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THE DONOR STRENGTH OF DIALKYLAMINO FUNCTIONS—A SYSTEMATIC STUDY OF δ_H/HMO π-ELECTRON DENSITY CORRELATIONS IN AMINOBENZENES[1,2]

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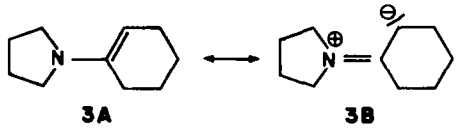
Abstract—From the resonance interaction between different NR_2 substituents and the arylic π-system in mono-, 1,3-bis- and 1,3,5-tris(dialkylamino)benzenes, quantitative parameters are derived for the relative donor strength of the pyrrolidino, dimethylamino, piperidino and morpholino group. Towards an uncharged π-system in the ground state, the donor potential decreases in the series Pyr > $N(CH_3)_2$ > Pip > Mor. The same order, though with somewhat different gradation, is observed for the aminobenzene/trinitrobenzene charge transfer complex absorptions, and for the polarographic oxidation potentials. The detailed analysis of the chemical shift/π-charge density correlations for methoxy and dialkylamino benzenes also reveals that these substituents exert a significant deshielding effect on protons in *ortho*-position. This additional downfield shift is probably due to steric interactions and strongly increases from the pyrrolidino to the piperidino group.

INTRODUCTION

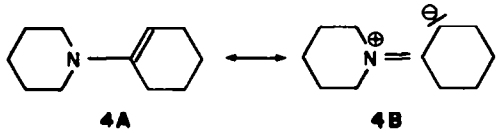
Dependence of enamine reactivity upon the nature of the nitrogen substituents is a well established fact.[4] Thus, 1 - *N* - pyrrolidino - cyclohexene reacts much more readily with electrophiles than 1 - *N* - piperidino - cyclohexene.[5] In view of the practically identical substrate structure, the difference in reactivity must arise from unlike stabilization of the positively charged transition state by the nitrogen lone pair. Since for electrophilic attack the transition state can be approximated by the cationic reaction intermediate (1, 2), this means that the weight of the immonium structure **B** is greater for the pyrrolidino **1** than for the piperidino compound **2**.

In enamine chemistry, this experimental behaviour has usually been rationalized in terms of H. C. Brown's generalization:[6] "Reactions which involve formation or retention of an *exo* double bond in a 5-ring derivative will be favoured over corresponding reactions which involve the formation or retention of an *exo* double bond in a 6-ring derivative." When, however, the relative stability of a number of isomer pairs with exo- and endocyclic double bonds, respectively, were determined by the hydrogenation method,[7] the endocyclic modification was found to be more stable in each case, even for five-membered rings. EHT calculations[8] are in agreement with the hydrogenation data but attempts at correlating reactivity with thermodynamical stabilities failed. In view of these discrepancies, the practicability of Brown's generalization for the heterocyclic moieties pyrrolidine and piperidine seems rather doubtful. The widespread application of enamines in preparative organic chemistry, on the other hand, makes it highly desirable to have some measure for the resonance interaction between NR_2 groups and double bonds—and thus for the reactivity of enamines.

The stronger donor potential for pyrrolidino vs piperidino nitrogen, noted above for transition state and cationic intermediate, must to some extent be reflected already in the ground state; so, greater weight of the dipolar structure **B** and thence higher C_β charge density is expected for pyrrolidino enamines (3 vs 4).

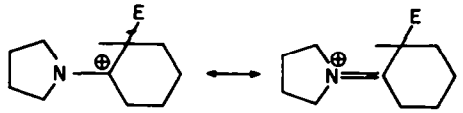


3A 3B

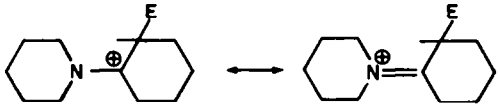


4A 4B

Gurowitz and Joseph[9] have indeed successfully used the β-proton chemical shift, as indicator of C_β electron density, to rationalize the isomer distribution of β-alkylated cyclohexenyl enamines in terms of varying NR_2 donor strength. For some electrophilic enamine reactions, reactivity could likewise be correlated with δ_{H_β}.[10–12] Especially with enamines of cyclic ketones, it is extremely difficult, though, to correctly assess and allow for steric and conformational effects on the chemical shift.[9,13–16] Symmetrical 1, 3, 5 - tris (dialkylamino) ben-



1A 1B



2A 2B

zenes,[17] on the other hand, which we have repeatedly used as model compounds for enamine reactions,[17,18] have a fixed (planar) geometry, and should thus be ideally suited for a quantification of the donor potential for the different NR_2 groups via the respective aryl proton shifts.

