^{1}H and ^{13}C NMR studies of *para*-substituted benzaldoximes for evaluation of the electron donor properties of substituted amino groups †

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^{1}H and ^{13}C NMR spectra of seventeen (*E*)-benzaldoximes and three acetophenone oximes, both carrying substituted *p*-amino groups, have been recorded and discussed from the point of view of substituent effect. The resonance effect of these substituents is not transmitted strongly to CH=NOH group. However, it is found that the chemical shift of C_{para} depends linearly on σ_R° values. This dependence has been used to calculate the resonance substituent constants for the less common amino groups and the 1-pyrrolidine group is found to be the most powerful electron donor among the substituents studied.

Introduction

Substituted amino groups, which are very interesting from the point of view of differentiation of their electron donor properties, comprise a wide range of members. Electronic effects of aromatic amino substituents depend on the geometry of the C_{Ar}–NR_2 fragment and it is determined by C_{Ar}–N distance, R–N–R valence angle, twist (torsion)[2,3] and bend angles,[4,5] both referring to mutual orientation of n_N and π_{Ar} orbitals, and also to the dihedral angle between the NR_2 and the ring planes (the pyramidalization or tilt angle[6]). The σ substituent constants of various amino groups differ almost exclusively due to the extent of benzene ring–nitrogen atom resonance.[7] Since the pK_a values of aniline derivatives involve contribution of steric inhibition to solvation,[8] basicity does not show properly the resonance between such groups and the aromatic ring. Instead, other data such as intensities of the UV[8,9] and IR bands,[2,10] dipole moments,[11,12] polarographic data[12,13] and exaltations of molar refraction[4,14] are more useful in prediction of the electron donor strength of amino groups. The σ_R° constant of the *p*-dimethylamino group based on the fluorine chemical shift in the spectrum of *N*,*N*-dimethyl-*p*-fluoroaniline, which is sensitive to very small perturbations in the π-charge density at fluorine atom produced by the substituent,[15] is equal to −0.52.[15] That group in *N*,*N*,2,6-tetramethyl-4-fluoroaniline is much twisted out of the ring plane but there is still some resonance interaction between the two parts of the molecule.[16] Both the ^{19}F chemical shift in the NMR spectrum of *N*,*N*,2-trimethyl-4-fluoroaniline[15] and intensity of the UV spectrum of ethyl *N*,*N*,3-trimethyl-4-aminobenzoate[17] show that the *ortho* methyl group produces a 56% steric inhibition of the resonance in the Ar–N fragment and this results in a reduction of the σ_R° constant of this *p*-dimethylamino group to −0.24.[15]

The chemical shift of the *para* carbon predicts well the electron donor strength of the amino groups.[8,18] It shows *N*-phenylaziridine to be the least conjugated of all *N*-phenyl cyclic amines studied.[4,8,19] It seems noteworthy that two *ortho* methyl groups decrease the N–methyl one-bond ^{13}C–^{1}H coupling constant in the spectra of *N*-methyl- and *N*,*N*-dimethyl-aniline by about 0.5 and 1.5 Hz, respectively.[20]

UV spectral data of *p*-aminonitrobenzenes,[9] *p*-aminoazobenzenes,[21] *p*-aminobenzenes[4] and complexes of aminobenzenes with 1,3,5-trinitrobenzene,[14] IR spectral data of aminobenzenes,[2,10] ^{19}F chemical shifts of fluoroanilines,[15] acidities of *p*-aminobenzoic acids,[13,22] rates of reduction of *p*-nitroanilines,[13] polarographic halfwave potentials of *p*-nitroanilines,[13] polarographic oxidation potentials of aminobenzenes[14] and dipole moments of aromatic amines[11,12] all show the following order of electron-donor strength of amino substituents: $(CH_2)_4N > Et_2N > Me_2N > (CH_2)_5N > NHMe > NH_2 > N(CH_2)_2$. Alkane bridges between C_{ortho} and N_{amino}, *e.g.* in julolidine derivatives, cause the nitrogen atom to reveal stronger donor properties than that in the 1-pyrrolidino group.[23]

The published ^{1}H, ^{13}C, ^{15}N and ^{17}O NMR spectra of aromatic oximes[24–30] have been mainly concerned with the configuration and with transmission of substituent effects to the CH=NOH group through the benzene ring. As found,[30] there are poor or very poor correlations between the ^{17}O NMR chemical shifts of the oximino oxygen and σ, σ^+ and σ_1 substituent constants for substituted benzaldoximes.

