Study of Substituent Effects on Conformational Equilibrium ($E \leftrightarrows Z$) of 2-(4-Substituted Anilino)-5-nitropyridines by Infrared Spectra, *X*-Ray Crystallography, and CNDO/2 Calculations

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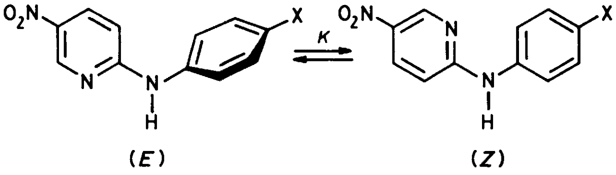
I.r. spectra of the amino stretching vibration bands (ν_{NH}) of 2-(4-substituted anilino)-5-nitropyridines with substituents NMe_2 (**1**), NH_2, OH, OMe, Me, H (**6**), Cl (**7**), Br (**8**), CO_2Et, CN, and NO_2 (**11**) were measured in CCl_4, $CHCl_3$, and CH_2Cl_2 solutions. The crystal structures of (**1**), (**6**), (**7**), and (**11**) were determined; (**1**) and (**6**) contain the *E*-isomer and (**7**) and (**11**) contain the *Z*-isomer. The ν_{NH} bands at lower and higher wavenumbers, $\nu_{NH}{}^{l}$ and $\nu_{NH}{}^{h}$, were assigned respectively to ν_{NH} of the *E*- and *Z*-isomer coexisting at equilibrium ($E \leftrightarrows Z$) in solution. For the respective solvents, the free energy difference ($\Delta G°$) estimated from the intensity ratio $\nu_{NH}{}^{h}:\nu_{NH}{}^{l}$ decreases linearly as the substituent σ constant increases in order from (**1**) to (**11**); the predominant form in solution of (**1**) is *E* and of (**11**) is *Z*. This agrees with the results of an i.r. study on the crystals of (**1**)—(**11**), *i.e.* that (**1**)—(**6**) are crystallized in the *E*-form (non-planar) and (**7**)—(**11**) are crystallized in the *Z*-form (planar). The differences between the total energies of the isomers (ΔE_{tot}) for (**1**)—(**11**), excluding (**8**), were calculated by the CNDO/2 method. The linear relation of ΔE_{tot} *versus* σ was considered to be representative of that of $\Delta G°$ obtained for each solvent *versus* σ, taking into account the dielectric effect of the solvent on it. The energy terms governing the change in ΔE_{tot} were selected to reveal important factors controlling the equilibrium, and the resonance and Coulombic interaction energies were attended. The substituent effect on the $\nu_{NH}{}^{l}$ and $\nu_{NH}{}^{h}$ frequencies were also investigated.

2-Anilinopyridines seem to coexist in the *E*- and *Z*-form at equilibrium in solution according to i.r. and u.v. studies.[1,2] Two ν_{NH} bands, $\nu_{NH}{}^{l}$ and $\nu_{NH}{}^{h}$, to be allotted to each isomer, appear at lower and higher wavenumbers, respectively.[1] However, the conformational isomers and the assignment of the bands have not been definitely confirmed.

For 2-(4-substituted anilino)-5-nitropyridines (**1**)—(**11**) we found a correlation between the intensity ratio $\nu_{NH}{}^{h}:\nu_{NH}{}^{l}$ and the substituent σ constant in CCl_4, $CHCl_3$, and CH_2Cl_2 solutions; the ratio increases as the σ constant increases. In the spectra of (**1**) and (**11**), the $\nu_{NH}{}^{l}$ band is more intense than $\nu_{NH}{}^{h}$ for the former and *vice versa* for the latter. A molecule in the *E*-form probably takes a non-planar conformation, the phenyl ring being twisted about the C(Ph)–N bond to reduce the repulsive interaction between the two hydrogen atoms of the different rings. On the other hand, a molecule in the *Z*-form may adopt a planar conformation. For a molecule substituted with a strong electron-withdrawing group, conjugation between the phenyl and the amino groups exists and therefore the molecule is most stabilized in the planar conformation. We supposed, therefore, that the molecule of (**11**) might predominantly take the *Z*-form and, hence, the $\nu_{NH}{}^{h}$ band might be attributed to the N–H in the *Z*-isomer. The molecule of (**1**), however, was expected to adopt the *E*-form.

X-Ray structure analyses for (**1**), (**6**), (**7**), and (**11**), taken to confirm the supposition, revealed that molecules (**1**) and (**6**) are of the *E*-form and (**7**) and (**11**) are of the *Z*-form. The amino groups in the former crystals form intermolecular hydrogen bonds with the pyridine N atoms and those in the latter ones form them with the nitro O atoms. As it is evident by inspection of the i.r. spectra that the hydrogen-bonding configurations in (**2**)—(**5**) and (**8**)—(**10**), respectively, are the same as those in (**1**) and (**6**) and in (**7**) and (**11**), molecules (**2**)—(**5**) are the *E*-isomer and (**8**)—(**10**) are the *Z*-isomer. Thus, molecules with the negative σ substituents are crystallized in the *E*-form and those with positive σ are crystallized in the *Z*-form. This corresponds well to the change in the predominant form exhibited in CH_2Cl_2 solution with increasing σ.



(**1**) X = NMe_2
(**2**) X = NH_2
(**3**) X = OH
(**4**) X = OMe
(**5**) X = Me
(**6**) X = H
(**7**) X = Cl
(**8**) X = Br
(**9**) X = CO_2Et
(**10**) X = CN
(**11**) X = NO_2

Substituent effects on the conformational equilibrium were treated theoretically using the results of the CNDO/2 calculations. In this paper, we discuss which factors play an important role in the equilibrium. The substituent effects on the $\nu_{NH}{}^{l}$ and $\nu_{NH}{}^{h}$ frequencies observed in solution are also discussed.

Experimental

Compounds (**1**), (**2**), (**8**), (**10**), and (**11**) were prepared as reported earlier[3] and compounds (**3**)—(**7**) and (**9**) were supplied by Hirauchi and Amano.[3] Deuteriated compounds (**1**)—(**11**), in which the amino groups were substituted by deuterium atoms, were prepared by evaporating acetone–D_2O solutions. Crystals used for *X*-ray analysis were obtained from ethyl acetate solution for (**1**) and ethyl alcohol solution for (**6**) and (**7**), and by sublimation for (**11**).

I.r. Spectroscopy.—I.r. spectra in CCl_4, $CHCl_3$, and CH_2Cl_2 solutions were recorded on a magnified wavenumber scale (×20) with JASCO DS-403G and A-702 spectrometers calibrated by the absorption bands of ammonia.[4] Compounds (**1**)—(**11**) were dissolved in these solvents at below 0.002 mol dm^{-3} (cell length 1, 2, 5, or 10 cm). The accuracy of the frequency of the ν_{NH} bands for these compounds was ± 0.2 cm^{-1}. I.r. spectra of crystals mulled in perfluorocarbon solvents were recorded on a magnified wavenumber scale (× 2) with a JASCO A-702 spectrometer calibrated with the absorption bands of ammonia and indene. All measurements were carried out at room temperature (27 ± 1 °C).