HMO π-ELECTRON DENSITY-CHEMICAL SHIFT CORRELATIONS

The direct proportionality relationship (1) between π-electron density and the chemical shift of aromatic and olefinic protons has found widespread application for analyzing, both qualitatively and quantitatively, the changes in electronic structure upon introduction of a substituent.[19-27]

$$\delta_{H_i} = q \cdot \rho_{C_i} \qquad (1)$$

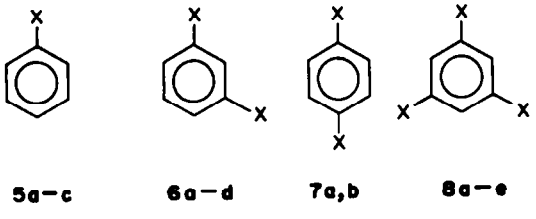
The underlying assumption, i.e. that within a given class of compounds, the chemical shift of a specific proton is determined primarily by the π charge density at the respective carbon, has for aromatic molecules been established to hold to at least first approximation.[19,24,27,28] Thus, Zweig *et al.* report good linear correlation between aryl proton shifts and HMO π-electron densities for the unsubstituted positions in a number of sterically unhindered dimethylamino and methoxy benzenes.[22,23]

The authors' assumption that there is no sterical interaction between two *ortho*-standing methoxyl groups,[22,29] is not tenable, though: veratrole, for instance, gives only one narrow singlet in the ^1H NMR for the two sets of aryl protons. The following correlations are therefore limited to those four benzene derivatives for each substituent which bear no mutually *ortho*-standing groups (**5–8**). Because of some (minor) discrepancies between Zweig's and our measurements,[3a] moreover, a new, internally consistent set of shift data will be used (see Experimental).

Within such a series of *meta*-substituted benzenes, the intramolecular ring current can be assumed as constant; intermolecular ring current and other medium effects may be minimized by using equimolar solutions in a common isotropic solvent. Of the other factors upon which the position of a nuclear magnetic resonance signal depends, anisotropic electrical and magnetic field gradients due to the substituent itself have been considered as negligible in the case of the methoxy and dimethylamino groups. Spiesecke and Schneider, in their fundamental paper,[30] had reported no significant anisotropic contribution to the ^1H shifts of trimethylamine and dimethylether; thence, Zweig *et al.* inferred that in substituted benzenes protons *ortho* to a $N(CH_3)_2$ or OCH_3 function likewise experience no additional anisotropic shift.[22]

In a detailed study of ^1H and ^{13}C shifts of simple aliphatic enamines,[16,31] this complete neglect of substituent anisotropy has since been demonstrated as unjustified. Within the aminobenzene series, this is exemplified, for instance, by the identical aryl proton shift, and consequently identical NR_2 donor strength, for the tripiperidino and trimorpholino compounds (**8d, e**) which is incompatible with the gradation known from enamine reactivity.[10] The assumptions upon which straightforward correlations of δ_H-values with π-electron densities have hitherto been based, evidently represent only a rough approximation of the actual chemical shift behaviour, and thus hold only for comparisons between groups of widely different mesomeric potential, such as between OR and NR_2.[22,23] In the evaluation of smaller chemical shift differences, the anisotropy factor may no longer be neglected since it has about the same magnitude as the differential shifts $\Delta\delta_{NR_2}$ between the individual dialkylamino groups and, even more crucially, differs for each NR_2 function.

In view of the approximations inherent in assessing the NR_2 substituent anisotropy (see below), the basic HMO formalism was used as an unsophisticated model for the π-electron density calculations. With respect to the choice of the parameters h and k which are needed to characterize heteroatoms in the Hückel formalism, though, there is no consensus in the literature; rather, values have been adapted in each case—more or less arbitrarily—to guarantee optimum linearity for the respective correlation. Heilbronner and Bock have justly raised strong objections to this practice.[32] In compliance with their recommendation, we have based our correlation for the methoxy-benzenes on the parameters $h_O = 2.00$ and $k_{C-O} = 0.80$ as originally proposed by Streitwieser;[33] for the dimethylamino nitrogen, Streit-



	X	
a	OCH_3	
b	$N(CH_3)_2$	
c		*(Pyr)*
d		*(Pip)*
e		*(Mor)*

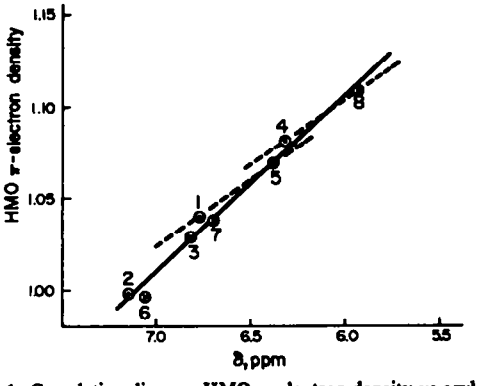


Fig. 1. Correlation diagram HMO π-electron density vs aryl proton chemical shift for the methoxy benzenes **5a–8a**: experimental δ-values (for the numbering of the correlation points, see Table 1).

weiser's values ($h_N = 1.50, k_{C-N} = 0.80$) were likewise used at the outset.

Methoxy benzenes. The HMO π-charge density/δ_H correlation plot for the methoxy benzenes **5a–8a** displays considerable deviations from linearity in a close-up view (Fig. 1). These divergencies are in fact systematic: the two straight lines connecting points ①/⑤ and ④/⑧ (Table 1, representing aryl positions with one and two *ortho*-OCH_3 groups, respectively) have identical slope, with a parallel displacement of about 0.1 ppm. These aryl proton shifts evidently are determined, *apart* from π-electron density, by an additional *ortho*-effect, i.e. the methoxyl group does indeed not behave magnetically isotropic.