Electron acceptor properties of the CH=NOH group (σ_R = 0.10)[7] preclude cross-conjugation to be important in *p*-aminobenzaldoximes. Thus, such compounds seem to be a very good model series to study the substituent effect. Since electronic properties of the less common amino groups are not known, the ^{1}H and ^{13}C NMR chemical shifts of *p*-aminobenzaldoximes are used in the present paper to evaluate their resonance substituent effects. The compounds under study have the formulae **1**–**20**.

Experimental

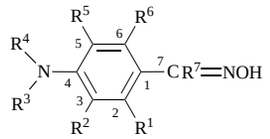
Syntheses

All melting points are uncorrected. The boiling points of all reaction products are expressed in the °C/mmHg units.

Most amines used in formylations are commercially available and known procedures were used to prepare others.[31,32] Lilolidine‡ bp 139–141/10 (lit. bp 90–100/0.5,[33] 112–113/5[34]) was prepared in overall 36% yield by reduction ($LiAlH_4$, standard procedure) of 4-oxolilolidine which, in turn, was obtained by

† For a preliminary report of this work, see ref. 1.

‡ The IUPAC name for lilolidine is 1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline. The name benzo[*h*,*i*]indolizidine has previously been used in the literature for lilolidine.[33,34]



	R^1	R^2	R^3	R^4	R^5	R^6	R^7
1	H	H	H	H	H	H	H
2	H	H	H	Me	H	H	H
3	H	H	Me	Me	H	H	H
4	H	H	Me	Et	H	H	H
5	H	H	Et	Et	H	H	H
6	Me	H	Me	Me	H	H	H
7	Me	H	Me	Me	H	Me	H
8	H	Me	Me	Me	H	H	H
9	H	H	$(CH_2)_4$		H	H	H
10	H	H	$(CH_2)_5$		H	H	H
11	H	H	$(CH_2)_6$		H	H	H
12	H	$(CH_2)_2$		Me	H	H	H
13	H	$(CH_2)_3$		H	H	H	H
14	H	$(CH_2)_3$		Me	H	H	H
15	H	$(CH_2)_4$		Me	H	H	H
16	H	$(CH_2)_2$		$(CH_2)_3$		H	H
17	H	$(CH_2)_3$		$(CH_2)_3$		H	H
18	H	H	H	H	H	H	Me
19	H	H	Me	Me	H	H	Me
20	H	H	$(CH_2)_5$		H	H	Me

cyclization–acylation of 1-(β-chloropropionyl)indoline.[34] To synthesise 1-methylindoline, 1-formylindoline (bp 168–173/15, lit. bp 115–117/2[35]) was first prepared in 94% yield from indoline and formic acid following the procedure used in formylation of *N*-methylaniline.[36] It was then reduced ($LiAlH_4$, standard procedure, 85% yield) to a product of bp 91–94/9 (lit. bps of 1-methylindoline are 68–73/1,[37] 120/12[38]). Kairoline (1-methyl-1,2,3,4-tetrahydroquinoline), bp 102–104/4 (lit. bp 160/12,[38] 80–81/0.4[39]) was obtained in 92% yield by reduction ($LiAlH_4$, standard procedure) of 1-formyl-1,2,3,4-tetrahydroquinoline which, in turn, was prepared in 80% yield by reductive formylation of quinoline with formic acid according to ref. 40. 1-Methyl-2,3-benzohexamethyleneimine (bp 120–125/16, lit. bp 59–60/0.2,[41] 160/12[38]) was obtained in a five-step synthesis (overall yield 34.5%) involving oximation of α-tetralone,[42] tosylation of α-tetralone oxime,[43,44] Beckmann rearrangement of the *O*-tosyl derivative of α-tetralone oxime (for details see synthesis of its *O*-benzenesulfonyl derivative[44]), methylation of homohydrocarbostyril[41,45] and reduction ($LiAlH_4$) of 1-methyl-homohydrocarbostyril.[41,45]