Calculations.—The CNDO/2 calculations for all the compounds, except (**8**), were carried out on a FACOM M-340R computer using a program written by Pople and Beveridge.[5] The geometries of the *E*- and *Z*-isomers of 2-anilino-5-nitropyridines, respectively, deduced from those of (**1**) and (**11**) in the crystals, were optimized by the MNDO method,[6] the twist angles of the pyridine and benzene rings being fixed at their averaged values observed for molecules A and B in the respective crystals. This was done because the method was unsuitable for estimating the rotational energy around the sp^2–sp^2 bond.[7] To set up the molecular models for the isomers of (**1**)—(**7**) and (**9**)—(**11**), the rotational isomers of 2-anilino-5-nitropyridines thus optimized were bound with the respective substituents to obtain a stable conformation referred to an analogous molecule with a common substituent,[8] *e.g.*, *p*-dimethylaminophenol for (**1**). For (**1**)—(**5**) and (**9**), models with substituents of other geometries related by a two-fold rotational axis along the C–X bond were also constructed. The molecule of (**8**) was excluded from the energy calculation, because the bromine atom could not be treated by the CNDO/2 method.

The conformational energies are given by the difference in total energies of the *E*- and *Z*-isomers. The total energy (E_{tot}) can be estimated as the sum (1) of one- and two-atomic terms where equations (2) and (3) apply.[9,10] The three terms of E_{AB} represent

$$E_{tot} = \sum_{A} E_A + \sum_{A<B} E_{AB} \tag{1}$$

$$E_A = \sum_{\mu}^{A} P_{\mu\mu} U_{\mu\mu} + \tfrac{1}{2}\sum_{\mu}^{A}\sum_{\nu}^{A}(P_{\mu\mu}P_{\nu\nu} + \tfrac{1}{2}P_{\mu\nu}^2)\gamma_{AA} \tag{2}$$

$$E_{AB} = \sum_{\mu}^{A}\sum_{\nu}^{B} 2P_{\mu\nu}\beta_{AB}^{\circ}S_{\mu\nu} - \sum_{\mu}^{A}\sum_{\nu}^{B}\tfrac{1}{2}P_{\mu\nu}^2\gamma_{AB} + (Z_A Z_B R_{AB}^{-1} - P_{AA}V_{AB} - P_{BB}V_{BA} + P_{AA}P_{BB}\gamma_{AB}) \tag{3}$$

resonance ($E_{AB}{}^{R}$), exchange ($E_{AB}{}^{E}$), and Coulombic interaction energies ($E_{AB}{}^{C}$), respectively. In addition, we calculated the non-bonding interaction energies of the N atom of the pyridine ring against the H atom of the NH group (E_{NH}), the X group (E_{NX}), the PhX group (E_{NPhX}), and the H(C12) atom of the benzene ring ($E_{NH(C)}$).

X-*Ray Analysis.*—Crystallographic details are listed in Table 1. A Rigaku AFC-5 diffractometer employing graphite-monochromatized Cu-K_α radiation was used. Three standard reflections monitored every 100 reflections showed no significant change during data collection. There were no absorption corrections. Structures were solved by MULTAN 78.[11] Hydrogen atoms were located on a difference density map. Positional parameters of all atoms and anisotropic thermal parameters of non-hydrogen atoms were refined by block-diagonal least-squares. The temperature factor of each hydrogen atom was set equal to B_{eq} of the bonded atom. $\Sigma(w|\Delta F|^2)$ was minimized, $w = 1/\sigma^2(F_o)$ for observed reflections with $|F_c| \geqq \sigma(F_o)$ and $|\Delta F| < 3\sigma(F_o)$, and $w = 0$ otherwise, $\sigma(F_o) = [\sigma_1{}^2(F_o) + c^2|F_o|^2]^{\frac{1}{2}}$, with $\sigma_1(F_o)$ from counting statistics.[12] Atomic scattering factors were calculated by $\Sigma[a_i\exp(-b_i\sin^2\theta/\lambda^2] + c\ (i = 1$—$4)$.[13] Calculations were performed by a FACOM M-340R computer at Shionogi Research Laboratories.

Results and Discussion

Assignment of the ν_{NH} *Bands.*—The i.r. parameters and the ΔG° values obtained for dilute CCl$_4$, CHCl$_3$, and CH$_2$Cl$_2$ solutions of (**1**)—(**11**) are listed in Table 2, together with the σ constants for the substituents.[14,15] Because the NO$_2$, CN, and CO$_2$Et groups have strong electron-withdrawing ability, their σ^- constants were used in place of the σ constants. The assignment of the $\nu_{NH}{}^{l}$ and $\nu_{NH}{}^{h}$ bands, described in the Introduction, is supported by the results of CNDO/2 calculations; the absolute value of the NH bond energy, which is approximately proportional to the force constant, is larger in the *Z*- than in the *E*-isomer.[16]

Substituent Effects on the NH *Stretching Frequencies.*—Figure 1 shows plots of the $\nu_{NH}{}^{l}$ and $\nu_{NH}{}^{h}$ frequencies *versus* the σ constant of the substituent in CHCl$_3$. Interestingly, the plots give correlations with the maximum near $\sigma = 0$. This behaviour strongly resembles that of 4′-substituted 4-nitrodiphenylamines in CHCl$_3$,[17] although the substituent effects on these ν_{NH} values are slightly suppressed for negative σ and enhanced for positive σ owing to the resonance interaction between the endo- and exo-cyclic nitrogen atoms. This indicates that the ν_{NH} value is primarily governed by the change in the hybridization of the N atom of the NH group in the former region[18–21] and in the polarization of the NH band in the latter.[19,22–24] Similar behaviour was obtained for the other solutions.

Substituent Effects on the Conformational Equilibrium (E $\rightleftarrows$ Z).—As shown in Table 2, the value of log ($\varepsilon^h/\varepsilon^l$) increases with increasing σ, where ε^l and ε^h are the absorption coefficients of the $\nu_{NH}{}^{l}$ and $\nu_{NH}{}^{h}$ bands, respectively. For the respective compounds, log ($\varepsilon^h/\varepsilon^l$) can be correlated with the dielectric constant of the solvent (*D*). In the conformational equilibrium ($E \rightleftarrows Z$), ΔG° is given by equations (4) and (5) where *K* is the equilibrium

$$\Delta G^\circ = -RT\ln K \tag{4}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{5}$$

constant and ΔH° and ΔS° are the differences of enthalpies and entropies, respectively. Assuming $\varepsilon^l N^h = \varepsilon^h N^l$, ΔG° is expressed by equation (6) where N^l and N^h are the number of molecules of

$$\Delta G^\circ = -2.303RT\log(\varepsilon^h/\varepsilon^l) \tag{6}$$

the *E*- and *Z*-isomer, respectively. Figure 2 shows plots of ΔG° calculated by equation (6) against σ. Good linear relationships were obtained for the various solvents. If the important factor controlling the equilibrium is the electrostatic interaction, ΔG° is proportional to $1/D$.[25] However, good linear relationships between ΔG° and *D* were obtained for (**1**)—(**9**) and (**11**) (*r* 0.99—1.00) and for (**10**) (*r* 0.97), where *r* is the correlation coefficient. The result suggests that the equilibrium is not governed primarily by electrostatic interactions in this case. This is not inconsistent with the theoretical results described in the next paragraph.