Consequently, an *ortho* increment $\Delta\delta_o$ is derived via linear regression analysis for the five aryl positions in anisole, resorcinol di- and phloroglucinol trimethylether (①, ③ – ⑤ and ⑧ in Table 1/Fig. 1). The −0.108 ppm per *o*-OCH_3 by which the experimental δ_H-values have to be corrected for best fit indicate that aryl protons experience additional deshielding from *ortho* methoxyl functions (caused either by anisotropic field gradients or steric effects of the substituent). The correlation for the corrected shift values is exceedingly good ($r = 0.9999_9$, Table 1; Fig. 2). Due to an intrinsic deficiency of the HMO formalism, however, points which represent aryl positions *meta* to a OCH_3 substituent (②, ⑦ in Fig. 2) still lie far outside the linear correlation.[a]

Inclusion of these *meta*-positions and the anisotropic downfield shift, causally connected with increasing π-charge density at the high field end of the shift range, thus combine to force a steeper slope for the simple correlation. Our final equation (2) therefore has a significantly less steep slope than the relationship, obtained for the uncorrected *o/p*-data, and than that reported by Zweig *et al.*[22]

$$[\text{HMO } \pi\text{-electron density}] = -7.26 \times 10^{-2}[\delta] + 1.5238. \quad (2)$$

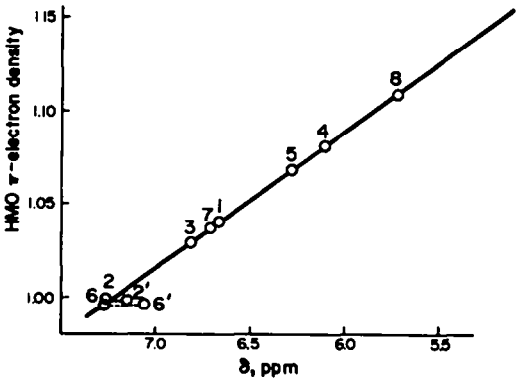


Fig. 2. Correlation diagram HMO π-electron density vs aryl proton chemical shift for the methoxy benzenes **5a–8a**: experimental δ-values corrected by $\Delta\delta_o = -0.108$ ppm (correlation line for *o/p*-positions ①, ③–⑤ and ⑧ only—for the numbering, see Table 1).

[a] These points (②, ⑦ in Fig. 2) can be forced onto the HMO correlation line for the *o/p*-positions only by an additional corrective term, $\Delta\delta_m$, of $+0.108_5$ ppm per *m*-OCH_3 function. After appropriate correction of the experimental δ-value, the point for hydroquinone dimethylether (⑦ in Fig. 2) also falls directly onto the correlation line—a nice confirmation for the validity of the corrective terms $\Delta\delta_o$ and $\Delta\delta_m$.

Dimethylamino benzenes. In adapting the HMO parameters for the $N(CH_3)_2$ group to the methoxy benzene correlation (2), h- and k-values may no longer both be chosen freely (contrary to the general practice in the literature). To accede as far as possible to the recommendation of Heilbronner and Bock,[32] we have retained the h_N-value of 1.50[33] for the $N(CH_3)_2$ nitrogen. In conjunction with Streitwieser's value of 0.80 for k_{C-N},[33] this gives a significantly smaller slope of the correlation line for those five positions in the sterically unhindered dimethylamino benzenes **5b–8b** which are either *ortho* and/or *para* to a $N(CH_3)_2$ substituent. With $k = 0.84$, on the other hand, both slope and intercept (Table 2) are identical with the values for the—uncorrected—methoxy correlation (Table 1). The individual points for the $N(CH_3)_2$ derivatives again show considerable scattering, the deviations—significantly—corresponding in both direction and relative magnitude to those found for the methoxy benzenes (as shown in Fig. 1). For the five *o/p*-positions in *N,N*-dimethylaniline and 1,3-bis- and 1,3,5 - tris (dimethylamino) - benzene (①, ③ – ⑤, and ⑧ in Table 2), therefore, that *ortho*-increment is determined for $0.80 \leqslant k_{C-N} \leqslant 0.90$, respectively, which gives the same slope for the dimethylamino correlation plot as in eqn (2). The correlation passes through an optimum for $k_{C-N} = 0.84$ (Fig. 3), with a corresponding anisotropy correction of −0.150 ppm which is significantly larger than for OCH_3.

As described, the HMO parameters for the OCH_3 and $N(CH_3)_2$ substituents have been adapted to best fit with ^1H shifts. Since no additional assumptions have been introduced and the internal consistency within the correlation has been strictly preserved, however, it should be possible now to also evaluate the finer nuances in mesomeric interaction between the different cyclic NR_2 moieties via a δ_H/HMO charge density correlation.