Some aldehydes and ketones were commercial products. *p*-(*N*,*N*-Dimethylamino)acetophenone was a gift from Dr Tomasz Bąk. Other aldehydes were obtained by the Vilsmeier–Haack[46] or Duff[47] methods and were purified by vacuum distillation or crystallization from aqueous ethanol. Detailed synthetic procedures will be given in another paper.[48]

p-Aminobenzaldoxime was obtained in 47% yield by reduction of *p*-nitrobenzaldoxime, according to the procedure used in synthesis of *p*-aminoacetophenone oxime.[49] The product was purified by crystallization from aqueous ethanol. Other aldoximes were obtained from their respective aldehydes by the standard procedure[50] and crystallized from aqueous ethanol. The yields were 26–91% (no attempts were made to improve the reaction efficiency). The synthetic procedure for ketoximes was slightly different. Thus, the mixture of the appropriate acetophenone (0.08 mmol), hydroxylamine hydrochloride (11.1 g, 0.16 mol), 96% aqueous ethanol (60 ml) and conc. hydrochloric acid (few drops) was refluxed for 1.5 h. The reaction mixture was then diluted with water (150 ml) and extracted with diethyl ether. Ketoximes were prepared in 51–69% yield by evaporation of solvent from the extract and recrystallization of the residue from 96% ethanol. Melting points (°C) of oximes: **1**, 126–130 (127–128[51]); **2**, 96.5–96.9; **3**, 147–148 (145–147[52]); **4**, 117–121; **5**, 89–91 (93[53]); **6**, 105–109 (107–109[52]); **7**, 134–135; **8**, 97–98 (97–98[52]); **9**, 190–192; **10**, 161–163; **11**, 110–114; **12**, 97–99; **13**, 147–151; **14**, 87–88; **15**, 107–109; **16**, 104–106.5; **17**, 126–128 (127–128[54]); **18**, 150–152 (153–154[55]); **19**, 218–222; **20**, 163–116.

NMR spectroscopy

NMR spectra of the saturated solutions of oximes in $[^2H_6]$acetone were recorded on a JEOL JNM GSX-270 FT NMR spectrometer working at 270.17 and 67.94 MHz for ^1H and ^{13}C observation, respectively. TMS (internal reference) and $[^2H_6]$acetone (lock) were used both in ^1H and ^{13}C NMR experiments. Other conditions are: ^1H: spectral width 3500 Hz, 32 K data points, digital resolution 0.21 Hz/point, pulse width 9.4 μs, flip angle 90 deg, number of scans 4, pulse delay 1 s, pulse sequence SGNON; ^{13}C: spectral width 15 000 Hz (^1H decoupled)/10 000 Hz (^1H coupled), 32 K data points (^1H decoupled)/64 K data points (^1H coupled), digital resolution 0.92 Hz/point (^1H decoupled) 0.32 Hz/point (^1H coupled), pulse width 7.8 μs, flip angle 90 deg, number of scans 100–400 (^1H decoupled)/*ca.* 9000 (^1H coupled), pulse delay 4 s, pulse sequence/decoupling SGBCM/continuous bilevel SGNON (^1H coupled).

In order to analyse accurately the ^1H NMR spectra, resolution enhancement was performed by combined exponential and trapezoidal windowing (T2 = 5% and T3 = 50%) and zero filling until the digital resolution was <0.05 Hz.

The data matrix for ^{13}C–^1H HETCOR was as follows: 10 000 Hz and 1024 points for the ^{13}C-axis and 1800–2000 Hz and 256 points for the ^1H-axis. An average value of $^1J(C,H) = 125$ Hz was used for the correlation between coupled nuclei.

Assignments of the signals in the aliphatic part of the spectra were possible from their homonuclear ^1H–^1H DFQ–COSY experiment. The signals of aromatic quaternary carbon atoms for compounds **9**, **13**, **15**, **16** and **17** were assigned with the help of the 2D ^{13}C–^{13}C INADEQUATE spectra (solutions in $[^2H_6]$acetone). Data matrix: 10 000 Hz and 1024 points in the f_1-axis and 20 000 Hz and 256 points in the f_2-axis. The number of scans was 256 (8*32). An average value of $^1J(C,C) = 36$ Hz was used for the correlation between coupled nuclei.