Partitioning of Total Energy.—The conformational energies, $\Delta E_{tot} = E_{tot}(Z\text{-isomer}) - E_{tot}(E\text{-isomer})$, along with the energy terms in equations (1) and (3), and the non-bonding interaction energies calculated by partitioning E_{tot}, are listed in Table 3. If the change in ΔS° in equation (5) is assumed to be negligible for the solvents examined, ΔG° may be expected to show a linear correlation with ΔE_{tot}. As shown in Figure 3, good linear relationships were obtained for the various solvents, the slope and the ΔG° value at $\Delta E_{tot} = 0$ tending to approach unity and zero, respectively, with decreasing dielectric constant of the solvent in the order from CH$_2$Cl$_2$ to CCl$_4$. This is reasonable

Table 1. Crystallographic details for (**1**), (**6**), (**7**), and (**11**)

	(**1**)	(**6**)	(**7**)	(**11**)
Formula	$C_{13}H_{14}N_4O_2$	$C_{11}H_9N_3O_2$	$C_{11}H_8ClN_3O_2$	$C_{11}H_8N_4O_4$
M	258.28	215.21	249.66	260.21
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
a/Å	9.875(2)	9.862(1)	10.343(4)	18.438(3)
b/Å	15.529(8)	11.209(1)	12.192(5)	5.534(1)
c/Å	9.696(4)	9.822(1)	9.418(4)	24.693(4)
α/°	118.15(5)	107.93(1)	93.04(4)	90.0
β/°	90.78(2)	90.87(1)	107.61(3)	114.57(1)
γ/°	95.58(2)	80.95(1)	77.03(3)	90.0
V/Å^3	1 301.9(11)	1 019.5(1)	1 102.9(8)	2 291.5(6)
No. of reflections used for least-squares refinement of cell dimensions ($20 < \theta < 25°$, $\lambda = 1.541\,78$ Å)	25	25	25	25
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Z	4	4	4	8
D_x/g cm^{-3}	1.318	1.402	1.503	1.508
Colour	Reddish orange	Yellow	Yellow	Yellow
Shape	Prism	Prism	Prism	Prism
Crystal dimensions/mm	0.2 × 0.2 × 0.1	0.2 × 0.2 × 0.3	0.2 × 0.2 × 0.3	0.2 × 0.3 × 0.1
μ(Cu-K_α)/cm^{-1}	7.7	8.4	30.3	10.2
$\theta_{max.}$/°	70	70	70	70
Scan mode	ω ($\theta < 15°$) ω—2θ ($\theta \geqq 15°$)	ω—2θ	ω—2θ	ω ($\theta < 15°$) ω—2θ ($\theta \geqq 15°$)
ω scan width/° $A + 0.2\tan\theta$				
A	1.2	1.2	1.2	1.3
ω scan speed/° min^{-1}	3	3	3	3
Measuring range	(h, $+k$, l)	($+h$, k, l)	(h, k, $-l$)	(h, $+k$, $+l$)
No. of reflections				
measured	4 992	3 982	4 346	4 357
unique	4 798	3 747	4 078	4 243
observed [$\lvert F_o\rvert > \sigma(F_o)$]	4 146	3 391	3 499	3 165
R	0.047	0.035	0.045	0.054
R_w	0.066	0.053	0.068	0.081
No. of reflections used for least-squares refinement	3 940	3 078	3 269	2 794
c^2	0.002 166	0.001 527	0.003 040	0.002 681

Table 2. I.r. spectral data for the NH group and the $\Delta G°$ values of 2-(4-substituted anilino)-5-nitropyridines in CCl_4, $CHCl_3$, and CH_2Cl_2[a]

		CCl_4				$CHCl_3$				CH_2Cl_2			
Compd.	σ[b]	$\nu_{NH}{}^h$/cm^{-1}	$\nu_{NH}{}^l$/cm^{-1}	log($\varepsilon^h/\varepsilon^l$)	$\Delta G°_{300K}$/kJ mol^{-1}	$\nu_{NH}{}^h$/cm^{-1}	$\nu_{NH}{}^l$/cm^{-1}	log($\varepsilon^h/\varepsilon^l$)	$\Delta G°_{300K}$/kJ mol^{-1}	$\nu_{NH}{}^h$/cm^{-1}	$\nu_{NH}{}^l$/cm^{-1}	log($\varepsilon^h/\varepsilon^l$)	$\Delta G°_{300K}$/kJ mol^{-1}
(**1**)	−0.83	3 437.9	3 408.0	−0.883	5.07	3 429.0	3 400.5	−0.690	3.96	3 419.3	3 394.2	−0.494	2.84
(**2**)	−0.66		*d*		(4.76)[c]	3 429.6	3 401.7	−0.675	3.88	3 419.3	3 394.5	−0.490	2.81
(**3**)	−0.357		*d*		(3.77)[c]	3 431.3	3 402.7	−0.535	3.07	3 420.7	3 395.7	−0.333	1.91
(**4**)	−0.268	3 439.7	3 409.6	−0.712	4.09	3 431.3	3 403.0	−0.527	3.03	3 420.8	3 395.8	−0.335	1.92
(**5**)	−0.170	3 438.3	3 409.7	−0.601	3.45	3 430.9	3 403.3	−0.463	2.66	3 420.6	3 395.7	−0.249	1.43
(**6**)	0	3 438.1	3 409.7	−0.465	2.67	3 431.2	3 403.4	−0.386	2.22	3 421.0	3 395.7	−0.160	0.92
(**7**)	0.227	3 438.4	3 408.4	−0.239	1.37	3 431.3	3 402.4	−0.160	0.92	3 420.8	3 395.2	0.026	−0.15
(**8**)	0.232	3 438.0	3 408.0	−0.236	1.36	3 431.2	3 402.4	−0.147	0.84	3 420.7	3 394.8	0.030	−0.17
(**9**)	0.678	3 435.2	3 406.9	−0.082	0.47	3 428.4	3 400.4	−0.002	0.01	3 418.4	3 392.8	0.141	−0.81
(**10**)	1.0		*d*		(−0.68)[c]	3 427.2	3 399.1	0.281	−1.61	3 416.6	3 389.8	0.388	−2.23
(**11**)	1.27	3 433.7	3 403.5	0.249	−1.43	3 425.7	3 398.3	0.323	−1.86	3 414.8	~3 388	~0.45	−2.58

[a] The dielectric constants of CCl_4, $CHCl_3$, and CH_2Cl_2 are 2.228 at 25 °C, 4.806 at 20 °C, and 8.93 at 25 °C, respectively. [b] The values were taken from ref. 25 except that those for the NMe_2 group were from ref. 26. [c] The value in parentheses was estimated using equation (a) in Figure 2. [d] The i.r. parameters were not obtained, because of low solubilities.

because energy calculations are done for molecules *in vacuo* (D 1). Therefore, we considered that the change in ΔE_{tot} with σ calculated for the molecular models reflected that in the equilibrium with σ.