Pyrrolidino, piperidino, and morpholino benzenes. The difference in overlap between a sp_2-carbon p_π orbital and the nitrogen lone pair of the various NR_2 groups could in principle be due to varying hybridization or different electronegativity of the N atom. Since our $^1H/^{13}C$ investigations of enamines have clearly demonstrated that, within the series of dialkylamino functions,

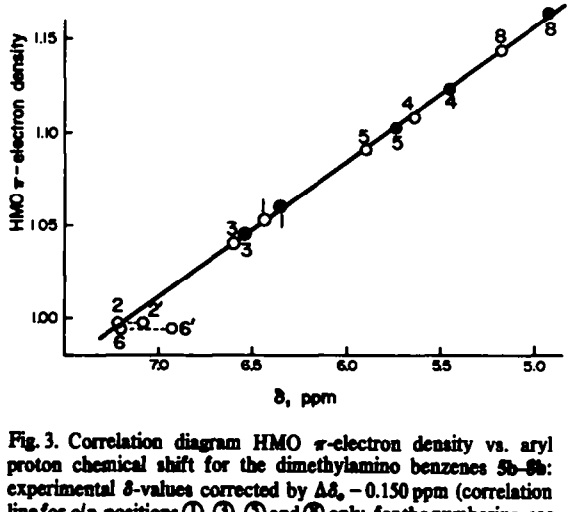


Fig. 3. Correlation diagram HMO π-electron density vs. aryl proton chemical shift for the dimethylamino benzenes **5b–8b**: experimental δ-values corrected by $\Delta\delta_o = -0.150$ ppm (correlation line for *o/p*-positions ①, ③–⑤ and ⑧ only–for the numbering, see Table 2); also entered are the correlation points for the *o/p*-positions in the pyrrolidino benzenes **5c–8c** (●, numbering analogous to dimethylamino benzenes).

Table 1. Methoxy benzenes **5a–8a**: HMO π-electron densities (calculated with $h_O = 2.00$, $k_{C-O} = 0.80$) and chemical shift values (in δ_{TMS} [ppm]) for the aryl protons (experimental data and values corrected by $\Delta\delta_o$ and/or $\Delta\delta_m$—see text)

-benzene		aryl-H position	correlation point no.	HMO π-electron density	experimental value	only aryl-H o and/or p to OCH_3	with optimized ortho-correct. $\Delta\delta_o$ = 0.108 ppm	with optimized meta-correct. $\Delta\delta_m$ + 0.104 ppm	with ortho- and meta-correction
1-methoxy	**5a**	2,6	1	1.0400	6.772	6.772	6.664		6.664
		3,5	2	0.9980	7.149			7.253	7.253
		4	3	1.0292	6.817	6.817	6.817		6.817
1,3-dimethoxy	**6a**	2	4	1.0812	6.317	6.317	6.101		6.101
		4,6	5	1.0684	6.382	6.382	6.274		6.274
		5	6	0.9958	7.060			7.268	7.268
1,4-dimethoxy	**7a**	2,3,5,6	7	1.0376	6.697		[6.589] [a]	6.693	6.693
1,3,5-trimethoxy	**8a**	2,4,6	8	1.1087	5.935	5.935	5.719		5.719
$[HMO\text{-}\pi] = a[\delta] + b$:			a		$-(9.6\pm0.5)10^{-2}$	$-(8.8\pm0.6)10^{-2}$	$-(7.26\pm0.02)10^{-2}$ [c]		$-(7.26\pm0.03)10^{-2}$
			b		1.683_5	1.630	1.5238		1.5238
			r [b]		-0.99_1	-0.99_4	-0.9999_9		-0.9999_6

[a] Not included in regression analysis. [b] Regression coefficient. [c] Final correlation/calibration line.

Table 2. Dimethylamino benzenes **5b**–**8b**: HMO π-electron densities (calculated with $h_N = 1.50$, $k_{C-N} = 0.84$) and chemical shift values (in δ_{TMS} [ppm]) for the aryl protons (experimental data and values corrected by $\Delta\delta_o$ and/or $\Delta\delta_m$—see text)

-benzene		aryl-H position	correlation point no.	HMO π-electron density	experimental value	only aryl-H *o* and/or *p* to $N(CH_3)_2$	with optimized *ortho*-correct. $\Delta\delta_o$ – 0.150 ppm	with optimized *meta*-correct. $\Delta\delta_m$ + 0.134 ppm	with ortho- and *meta*-correction
1-dimethylamino	**5b**	2,6	1	1.0530	6.590	6.590	6.440		6.440
		3,5	2	0.9975	7.085			7.219	7.219
		4	3	1.0402	6.598	6.598	6.598		6.598
1,3-bis(dimethylamino)	**6b**	2	4	1.1084	5.940	5.940	5.640		5.640
		4,6	5	1.0911	6.044	6.044	5.894		5.894
		5	6	0.9949	6.927			7.195	7.195
1,4-bis(dimethylamino)	**7b**	2,3,5,6	7	1.0496	6.58_5 [d]		[6.43] [a]	6.568	[6.57] [a]
1,3,5-tris(dimethylamino)	**8b**	2,4,6	8	1.1446	5.478	5.478	5.178		5.178
$[HMO\text{-}\pi] = a[\delta] + b$:			a		$-(9.6\pm0.6)10^{-2}$	$-(8.8\pm0.6)10^{-2}$	$-(7.25\pm0.1)10^{-2}$ [c]		$-(7.26\pm0.1)10^{-2}$
			b		1.673	1.630	1.5191		1.5192
			r [b]		-0.98_8	-0.99_3	-0.9996_4		-0.9996_2

[a] Not included in regression analysis. [b] Regression coefficient. [c] Final correlation/calibration line. [d] Due to rapid oxidation in CCl_4, no reliable $\delta_{N\text{-}ar}$-value could be obtained.

the electronegativity of the heteroatom does not vary significantly,[16] the $N(CH_3)_2$ h-value of 1.50 for the coulomb integral perturbation parameter was retained also for the cyclic dialkylamino functions.

