH$_2$-py; **5**, 4NMe$_2$-py; **6**, NH$_3$; **7**, pip; **8**, en; **9**, tn; **10**, tmen

(7.92);[17] *i.e.*, in the latter two cases, the basicity of the free end of the mono-co-ordinated diamine is found, after statistical correction, to be *ca.* 85% that of the free amine.

(*ii*) Because of solvation, pK_a^L values do not simply relate to the donor capacity of L and direct comparisons between amines belonging to different classes, based on pK_a values alone, are too simplistic.

However, while solvation effects restrict the comparison to isostructural species when correlations such as (4) are concerned,[18] they should play only a minor role in the case of correlation (2) insofar as the solvation free energy changes, due to hydrogen-bonding of L with the solvent, of reactions (1) and (3) compensate each other in equation (2).

The fact that the pK_a^c value of NH$_3$ (and possibly those of en and tn) differs by *only* 0.3 units from the value expected from equation (2) seems to indicate that the behaviour of aliphatic amines closely parallels that of the pyridine derivatives. Further investigations with a wider range of amines having sp^3 nitrogen atoms would be necessary to establish this point conclusively.

The relatively high acidity of the complexes containing the pip and tmen ligands (see Fig. 2) is very likely a consequence of their bulkiness. A referee suggested that steric hindrance would cause an increase in the Pt–N bond length, which would automatically reduce the electron donation from L to Pt.

It may be of importance to consider also the steric hindrance to the approach of a hydrated proton to an amino group caused by bulky substituents close to it.[19] For instance, introduction of two methyl groups into *ortho* positions in the anilinium ion decreases the pK_a value by *ca.* 1.4 units[20] relative to PhNH$_3^+$. A molecular model of the cation [Pt(8NH$_2$-quin)(pip)$_2$]$^{2+}$ indicates that, because of non-bonding interactions, the two piperidine rings will probably lie nearly perpendicular to the co-ordination plane with the N–H bonds facing each other. Under these conditions, the two α-methylene groups of the amine *cis* to the reaction centre will extend over it by nearly the same amount as the two *cis* methyl groups in the tmen derivative do. Assuming normal bond lengths and angles, the distance of the α-carbon atoms from the reaction centre is estimated to be, on average, nearly the same of that of the methyl carbons from nitrogen in 2,6-dimethylaniline.

Acknowledgements

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