In order to identify the important factors controlling the equilibrium, the regression analysis was done between ΔE_{tot} and its components described above. For (**1**)—(**5**) and (**9**), the energy values for the conformational isomers of the substituent were averaged because of the smallness of their differences. The correlation equations are presented in Table 4. $\Delta\sum_{A<B}E_{AB}$ correlates well with ΔE_{tot} with a positive slope, while $\Delta\sum_{A}E_{A}$ shows a correlation with a negative slope. This suggests that the effective terms governing the change in the equilibrium may be detected by analysing $\Delta\sum_{A<B}E_{AB}$ consisting of the energy terms

Table 3. Energy differences (kJ mol^{-1}) between *E*- and *Z*-isomers for 2-(4-substituted anilino)-5-nitropyridines by CNDO/2 calculations

Compd.	g^a	ΔE_{tot}	$\Delta\sum_{A} E_A$	$\Delta\sum_{A<B} E_{AB}$	$\Delta E_{AB}{}^R$	$\Delta E_{AB}{}^E$	$\Delta E_{AB}{}^C$	ΔE_{NH}	ΔE_{NX}	ΔE_{NPhX}	$\Delta E_{NH(C)}$
(1)	$+z$	7.502	11.929	−4.427	−13.305	−9.937	18.815	−8.008	0.473	3.728	−5.699
	$-z$	6.703	9.238	−2.535	−12.142	−9.991	19.598	−7.983	0.418	3.753	−5.699
(2)	$+z$	7.980	10.770	−2.790	−12.426	−10.000	19.636	−8.088	0.393	3.648	−5.669
	$-z$	6.992	7.699	−0.707	−11.485	−10.401	21.179	−8.008	0.393	3.703	−5.669
(3)	$+y$	6.469	9.004	−2.535	−13.054	−10.192	20.711	−7.849	0.498	4.515	−5.828
	$-y$	6.498	8.821	−2.323	−12.816	−10.201	20.694	−7.929	0.891	3.544	−5.908
(4)	$+y$	6.804	10.660	−3.856	−13.373	−9.930	19.447	−8.008	0.632	3.464	−5.774
	$-y$	6.795	8.272	−1.477	−12.736	−10.192	21.451	−7.849	0.841	3.569	−5.883
(5)	$+y$	5.084	13.368	−8.284	−15.154	−10.845	17.715	−7.770	0.159	3.966	−5.644
	$-y$	5.256	14.436	−9.180	−15.257	−10.821	16.898	−7.850	0.158	3.964	−5.644
(6)		4.505	14.673	−10.168	−19.477	−10.686	19.995	−7.845	0.054	3.912	−5.699
(7)		2.372	15.962	−13.590	−19.355	−11.092	16.857	−7.560	0.920	3.230	−6.197
(9)	$+y$	2.456	15.393	−12.937	−16.594	−9.594	13.251	−7.586	0.368	3.966	−5.883
	$-y$	2.322	15.548	−13.226	−16.811	−9.544	13.129	−7.586	−0.054	3.674	−5.828
(10)		2.942	15.694	−12.752	−17.472	−10.765	15.485	−7.615	0.368	3.569	−6.012
(11)		−0.401	13.933	−14.334	−18.564	−10.205	14.435	−7.192	0.657	2.782	−6.590

[a] $+z$ or $-z$ shows the sign of the z co-ordinate axis of C atoms in NMe_2 and H atoms in NH_2 and $+y$ or $-y$ shows the sign of the y co-ordinate axis of H atom in OH group and C atom in OMe group, H atoms in Me group, and O atom of $C{=}O(CO_2Et)$ group.

Table 4. Correlations between ΔE_{tot} (kJ mol^{-1}) and the other energy differences by CNDO/2 calculations; $\Delta E_{tot} = AY + B$ ($n = 10$)

Equation	Y	A	B	r
(7)	$\Delta\sum_{A} E_A$	−0.710	13.556	0.79
(8)	$\Delta\sum_{A<B} E_{AB}$	0.470	8.376	0.94
(9)	$\Delta E_{AB}{}^R$	0.740	16.132	0.84
(10)	$\Delta E_{AB}{}^E$	0.991	14.745	0.18
(11)	$\Delta E_{AB}{}^C$	0.805	−9.852	0.85
(12)	ΔE_{NH}	−9.827	−71.645	0.98
(13)	ΔE_{NX}	−0.675	4.794	0.08
(14)	ΔE_{NPhX}	4.536	−11.955	0.66
(15)	$\Delta E_{NH(C)}$	7.279	47.474	0.83

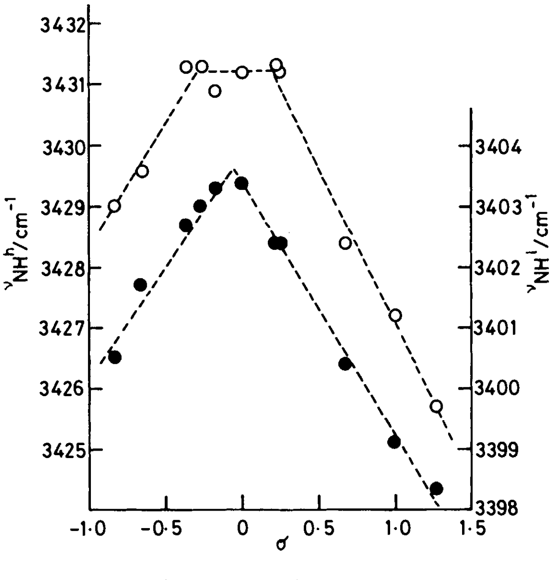


Figure 1. Plots of $\nu_{NH}{}^h$ (○) and $\nu_{NH}{}^l$ (●) against σ in 2-(4-substituted anilino)-5-nitropyridines in $CHCl_3$

$\Delta E_{AB}{}^R$, $\Delta E_{AB}{}^E$, and $\Delta E_{AB}{}^C$. As shown by equations (9)—(11) in Table 4, the first (resonance interaction) and the third (Coulombic interaction) energy terms correlate similarly with ΔE_{tot}, but the second one does not.