In the pyrrolidino benzenes—this becomes evident from the aryl proton spectra already by inspection—the *ortho*-protons experience only a small additional deshielding effect. Nevertheless, the same optimization procedure as for the $N(CH_3)_2$ derivatives is applied to the data pairs representing the five *o/p*-positions in **5c**, **6c** and **8c**. The regression analysis yields k = 0.90 for the Pyr substituent, together with a small *ortho*-increment of −0.056 ppm/*o*-Pyr group. When, after appropriate correction, the five correlation points for the *o/p*-positions in mono-, 1,3-di- and 1,3,5-tripyrrolidinobenzene are entered into the correlation plot for the dimethylamino compounds (●, Fig. 3), the mutual compatibility of the two data sets, and thence of the respective overlap integrals (k-values), is immediately apparent.

By the same procedure, a k-value of 0.79 can be derived for the piperidino substituent. As indicated already by the enamine data,[16,30] the fit for this NR_2 group requires a very large corrective term, $\Delta\delta_o$ −0.243 ppm. Since, furthermore, the numerical evaluation of the ^1H spectra of piperidinobenzene **5d** and 1,3-di-piperidinobenzene **6d** is none too good,[3a] k_{Pip} is *a priori* not as reliable in its relative magnitude as the values for $N(CH_3)_2$ and Pyr.

The difference in NR_2 donor strength becomes especially manifest in the barriers of rotation around the C^2–NO partial double bond in the 1,3,5-tris(dialkylamino)-2-nitrosobenzenes **9**.[34] We shall use these quantities, therefore, to derive k-values also for the piperidino and morpholino substituents.

The energy of activation for this rotational process is facilely simulated in the HMO formalism. In conjunction with the experimental $\Delta G_C^{\ddagger}$-values determined by dynamic ^1H NMR spectroscopy[35] (Table 3), the HMO-ΔE_π-values for tris(dimethylamino)- and tripyrrolidino-nitrosobenzene (**9b**, **c**) set up a new correlation line ($\Delta G_C^{\ddagger}/\Delta E_\pi$-plot, Fig. 4). With this relationship, $\Delta G_C^{\ddagger}$ for the piperidino and morpholino compound (**9d**, **e**)[b] can be correlated with the respective ΔE_π-values (Fig. 4/Table 3) which in turn determine a specific overlap integral for each of the two NR_2 functions. The k-values thus obtained are 0.775 for the piperidino and 0.74 for the morpholino group. For a cross-check, ΔE_π (HMO) activation barriers are calculated for three further triaminonitrosobenzenes with different NR_2 functions (**9f–h**, Table 3) and compared with the experimental $\Delta G_C^{\ddagger}$-values;[35] the points fit perfectly onto the correlation line in Fig. 4.

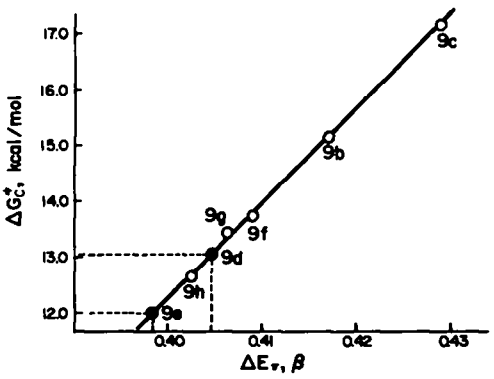


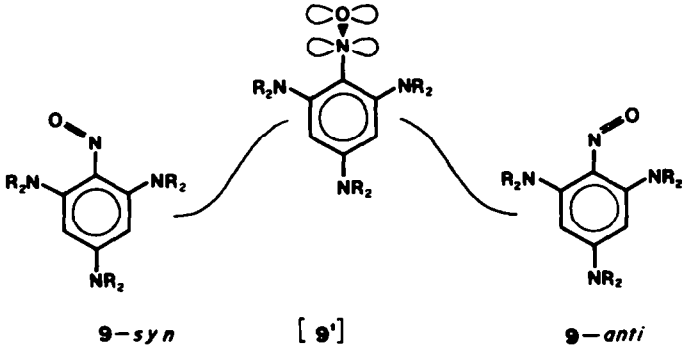
Fig. 4. Barriers of rotation around the C^2–NO partial double bond in 1,3,5-tris(dialkylamino)-2-nitrosobenzenes **9**: correlation diagram for $\Delta G_C^{\ddagger}$-values (determined by temperature-dependent ^1H NMR) vs activation barriers simulated by HMO calculations (see text, Table 4).

CONCLUSIONS

Even though in a rather roundabout manner, we have thus successfully derived quantitative parameters for the mesomeric potential of the different NR_2 substituents.

	Pyrrolidino	$N(CH_3)_2$	Piperidino	Morpholino
k	0.90	0.84	0.775	0.74

Since they are calibrated against ^1H chemical shift data, i.e. against a ground state property, these parameters of course mirror only the relative donor strength of the NR_2 substituents towards an acceptor π-system in its (uncharged) ground state. They take no account of the "sleeping" potential of each dialkylamino group for stabilization of a partial or full positive charge which would be necessary, though, to allow exact predictions on the influence of the individual NR_2 moieties upon enamine reactivity.