The 2D ^{13}C–^{13}C INADEQUATE correlation map of oxime **16** was recorded in saturated $[^2H_6]$DMSO solution at 30 °C with a Bruker Avance DRX500 spectrometer working at 125.76 MHz equipped with a 5 mm broadband direct detection probehead. The spectral width was 23 000 Hz (180 ppm), number of scans 160 and composite pulse decoupling (WALTZ-16) was used to decouple protons during the pulse sequence. The delay transmitting the correlation between coupled neighbouring ^{13}C-nuclei was set to correspond the direct coupling constants of $^1J(^{13}C,^{13}C) = 36$ Hz.

Results and discussion

All oximes studied are the *syn*, *i.e. E* isomers. Although a coplanar arrangement of the ring and the CH=NOH group in compounds carrying two methyls *ortho* to the oxime group may lead to serious steric repulsion, oxime **7** has also been assigned the *E* configuration.[24]

The ^1H and ^{13}C NMR chemical shifts for the oximes **1**–**20** are collected in Tables 1, 2, 4 and 5. As seen, the chemical shift of C7 changes in a narrow range (1.48 ppm) from 148.65 for **6** to 150.13 ppm for **16**. The values of δ_{C7} in the spectra of ketoximes **18**–**20** are >154 ppm. There is no linear relationship between the chemical shift of C7 and σ_R^o substituent constants of the different amino groups for the compounds studied. It is known[27,29,30] that the chemical shift of C7 in the spectra of *p*-substituted benzaldoximes depends mainly on the substituent inductive effect and its resonance is of reduced importance. Moreover, multiparameter correlations of δ_{C7} with inductive and resonance substituent constants[56] and with semiempirical parameters that represent the paramagnetic interaction

Table 1 ^{13}C chemical shifts of aromatic and α-methine carbons in the spectra of oximes **1**–**20** (δ in ppm from TMS, in [$^2H_6$]acetone)

	C1	C2	C3	C4	C5	C6	C7
1	122.57	128.74	114.91	150.73	114.91	128.74	149.61
2	122.05	128.73	112.51	152.06	112.51	128.73	149.62
3	121.86	128.52	112.75	152.24	112.75	128.52	149.42
4	121.43	128.70	112.58	150.81	112.58	128.70	149.46
5	121.01	128.86	112.17	149.35	112.17	128.86	149.50
6	120.10	138.07	114.55	151.91	110.78	128.75	148.65
7	119.55	139.07	113.14	151.21	113.14	139.07	149.16
8	128.02	130.05	132.53	154.92	119.07	126.05	149.20
9	121.10	128.67	112.35	146.45	112.35	128.67	149.63
10	123.98	128.47	116.11	153.59	116.11	128.47	149.23
11	121.01	128.87	111.83	150.59	111.83	128.87	149.46
12	123.29	122.55	131.52	155.42	106.75	128.41	149.80
13	121.05[a]	128.67	121.56[a]	147.62	114.25	126.43	149.68
14	123.22	127.54	121.41	148.46	111.08	127.07	149.62
15	126.09	126.34	135.44	154.64	116.76	128.79	149.31
16	124.10	126.74	129.57	*b*	119.16	120.90	150.13
16[c]	122.84	125.68[d]	128.45	151.01	118.03	119.83[e]	148.88[f]
17	121.00	126.34	121.80	144.70	121.80	126.34	149.61
18	126.61	127.58	114.65	149.97	114.65	127.58	154.32
19	126.01	127.42	122.62	151.89	112.62	127.42	154.07
20	128.05	127.33	115.95	153.14	115.95	127.33	154.01

[a] Signals may be interchanged. [b] Due to limited solubility of this compound in acetone, the quality of its INADEQUATE spectra is poor and this signal is not seen in the spectrum. [c] In [$^2H_6$]DMSO at 125.758 MHz. [d] ^1J(C2,H2) = 155.2 Hz. [e] ^1J(C6,H6) = 158.14 Hz. [f] ^1J(C7,H7) = 160.4 Hz.