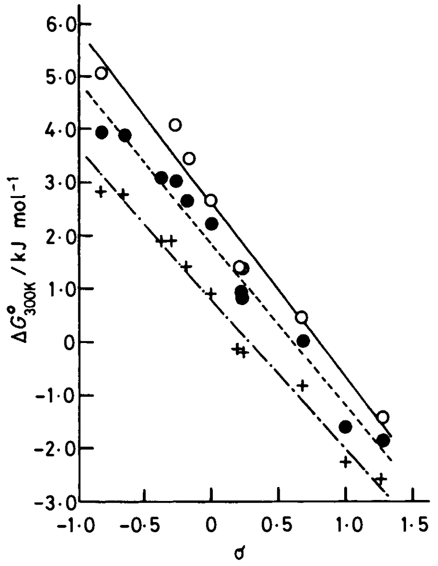


Figure 2. Plots of ΔG°_{300K} in CCl_4 (○), $CHCl_3$ (●), and CH_2Cl_2 (+) against σ in 2-(4-substituted anilino)-5-nitropyridines. Regression analysis gave the equations: (a) in CCl_4, $\Delta G^\circ = -3.276\sigma + 2.598$ ($n = 8$, $r = 0.98$); (b) in $CHCl_3$, $\Delta G^\circ = -3.061\sigma + 1.869$ ($n = 11$, $r = 0.99$); (c) in CH_2Cl_2, $\Delta G^\circ = -2.804 + 0.821$ ($n = 11$, $r = 0.99$), where n is the number of data points and r is the correlation coefficient coefficient

The *X*-ray study revealed that the phenyl group of the *E*-isomer twists about the C(Ph)–N bond, but that of *Z*-isomer does not. The conjugation between the phenyl and amino groups is more remarkable in the *Z*- than in the *E*-isomer. Therefore, in the case of a molecule substituted with an electron-withdrawing group, the absolute value of $E_{AB}{}^R$ for the *Z*-isomer is larger than that of the *E*-isomer. This leads to a decrease in ΔE_{tot} and makes the equilibrium, $E \rightleftarrows Z$, lie to the right.

The non-bonding interaction energies, shown in Table 3, which were considered to vary according to the conversion of the molecular conformations were calculated to elucidate the factors affecting $\Delta E_{AB}{}^C$. However, the changes in their differences with σ were so small that no conclusions could be drawn.

Table 5. Atomic co-ordinates ($\times 10^4$, and $\times 10^3$ for hydrogen)

(1)

Molecule A	x	y	z		x	y	z
N(1)	3 681(1)	4 645(1)	3 747(2)	C(18)	3 764(2)	10 958(1)	8 382(3)
C(2)	3 832(1)	5 603(1)	4 065(2)	C(19)	1 280(2)	10 525(1)	7 952(3)
C(3)	4 644(2)	5 926(1)	3 177(2)	H(C3)	467(2)	660(1)	337(2)
C(4)	5 369(2)	5 272(1)	2 030(2)	H(C4)	594(2)	545(1)	128(2)
C(5)	5 259(2)	4 309(1)	1 777(2)	H(C6)	428(2)	335(1)	245(2)
C(6)	4 403(2)	4 027(1)	2 636(2)	H(N10)	259(2)	587(1)	568(3)
N(7)	6 029(1)	3 598(1)	619(2)	H(C12)	513(2)	770(1)	609(3)
O(8)	6 737(2)	3 841(1)	−185(2)	H(C13)	497(2)	936(1)	710(3)
O(9)	5 968(2)	2 781(1)	519(2)	H(C15)	73(2)	873(1)	698(2)
N(10)	3 133(1)	6 192(1)	5 270(2)	H(C16)	101(2)	706(1)	602(2)
C(11)	3 063(1)	7 213(1)	5 871(2)	H(C18)	340(2)	1 158(2)	880(3)
C(12)	4 194(2)	7 903(1)	6 227(2)	H′(C18)	441(3)	1 090(2)	764(3)
C(13)	4 062(2)	8 891(1)	6 854(2)	H″(C18)	437(3)	1 091(2)	920(3)
C(14)	2 779(2)	9 236(1)	7 141(2)	H(C19)	69(2)	1 013(2)	696(3)
C(15)	1 645(2)	8 534(1)	6 813(2)	H′(C19)	81(2)	1 048(2)	888(3)
C(16)	1 794(1)	7 551(1)	6 203(2)	H″(C19)	133(2)	1 121(2)	840(3)
N(17)	2 620(2)	10 215(1)	7 717(2)				

Molecule B							
N(1)	1 245(1)	5 296(1)	6 795(2)	C(18)	2 424(3)	−779(2)	3 430(3)
C(2)	1 052(1)	4 328(1)	6 414(2)	C(19)	2 297(2)	−848(1)	840(3)
C(3)	63(2)	3 959(1)	7 102(2)	H(C3)	−3(2)	326(1)	678(2)
C(4)	−743(2)	4 589(1)	8 152(2)	H(C4)	−146(2)	436(1)	862(2)
C(5)	−530(2)	5 576(1)	8 529(2)	H(C6)	64(2)	656(1)	806(2)
C(6)	468(2)	5 897(1)	7 843(2)	H(N10)	242(2)	411(1)	491(2)
N(7)	−1 354(2)	6 271(1)	9 634(2)	H(C12)	213(2)	263(1)	667(2)
O(8)	−2 244(1)	5 988(1)	10 221(2)	H(C13)	236(2)	99(1)	553(3)
O(9)	−1 143(2)	7 126(1)	9 922(2)	H(C15)	212(2)	83(1)	124(2)
N(10)	1 852(1)	3 767(1)	5 296(2)	H(C16)	181(2)	250(1)	236(2)
C(11)	1 937(1)	2 742(1)	4 651(2)	H(C18)	323(3)	−42(2)	438(3)
C(12)	2 091(2)	2 278(1)	5 555(2)	H′(C18)	166(3)	−69(2)	406(3)
C(13)	2 229(2)	1 283(1)	4 859(2)	H″(C18)	264(3)	−145(2)	268(3)
C(14)	2 243(2)	716(1)	3 224(2)	H(C19)	138(3)	−82(2)	44(3)
C(15)	2 109(2)	1 202(1)	2 336(2)	H′(C19)	238(3)	−150(2)	54(3)
C(16)	1 949(2)	2 187(1)	3 036(2)	H″C(19)	297(2)	−61(2)	40(3)
N(17)	2 415(2)	−269(1)	2 524(2)				

(6)

Molecule A							
N(1)	6 345(1)	9 545(1)	5 839(1)	C(14)	6 743(1)	15 483(1)	7 558(1)
C(2)	6 169(1)	10 765(1)	6 704(1)	C(15)	7 943(1)	14 654(1)	7 006(1)
C(3)	5 350(1)	11 176(1)	7 969(1)	C(16)	7 977(1)	13 357(1)	6 617(1)
C(4)	4 615(1)	10 344(1)	8 285(1)	H(C3)	529(1)	1 199(1)	862(1)
C(5)	4 723(1)	9 123(1)	7 322(1)	H(C4)	405(1)	1 060(1)	919(2)
C(6)	5 610(1)	8 753(1)	6 148(1)	H(C6)	576(1)	793(1)	548(1)
N(7)	3 918(1)	8 225(1)	7 556(1)	H(N10)	745(1)	1 110(1)	541(1)
O(8)	3 352(1)	8 471(1)	8 735(1)	H(C12)	473(2)	1 334(1)	725(2)
O(9)	3 817(1)	7 267(1)	6 564(1)	H(C13)	466(2)	1 553(2)	800(2)
N(10)	6 881(1)	11 526(1)	6 247(1)	H(C14)	673(2)	1 640(1)	786(2)
C(11)	6 792(1)	12 859(1)	6 761(1)	H(C15)	880(2)	1 498(1)	688(2)
C(12)	5 583(1)	13 685(1)	7 294(1)	H(C16)	884(1)	1 278(1)	627(1)
C(13)	5 572(1)	14 990(1)	7 700(2)				