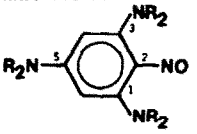


9–*syn* [**9'**] **9**–*anti*

[b] The $\Delta G_C^{\ddagger}$-values are used because they are derived from exactly determinable experimental data;[36] a correlation based on $\Delta H_C^{\ddagger}$, calculated from $\Delta G_C^{\ddagger}$ with the $\Delta S^{\ddagger}$-value for the C^1–NO rotation in 4-dimethylaminonitrosobenzene,[37] yields identical results.

Better than by ground state π-electron densities, the charged transition state of an electrophilic attack is approximated by the charge transfer complex with a strong electron acceptor or by the radical cation formed upon one-electron oxidation of an aminobenzene. In Table 4, the (HMO) π-energy of the highest occupied molecular

Table 3. Activation barriers for rotation around the C^2–NO partial double bond in the 1, 3, 5 - tris(dialkylamino) - 2 - nitrosobenzenes **9b–h**



	NR_2^1	NR_2^3	NR_2^5	$\Delta G_c^{\ddagger}$ [a] [kcal/mol]	$\Delta E_{\pi\text{-HMO}}$ [b] [β]
9c	*Pyr*	*Pyr*	*Pyr*	17.2	0.4289
9b	$N(CH_3)_2$	$N(CH_3)_2$	$N(CH_3)_2$	15.1_5	0.4169
9d	*Pip*	*Pip*	*Pip*	13.0_5	0.4047
9e	*Mor*	*Mor*	*Mor*	12.0	0.3983
9f	$N(CH_3)_2$	*Pip*	*Pip*	13.7_5	0.4090
9g	*Mor*	*Pip*	$N(CH_3)_2$	13.4	0.4062
9h	*Mor*	*Pip*	*Pip*	12.6_5	0.4024

[a] Determined by temperature-dependent ^1H NMR in $CDCl_3$.[37]

[b] Calculated as detailed in the text; for the nitroso function, the following heteroatom parameters were used: h_N 0.50, h_O 1.00, $k_{N=O}$ 1.00, k_{C^2-N} 0.80 and 0.00, respectively.[34]

Table 4. Mono-, 1, 3-bis- and 1, 3, 5-tris(dialkylamino)benzenes: energies of highest occupied molecular orbital [β], trinitrobenzene CT complex band energies (only longest wavelength CT band), and polarographic halfwave oxidation potentials

-benzene		ε_{HOMO} [β] [a]	ν_{CT} [cm^{-1}] [b] (TNB complex)	$E_{1/2}^{ox}$ [V] [c] (*vs.* $Ag/Ag^{\oplus}$)
1-pyrrolidino	**5c**	- 0.7012	19500	
1-dimethylamino	**5b**	- 0.7266	20700	0.45
1-piperidino	**5d**	- 0.7545	21500	
1-morpholino	**5e**	- 0.7696	23600	
1,3-dipyrrolidino	**6c**	- 0.6357	18100	0.11
		- 0.7937 [d]		
1,3-bis(dimethylamino)	**6b**	- 0.6635	20000	
		- 0.8148 [d]		
1,3-dipiperidino	**6d**	- 0.6944	21000	0.25
		- 0.8376 [d]		
1,3,5-tripyrrolidino	**8c**	- 0.6357 [e]	16000	0.01
1,3,5-tris(dimethylamino)	**8b**	- 0.6635 [e]	17500	0.13
1,3,5-tripiperidino	**8d**	- 0.6944 [e]	18900	0.18
1,3,5-trimorpholino	**8e**	- 0.7114 [e]	20600	0.35

[a] For the heteroatom parameters, the *h*- and *k*-values were used as described in the text. [b] In CH_2Cl_2 (UVASOL *Merck*), determined from equimolar solutions of amino- and trinitrobenzene at several different concentrations (range $1 - 5 \times 10^{-2}$ m), rounded to the nearest 100 cm^{-1}. [c] Measured at a rotating platinum electrode in CH_3CN against $Ag/Ag^{\oplus}$ (10^{-2} m in CH_3CN) as reference, supporting electrolyte 10^{-1} m $LiClO_4$. [d] Second highest occupied molecular orbital. [e] Doubly degenerate HOMO's.

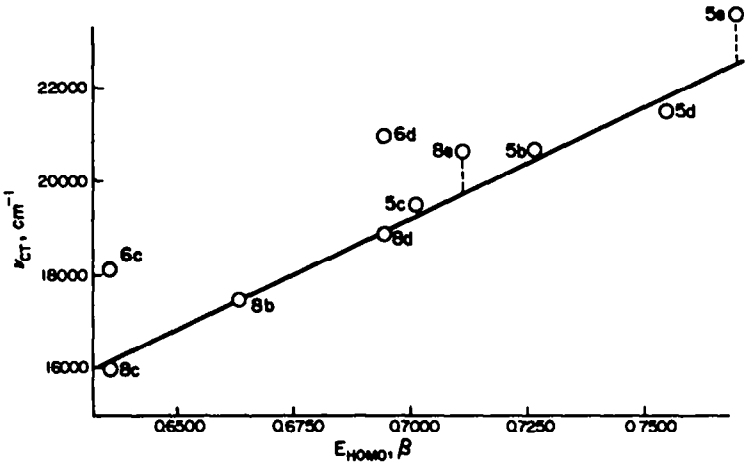


Fig. 5. Correlation diagram CT band energy of dialkylaminobenzene/trinitrobenzene charge transfer complexes (in CH_2Cl_2, only longest wavelength CT absorption included) vs energy of highest occupied molecular orbital (in β).