Table 2 ^{13}C chemical shifts of the side-chain carbons in the spectra of oximes **1**–**21** (δ in ppm from TMS, in [$^2H_6$]acetone)

	N*C*	NC*C*	NC_2C and NC_3C	C*C*H$_3$
2	29.83	—	—	—
3	40.27	—	—	—
4	46.93[a]	11.44	—	—
	37.41[b]			
5	44.85	12.86	—	—
6	40.20	—	—	20.63
7	40.22	—	—	22.27
8	44.10	—	—	18.68
9	48.12	26.01	—	—
10	50.17	26.31	25.07	—
11	49.81	28.12	27.56	—
12	56.13[a]	28.67	—	—
	35.41[b]			
13	42.17	27.79	22.56	—
14	51.53[a]	22.81	28.39	—
	38.81[b]			
15	57.18[a]	30.12	26.13	—
	43.01[b]		35.52	
16	47.20[c]	23.54[d]	24.54	—
	55.08[e]	28.80[f]		
16[g]	46.02[c]	22.40[d]	23.45	—
	54.13[e]	27.85[f]		
17	50.49	28.40	22.62	—
18	—	—	—	11.31
19	40.38	—	—	11.22
20	50.12	26.26	25.07	11.26

[a] N*C*H$_2$. [b] N*C*H$_3$. [c] NCH$_2$*C*H$_2$CH$_2$. [d] NCH$_2$*C*H$_2$CH$_2$. [e] N*C*H$_2$CH$_2$. [f] NCH$_2$*C*H$_2$. [g] In [$^2H_6$]DMSO at 125.758 MHz.

between the substituent and carbon atom[57] are of better quality.[27]

The chemical shift of C1, *i.e.* the *para* carbon atom with respect to the amino substituent is the most appropriate from the point of view of electron donor strength of the amino substituent. Since sensitivity of 2D ^{13}C–^{13}C INADEQUATE experiment for compounds **9**, **13**, **15**, **16** and **17** was good enough (see Fig. 1), the respective spectra were recorded to distinguish between the signals of different quaternary carbon atoms.

The ^{13}C chemical shifts for both aldoximes **1**–**17** and ketoximes **18**–**20** vary from 119.55 for **7** and 120.10 for **6** to 128.02 for **8** and 128.05 ppm for **20**. Thus, the chemical shift dispersion of δ_{C1}, *i.e.* 8.50 ppm, is wider than that for δ_{C7}. Although, resonance and inductive effects of the *para* substituent on δ_{C1} in the spectra of benzaldoximes are comparable by their magnitudes,[27] only δ_{Cl} values in the spectra of *p*-aminobenzaldoximes studied were found to be linearly dependent on σ_R^o. The correlation obtained is: $\delta_{C1} = 132.44 + 19.34\sigma_R^o$ for compounds **1**–**3**, **5** and **8**–**10** (correlation coefficient = 0.974, standard deviation = 2.45, standard error = 0.93). From its decreased value of σ_R^o it is clear that the dimethylamino group in **8** is considerably twisted out of the ring plane. In order to determine the resonance effect of the less common amino groups, the above equation was used to calculate the respective σ_R^o values. They are given in Table 3.

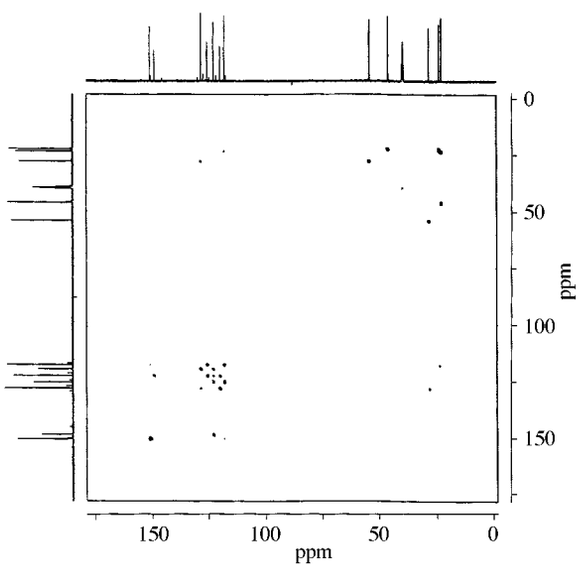


Fig. 1 The 2D ^{13}C–^{13}C INADEQUATE correlation map of oxime **16** in saturated [$^2H_6$]DMSO solution at 30 °C