Molecule B							
N(1)	8 786(1)	10 314(1)	3 567(1)	C(14)	8 138(1)	4 440(1)	1 813(1)
C(2)	9 057(1)	9 058(1)	2 828(1)	C(15)	8 173(1)	5 069(1)	3 259(1)
C(3)	10 059(1)	8 555(1)	1 703(1)	C(16)	8 261(1)	6 350(1)	3 733(1)
C(4)	10 805(1)	9 362(1)	1 359(1)	H(C3)	1 030(1)	770(1)	122(1)
C(5)	10 514(1)	10 646(1)	2 123(1)	H(C4)	1 153(1)	906(1)	59(1)
C(6)	9 506(1)	11 085(1)	3 199(1)	H(C6)	931(1)	1 200(1)	378(1)
N(7)	11 271(1)	11 545(1)	1 821(1)	H(N10)	775(1)	873(1)	404(2)
O(8)	12 161(1)	11 157(1)	870(1)	H(C12)	812(2)	691(1)	67(2)
O(9)	11 008(1)	12 657(1)	2 552(1)	H(C13)	815(2)	467(1)	−11(2)
N(10)	8 301(1)	8 346(1)	3 309(1)	H(C14)	806(2)	351(1)	149(2)
C(11)	8 288(1)	7 022(1)	2 755(1)	H(C15)	813(2)	462(1)	396(2)
C(12)	8 219(1)	6 400(1)	1 306(1)	H(C16)	831(2)	682(1)	476(1)
C(13)	8 161(1)	5 101(1)	847(1)				

Table 5. *continued*

(7)

Molecule A	*x*	*y*	*z*		*x*	*y*	*z*
N(1)	4 751(2)	2 174(1)	7 605(2)	C(14)	3 016(2)	1 667(2)	1 784(2)
C(2)	3 931(2)	3 193(1)	7 193(2)	C(15)	2 253(2)	2 757(2)	1 774(2)
C(3)	3 687(2)	4 033(2)	8 228(2)	C(16)	2 377(2)	3 319(1)	3 104(2)
C(4)	4 321(2)	3 811(2)	9 707(2)	Cl	2 828(1)	9 500(4)	116(1)
C(5)	5 201(2)	2 766(2)	10 122(2)	H(C3)	305(3)	478(2)	783(3)
C(6)	5 373(2)	1 978(2)	9 053(2)	H(C4)	414(3)	435(2)	1 040(3)
N(7)	5 914(2)	2 507(2)	11 672(2)	H(C6)	594(3)	127(2)	937(3)
O(8)	5 751(2)	3 230(2)	12 592(2)	H(N10)	281(3)	411(2)	557(3)
O(9)	6 651(2)	1 558(1)	12 026(2)	H(C12)	459(3)	141(2)	526(3)
N(10)	3 285(2)	3 451(1)	5 719(2)	H(C13)	443(3)	40(2)	304(3)
C(11)	3 258(2)	2 807(1)	4 441(2)	H(C15)	161(3)	314(2)	88(3)
C(12)	4 024(2)	1 709(2)	4 418(2)	H(C16)	188(3)	409(2)	305(3)
C(13)	3 887(2)	1 148(2)	3 094(2)				

Molecule B							
N(1)	−534(2)	9 004(1)	6 391(2)	C(14)	−1 725(2)	12 925(2)	8 873(2)
C(2)	−1 447(2)	9 581(1)	5 214(2)	C(15)	−2 509(2)	13 280(2)	7 450(2)
C(3)	−1 792(2)	9 123(2)	3 771(2)	C(16)	−2 614(2)	12 505(2)	6 323(2)
C(4)	−1 171(2)	8 049(2)	3 565(2)	Cl	−1 547(1)	13 903(1)	10 297(1)
C(5)	−213(2)	7 449(1)	4 805(2)	H(C3)	−246(3)	959(2)	296(3)
C(6)	77(2)	7 941(2)	6 168(2)	H(C4)	−143(3)	773(2)	252(3)
N(7)	469(2)	6 301(1)	4 625(2)	H(C6)	74(3)	753(2)	705(3)
O(8)	63(2)	5 836(1)	3 449(2)	H(N10)	−263(3)	1 099(2)	452(3)
O(9)	1 449(2)	5 837(1)	5 663(2)	H(C12)	−66(3)	1 024(2)	838(3)
N(10)	−2 097(2)	10 670(1)	5 371(2)	H(C13)	−59(3)	1 162(2)	1 017(3)
C(11)	−1 951(2)	11 377(1)	6 615(2)	H(C15)	−299(3)	1 402(2)	727(3)
C(12)	−1 200(2)	11 030(2)	8 067(2)	H(C16)	−317(3)	1 272(2)	528(3)
C(13)	−1 089(2)	11 806(2)	9 200(2)				

(11)

Molecule A							
N(1)	1 152(1)	10 617(4)	2 654(1)	C(15)	68(2)	13 331(6)	4 263(1)
C(2)	1 463(1)	12 643(5)	2 960(1)	C(16)	552(2)	14 103(5)	4 010(1)
C(3)	2 114(2)	13 831(6)	2 923(1)	N(17)	−857(2)	10 281(5)	4 333(1)
C(4)	2 446(2)	12 901(5)	2 568(1)	O(18)	−1 192(2)	8 362(5)	4 162(1)
C(5)	2 128(2)	10 795(5)	2 261(1)	O(19)	−922(2)	11 520(5)	4 727(1)
C(6)	1 486(2)	9 693(6)	2 305(1)	H(C3)	230(2)	1 515(7)	316(2)
N(7)	2 484(2)	9 726(5)	1 890(1)	H(C4)	294(2)	1 375(7)	256(2)
O(8)	3 048(2)	10 723(6)	1 857(1)	H(C6)	126(2)	822(7)	209(2)
O(9)	2 201(2)	7 890(6)	1 613(1)	H(N10)	141(2)	1 525(7)	353(2)
N(10)	1 171(1)	13 673(4)	3 345(1)	H(C12)	33(2)	960(7)	314(1)
C(11)	644(1)	12 739(5)	3 559(1)	H(C13)	−60(2)	835(7)	346(2)
C(12)	223(2)	10 665(5)	3 361(1)	H(C15)	5(2)	1 438(7)	458(2)
C(13)	−266(2)	9 855(6)	3 617(1)	H(C16)	82(2)	1 528(7)	415(2)
C(14)	−346(2)	11 195(6)	4 063(1)				