orbital as model parameter is contrasted with the charge transfer band energy of CT complexes between trinitrobenzene (see Experimental) and all the aminobenzenes;[38] some polarographic halfwave oxidation potentials (determined in CH_3CN vs $Ag/Ag^{\oplus}$[39]) are likewise included.

When the trinitrobenzene ν_{CT}-values (Table 4) for mono- and 1,3,5-trisubstituted benzene derivatives[c] of Pyr, $N(CH_3)_2$ and Pip are plotted against the HMO π-energy of the highest occupied MO of the aminobenzene, a good linear correlation is obtained (Fig. 5). The divergencies in each case are within the experimental error limit of ± 5 nm for the CT maximum; the two morpholino derivatives, **5e** and **8e**, on the other hand, lie definitely outside the correlation. This could be due either to a slightly different CT complex configuration (perhaps an effect of the γ-oxygen atoms), or to the k-value for the morpholino group being too large (a good fit would require $k_{Mor} \simeq 0.70$).

For the triaminobenzene $E^{ox}_{1/2}$-values (Table 4), the trend $Pyr > N(CH_3)_2 > Pip > Mor$ is likewise observed, but again one point (this time for the piperidino compound) falls definitely outside the linear correlation. Also, the oxidation potential of the diamino derivatives **6** in each case is higher than that of the corresponding triaminobenzenes **8**—contrary to the predictions from HOMO energies (see Table 4). Clearly, for such finer differentiations, both the simple, straightforward correlation technique and the HMO formalism are strained too much.

If one keeps this reservation in mind, though, the k-parameters derived above nevertheless represent a useful tool also for energy and reactivity correlations.

EXPERIMENTAL

All compounds (available commercially or prepared according to the literature[17,40]) were redistilled or recrystallized, respectively, from light petrol ether before the NMR measurements.

The NMR spectra were taken of 0.5 molar CCl_4 solutions at 30°C; the chemical shifts are given in δ [ppm] relative to TMS as internal standard. The spectra were run either on a Varian A60 in CW sweep mode or on a Bruker HX90E in Pulse-Fourier-Transform technique (with $(CD_3)_2CO$ as ^{2}D-lock in the inner tube of a coaxial cell unit); 16k interferograms were utilized with a spectral width of 892.8571 Hz (corresponding to 0.1090 Hz ≙ 0.001 ppm per address). In the case of those compounds which give only singlet aryl proton signals, the listed chemical shifts are the average of three sweeps in each direction or of five separate FT spectra, respectively. For the complex ^{1}H spectra of anisole and *N,N*-dimethylaniline, an exact computational analysis by Castellano *et al.*[41] is available; the spectra of the corresponding two *meta*-disubstituted derivatives, resorcinol dimethylether **6a** and *N,N,N',N'*-tetramethyl-*m*-phenylenediamine **6b**, were re-measured and numerically evaluated by ourselves.[3a] For the numerical analysis and the HMO calculations, standard programs were used.

The charge transfer complex spectra were measured on a Beckman ACTA M VI UV/VIS spectrophotometer in tandem cell cuvettes (HELLMA, Mülheim/Baden) with an overall pathlength of 0.877 cm.[38] Of the CT acceptors commonly used, chloranil and even more so tetracyanoethylene undergo rapid chemical reaction with aminobenzenes; in the case of TCNE and tripyrrolidinobenzene, for instance, the CT complex is extremely transient, the σ-complex intermediate of aromatic electrophilic substitution being formed almost immediately.[3a] Even if the CT bands can be observed by rapidly scanning after mixing the components, a correct evaluation of λ_{max} is not possible. Trinitrobenzene, on the other hand, gives well-defined, perfectly reproducible CT bands for mono-, bis- and tris(dialkylamino)benzenes.

For details of the triamino-nitrosobenzene rotation barrier determinations and the polarographic oxidation potential measurements, see the respective references.[35,39]

REFERENCES

[1]XIV. Communication on *Aminobenzenes* XIII. Communication: F. Effenberger and P. Menzel, *Chem. Ber.* **110**, 1342 (1977).

[2]At the same time, IV. Communication on *Conformation and Reactivity of Electron-rich π-Systems* III. Communication: P. Fischer, K. E. Mack, E. Mössner and F. Effenberger, *Chem. Ber.* **110**, 181 (1977).

[3]In part taken from the Ph.D. Thesis of [a]P. Fischer, Universität Stuttgart (1970), [b]W. W. Schoeller, Universität Stuttgart (1969), [c]W. D. Stohrer, Universität Stuttgart (1969).

[4]E. J. Stamhuis in *Enamines: Their Synthesis, Structure and Reactions* (Edited by A. G. Cook), pp. 101–113. Marcel Dekker, New York (1969); M. E. Kuehne, *Ibid.* pp. 342 ff.