The chemical shift of C4, *i.e.* the *ipso* carbon atom with respect to the amino substituent, for compounds **1**–**20** changes in a very wide range from 130.88 to 155.42 ppm ($\Delta\delta$ = 24.54 ppm) but no simple dependence between δ_{C4} and the type of substituent was found. It should be mentioned that multiparameter correlation between the chemical shift of C4, *i.e.* the *ipso* carbon, and the substituent constants in the NMR spectra of *p*-substituted benzaldoximes was observed.[27] Although the contribution of the inductive effect is more than seven times that of the resonance effect, the paramagnetic interaction between the substituent and C4 is that which most contributes to δ_{C4}.[57]

Table 3 σ_R^o substituent constants of amino groups

R	σ_R^o
NH_2	−0.48[a]
NHMe	−0.52[a]
NMe_2	−0.53[a]
N(Me)Et	−0.57[b]
NEt_2	−0.57[a]
1-NMe_2; 3-Me	−0.64[b]
1-NMe_2; 3,5-Me_2	−0.67[b]
1-NMe_2; 2-Me	−0.24[a]
$N(CH_2)_4$	−0.63[a]
$N(CH_2)_5$	−0.47[a]
$N(CH_2)_6$	−0.59[b]
1-N(Me)[2-$(CH_2)_2$]	−0.47[b]
1-NH[2-$(CH_2)_3$]	—
1-N(Me)[2-$(CH_2)_3$]	−0.48[b]
1-N(Me)[2-$(CH_2)_4$]	−0.33[b]
1-N[2-$(CH_2)_2$][6-$(CH_2)_3$]	−0.43[b]
1-N{2,6-[$(CH_2)_3]_2$}	−0.59[b]

[a] Literature values.[2,10,15] [b] Calculated from equation $\sigma_R^o = (\delta_{C1} - 132.44)/19.34$.

Table 4 ^{1}H chemical shifts of aromatic, α-methine and oximino protons in the spectra of oximes **1**–**20** (δ in ppm from TMS, in [$^2H_6$]acetone)

	H2	H3	H5	H6	H7	NO*H*
1	7.32	6.66	6.66	7.32	7.96	9.67
2	7.37	6.59	6.59	7.37	7.96	9.63
3	7.44	6.71	6.71	7.44	7.99	9.71
4	7.42	6.69	6.69	7.42	7.99	9.69
5	7.40	6.68	6.68	7.40	7.96	9.62
6	—	6.54	6.56	7.49	8.23	9.73
7	—	6.44	6.44	—	8.34	9.83
8	7.40	—	7.01	7.35	8.02	9.98
9	7.41	6.56	6.56	7.41	7.97	9.63
10	7.44	6.92	6.92	7.44	8.00	9.80
11	7.40	6.71	6.71	7.40	7.96	9.63
12	7.34	—	6.41	7.21	7.98	9.73
13	7.11	—	6.45	7.13	7.90	9.56
14	7.16	—	6.53	7.22	7.93	9.65
15	7.35	—	6.88	7.33	8.03	9.95
16	6.96	—	—	7.16	7.93	9.63
17	6.95	—	—	6.95	7.85	9.55
18	7.42	6.64	6.64	7.42	—	~9.7[a]
19	7.54	6.71	6.71	7.54	—	9.75
20	7.54	6.90	6.90	7.54	—	9.87

[a] Very weak signal.

The chemical shift of H7 and that of the oxime proton, NO*H*, in the spectra of oximes studied changes in a similar narrow range, *i.e.* 0.49 and 0.43 ppm, respectively. Although, δ_{C7} for both *E* and *Z* ring-substituted benzaldoximes correlates well with the σ constants,[29] no linear relationship between the shift of H7 and NO*H*, and σ_R^o values was found for the compounds studied.

The results obtained show that the resonance effect of *p*-amino groups is not transmitted strongly to the CH=NOH group which is in disagreement with the X-ray studies on *p*-dimethylaminobenzaldoxime.[58] Since the inductive substituent constants of amino groups are scarce and those that are available differ only slightly from each other, no correlation between the shift of C7 and σ_1 values can be obtained (such a procedure was used for some other *p*-substituted benzaldoximes[28]).