Molecule B							
N(1)	5 570(2)	1 293(5)	4 271(1)	C(15)	7 643(2)	8 632(6)	5 074(1)
C(2)	6 022(2)	1 761(5)	3 969(1)	C(16)	7 410(2)	6 869(6)	4 653(1)
C(3)	5 947(2)	438(7)	3 468(1)	N(17)	7 474(1)	10 725(4)	5 889(1)
C(4)	5 408(2)	−1 375(7)	3 268(2)	O(18)	7 108(2)	10 939(5)	6 201(1)
C(5)	4 958(2)	−1 874(6)	3 582(1)	O(19)	8 033(1)	12 043(4)	5 939(1)
C(6)	5 038(2)	−536(6)	4 076(1)	H(C3)	627(3)	64(8)	323(2)
N(7)	4 385(2)	−3 875(6)	3 395(1)	H(C4)	526(2)	−229(8)	288(2)
O(8)	4 290(2)	−4 952(8)	2 938(1)	H(C6)	470(2)	−77(8)	428(2)
O(9)	4 074(2)	−4 495(5)	3 720(1)	H(N10)	685(2)	376(8)	393(2)
N(10)	6 589(2)	3 574(5)	4 156(1)	H(C12)	615(2)	446(7)	501(2)
C(11)	6 803(2)	5 251(5)	4 608(1)	H(C13)	646(2)	735(7)	570(2)
C(12)	6 450(2)	5 393(5)	4 992(1)	H(C15)	806(2)	983(8)	511(2)
C(13)	6 674(2)	7 182(6)	5 417(1)	H(C16)	765(2)	674(7)	435(2)
C(14)	7 259(2)	8 802(5)	5 450(1)				

Table 6. I.r. bands ν_{NH} and ν_{ND} of 2-(4-substituted anilino)-5-nitropyridines and their deuteriated compounds (perfluorocarbon solvent mull)

Compound	ν_{NH}/cm^{-1}				ν_{ND}/cm^{-1}			ν_{NH}/ν_{ND}^{e}
(**1**)	3 234	3 169	$\sim$2 960^{c}	($\sim$2 980)^{d}	2 320^{c}	2 144		1.28
					2 287			
(**2**)^{a}	3 223	3 176	$\sim$2 980^{c}	($\sim$2 990)^{d}	2 306^{c}	2 136		1.29
(**3**)^{b}	3 239	3 200	$\sim$3 000^{c}	($\sim$3 010)^{d}	2 307^{c}	2 139		1.30
(**4**)	3 236	3 189	$\sim$2 980^{c}	($\sim$2 990)^{d}	2 291^{c}	2 139		1.30
(**5**)	3 235	3 184	$\sim$3 000^{c}	($\sim$3 020)^{d}	2 302^{c}	2 137		1.30
(**6**)	3 235	3 188	$\sim$3 000^{c}	($\sim$3 020)^{d}	2 305^{c}	2 141		1.30
(**7**)	3 352^{c}	3 219	3 141		2 541	2 462^{c}	2 416	1.36
(**8**)	3 356^{c}	3 223	3 142		2 509	2 462^{c}	2 415	1.36
(**9**)	3 314^{c}	3 230	3 158		2 434	2 400^{c}	2 369	1.38
		3 219	3 124					
(**10**)	3 376	3 228	3 152		2 511	2 445^{c}	2 416	1.36
	3 335^{c}							
(**11**)	3 350	3 237	3 163		2 511	2 481	2 416	1.35
	3 328^{c}					2 457^{c}		

[a] The $\nu_{NH}(\nu_{ND})$ bands of the $NH_2(ND_2)$ group were observed at 3 467 (2 599) and 3 377 (2 446) cm^{-1}. [b] The $\nu_{OH}(\nu_{OD})$ bands of the OH(OD) group were observed at 3 432 (2 549) and 3 386 (2 524) cm^{-1}. [c] Main band. [d] The values in parentheses show the centre of gravity frequency for the ν_{NH} bands of the NH group. [e] Deuterium isotope frequency rate of the main band.

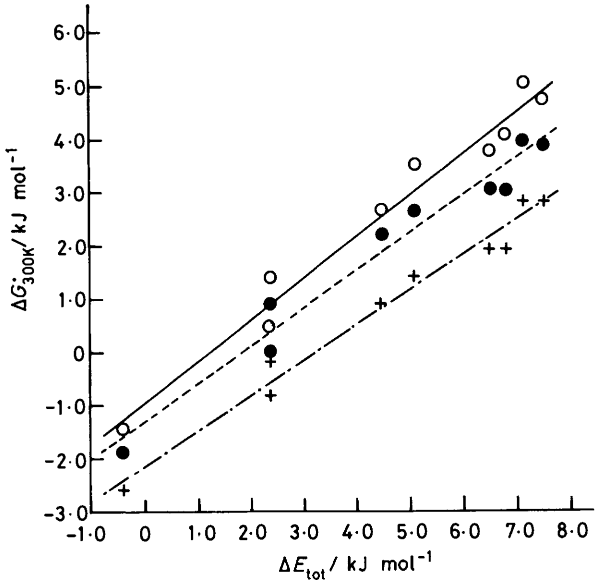


Figure 3. Plots of ΔG°_{300K} in CCl_4 (○), $CHCl_3$ (●), and CH_2Cl_2 (+) against ΔE_{tot} in 2-(4-substituted anilino)-5-nitropyridines. Regression analysis gave the equations, excluding (10): (a) in CCl_4, $\Delta G^{\circ} = 0.790\ \Delta E_{tot} - 0.987$ ($n = 9$, $r = 0.99$); (b) in $CHCl_3$, $\Delta G^{\circ} = 0.707\ \Delta E_{tot} - 1.302$ ($n = 9, r = 0.98$); (c) in CH_2Cl_2, $\Delta G^{\circ} = 0.659\ \Delta E_{tot} - 2.148$ ($n = 9$, $r = 0.99$)

Crystal and Molecular Structure of (**1**), (**6**), (**7**), *and* (**11**).—The asymmetric unit in the crystals contains two independent molecules A and B. The atomic co-ordinates are listed in Table 5. Tables of anisotropic thermal parameters and bond lengths and angles are listed in Supplementary Publication No. SUP 56646 (8 pp.).*

The molecules of (**1**) and (**6**) are in the *E*-form and those of (**7**) and (**11**) in the *Z*-form as seen in Figure 4. For all the molecules, the nitro groups are almost coplanar with the pyridine rings and the N(10)–C(11) bonds are nearly in the planes: the torsion angles C(3)–C(2)–N(10)–C(11) in molecules A and B are −0.3(3) and 3.8(3)° for (**1**), 11.3(2) and 4.4(2)° for (**6**), 176.8(3) and 177.1 (2)° for (**7**), and 167.3(3) and 177.4(4)° for (**11**). In (**1**) and (**6**), the benzene rings are twisted about the N(10)–C(11) bonds and the bond angles of C(3)–C(2)–N(10) are enlarged to reduce the repulsive interaction between H(C3) and H(C12). The rings in (**7**) and (**11**), on the other hand, show little twisting. The torsion angles of C(2)–N(10)–C(11)–C(12) are 48.6(3) and 49.5(3)° for (**1**), 33.5(2) and 45.9(2)° for (**6**), 4.9(4) and 9.7(4)° for (**7**), and 9.1(5) and 0.6(7)° for (**11**). The N(10) atoms adopt the trigonal configuration. In the dimethylamino groups of (**1**), the N(17) atoms of molecules A and B deviate from the planes through C(14), C(18), and C(19) in opposite directions by 0.089(2) and 0.094(2) Å, respectively.