[5]G. Stork, A. Brizzolara, H. K. Landesman, J. Szmuszkovicz and R. Terrell, *J. Am. Chem. Soc.* **85**, 207 (1963).

[c]For the diamino compounds, which have two close-lying HOMO's (see Table 4), the corresponding two CT absorptions are not resolved. Superposition of both bands in the actual spectrum produces an extremely broad absorption, with an apparent λ_{max} intermediate between the true values for the first and second CT maximum; these ν_{CT}-data are therefore excluded from the correlation.

[6]H. C. Brown, J. H. Brewster and H. Shechter, *J. Am. Chem. Soc.* **76**, 467 (1954); H. C. Brown, *J. Org. Chem.* **22**, 439 (1957).
[7]R. B. Turner and R. H. Garner, *J. Am. Chem. Soc.* **80**, 1424 (1958).
[8]M. Scholz and H. J. Köhler, *Tetrahedron* **25**, 1863 (1969).
[9]W. D. Gurowitz and M. A. Joseph, *J. Org. Chem.* **32**, 3289 (1967).
[10]M. E. Kuehne and T. Garbacik, *J. Org. Chem.* **35**, 1555 (1970).
[11]K. Nagarajan and S. Rajappa, *Tetrahedron Letters* 2293 (1969).
[12]E. J. Cone, R. H. Garner and A. W. Hayes, *J. Org. Chem.* **37**, 4436 (1972).
[13]F. P. Colonna, G. Pitacca and E. Valentin, *Tetrahedron* **27**, 5481 (1971).
[14]H. W. Dürbeck and L. L. Duttka, *Tetrahedron* **29**, 4285 (1973).
[15]D. Tourwé, G. van Binst, S. A. G. de Graaf and U. K. Pandit, *Org. Magn. Res.* **7**, 443 (1975).
[16]D. Müller, Ph.D. Thesis, Universität Stuttgart (1977).
[17]F. Effenberger and R. Niess, *Chem. Ber.* **101**, 3787 (1968).
[18a]F. Effenberger, K. Nagel and W. Agster, *Angew. Chem.* **81**, 619 (1971); [b]P. Fischer, K. E. Mack, E. Mössner and F. Effenberger, *Chem. Ber.* **110**, 181 (1977); [c]P. Menzel, W. Seufert and F. Effenberger, *Chem. Ber.* to be published.
[19]G. Fraenkel, R. E. Carter, A. McLachlan and J. H. Richards, *J. Am. Chem. Soc.* **82**, 5846 (1960).
[20]H. Spiesecke and W. G. Schneider, *J. Chem. Phys.* **35**, 731 (1961).
[21]C. MacLean and E. L. Mackor, *Mol. Phys.* **4**, 241 (1961).
[22]A. Zweig, J. E. Lehnsen, J. E. Lancaster and M. T. Neglia, *J. Am. Chem. Soc.* **85**, 3940 (1963).
[23]A. Zweig, J. E. Lancaster, M. T. Neglia and W. H. Jura, *J. Am. Chem. Soc.* **86**, 4130 (1964).
[24]T. K. Wu and B. P. Dailey, *J. Chem. Phys.* **41**, 2796 (1964).
[25]F. W. Wehrli, E. Pretsch and W. Simon, *Helv. Chim. Acta* **50**, 2189 (1967).
[26]B. M. Lynch, *Tetrahedron Letters* 1357 (1969).
[27]For recent reviews on the subject see: [a]D. G. Farnum, *Adv. Phys. Org. Chem.* **11**, 123 (1975); [b]W. G. Hehre, R. W. Taft and R. D. Topsom, *Progr. Phys. Org. Chem.* **12**, 169 ff. (1976).
[28]N. Jun, *Bull. Chem. Soc. Japan* 1637 (1975).
[29]A. Zweig, J. E. Lehnsen and M. A. Murray, *J. Am. Chem. Soc.* **85**, 3933 (1963).
[30]H. Spiesecke and W. G. Schneider, *J. Chem. Phys.* **35**, 722 (1961).
[31]P. Fischer and D. Müller, *Angew. Chem.* to be published.
[32]E. Heilbronner and H. Bock, *Das HMO-Modell und seine Anwendung*, p. 156, Verlag Chemie, Weinheim (1968).
[33]A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists*, p. 135. Wiley, New York (1961).
[34]F. Effenberger, W. Kurtz and P. Fischer, *Chem. Ber.* **107**, 1285 (1974).
[35]P. Fischer, W. Kurtz and F. Effenberger, *Chem. Ber.* **107**, 1305 (1974).
[36]H. Kessler, *Angew. Chem.* **82**, 237 (1970).
[37]P. K. Korver, P. J. van der Haak and T. J. de Boer, *Tetrahedron* **22**, 3157 (1966).
[38]P. Fischer, unpublished results.
[39]U. Schirmer, Ph.D. Thesis, Universität Stuttgart (1973).
[40]F. Effenberger, G. Prossel, E. Auer and P. Fischer, *Chem. Ber.* **103**, 1456 (1970).
[41]S. Castellano, C. Sun and R. Kostelnik, *Tetrahedron Letters* 5205 (1967).