X-Ray determination[58] shows that the molecule *p*-(*N*,*N*-dimethylamino)benzaldoxime is planar with angles $\angle C_{Me}NC_{Me'}$ and $\angle C_{Me}NC_{Ar}$ equal to 115.5°, and 121.7° (120.7°), respectively. The C_{Ar}–N distance (1.380 Å) indicates this bond to have significant double bond character. The angle $\angle C_{Me}NC_{Me}$ shows the amine nitrogen atom to have sp^2 hybridization. Other bond lengths and valence angles confirm also that there is an electron transfer from the amino nitrogen to oximino oxygen. However, the NMR results presented in Tables 1 and 4 show this is not the case for *p*-(*N*,*N*-dimethylamino)benzaldoxime and the other oximes studied. Moreover, those data indicate that hybridization of the amino nitrogen atom in the compounds studied is more sp^3 than sp^2-like.

Table 5 ^{1}H chemical shifts of the side-chain protons in the spectra of oximes **1**–**20** (δ in ppm from TMS, in [$^2H_6$]acetone)

	N*H*	NC*H*	NC_2H	NC_3H and NC_4H	CCH_3
1	4.90	—	—	—	—
2	5.24	2.83	—	—	—
3	—	2.96	—	—	—
4	—	3.43[a]	1.09	—	—
		2.93[b]			
5	—	3.41	1.15	—	—
6	—	2.95	—	—	2.37
7	—	2.94	—	—	2.35
8	—	2.69	—	—	2.29
9	—	3.28	2.00	—	—
10	—	3.23	1.64[c]	1.64[c]	—
11	—	3.51	1.78	1.53	—
12	—	3.31[a]	2.89	—	—
		2.74[b]			
13	5.30	3.29	1.86	2.71	—
14	—	3.23[a]	1.91	2.69	—
		2.87[b]			
15	—	2.92[a]	1.71	1.58	—
		2.84[b]		2.74	
16	—	2.98[d]	2.04[e]	2.62	—
		3.28[f]	2.87[g]		
17	—	3.18	1.92	2.69	—
18	~4.4[h]	—	—	—	2.14
19	—	2.96	—	—	2.15
20	—	3.20	1.63[d]	1.63[d]	2.16

[a] NCH_2. [b] NCH_3. [c] Centre of the multiplet. [d] $NCH_2CH_2CH_2$. [e] NCH_2-CH_2CH_2. [f] NCH_2CH_2. [g] NCH_2CH_2. [h] Very weak signal.

The conformation of indoline and of its homologs is not known. Absorption bands in the spectra of *N*-alkylindolines have significantly reduced intensity, and are red shifted, as compared to the spectra of *N*,*N*-dialkylanilines.[59] Both differences in hybridization of nitrogen atoms in those compounds and conformational equilibria of the five-membered ring in indoline can account for this behaviour but no definitive explanation of extent of the benzene ring–nitrogen resonance in that compound was given.[59] On the other hand, molecular models show that hybridization of the N atom in indolines can be both of sp^2 and sp^3 type, and the five-membered ring can be both planar and puckered. Moreover, deformation of the benzene ring in anilines carrying short C_{Ar}–N bridges can also occur.

The derived σ_R^o values show piperidino to be the most powerful donor among the studied amino substituents. The propane bridge between the amino N atom and *ortho* position was found to enable the resonance to be more effective than that in the systems that contain shorter and longer bridges. Finally, in disagreement with earlier work,[23] the σ_R^o values show that the amino nitrogen atom in julolidine is a weaker electron donor than that in pyrrolidine. It is noteworthy that the observed order of the substituents resembles, in general, that based on values of E_{HOMO} and positions of the CT bands in the spectra of complexes of aminobenzenes with 1,3,5-trinitrobenzene,[14] UV spectral data of *p*-aminoazobenzenes,[21] dipole moments of aromatic amines,[11,12] polarographic oxidation potentials of aminobenzenes[14] and polarographic halfwave potentials of *p*-nitroanilines.[13] Other spectral studies, now in progress, are expected to show the accuracy of estimation of the σ values obtained.

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