The bond lengths and angles for the molecules A and B in each crystal are almost equal. The N(10)–C(11) bonds [averaged values for (**1**), (**6**), (**7**), and (**11**) being 1.419(2), 1.414(1), 1.403(2), and 1.381(4) Å, respectively] are shortest in (**11**), while the C(2)–N(10) [1.349(2), 1.361(1), 1.367(2), 1.389(4) Å] and C(5)–N(7) bonds [1.441(2), 1.447(1), 1.442(2), 1.461(4) Å] are shortest in (**1**). This indicates that the resonance interaction between N(10) and the phenyl part is enhanced in the planar molecule by a strong electron-withdrawing group and the contribution of the quinonoid structure to the pyridine part is significant in the non-planar molecules.

In the crystals of (**1**) and (**6**), molecules A and B are associated to form a dimer unit by intermolecular hydrogen bonds (Figure 4). On the other hand, the molecules in (**7**) and (**11**) are alternately arranged to form an infinite hydrogen-bonded chain. The hydrogen bonds in the former crystal are between the N(10) and the pyridine N atoms, and those in the latter crystals are between the N(10) and the nitro group O atoms. These bonds may arise because pyridine N atoms in the non-planar molecules can form hydrogen bonds as proton acceptors, but those in the planar molecules cannot form them owing to steric hindrance. Based on the difference in the types of hydrogen bonds found in the crystals of the *E*- and *Z*-isomers, the molecules in (**2**)—(**5**) and (**8**)—(**10**) could be identified with the respective isomers by an i.r. spectral study as described below.

The ν_{NH} *and* ν_{ND} *Bands in Crystals*.—The ν_{NH} and ν_{ND} bands for the amino groups of (**1**)—(**11**) and their deuteriated compounds in crystals are listed in Table 6, together with

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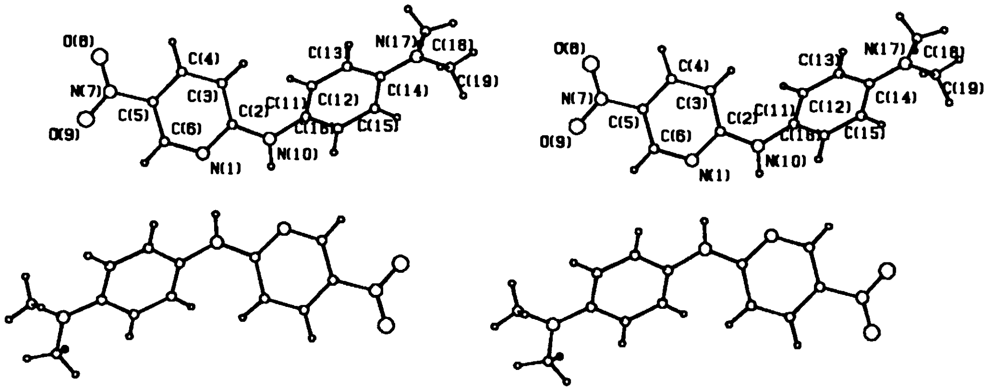
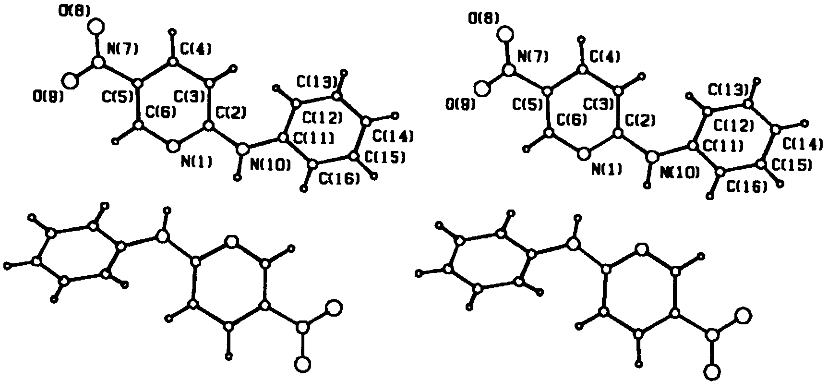
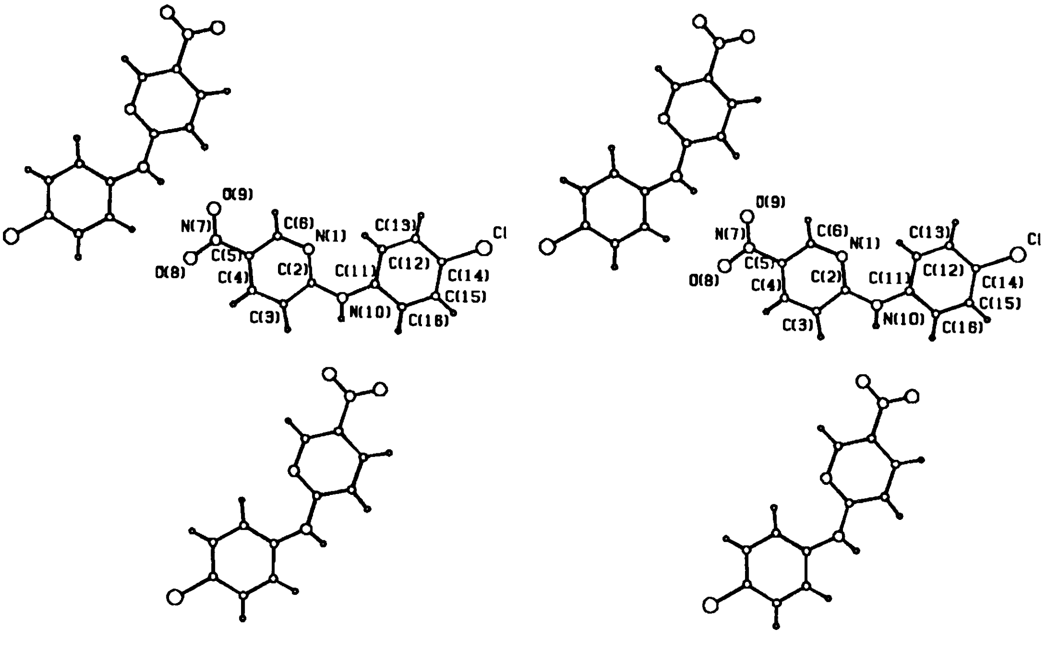
* For details see Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1986, Issue 1.


O(8)
N(7)
O(9)
C(5)
C(4)
C(3)
C(6)
C(2)
N(1)
N(10)
C(11)
C(12)
C(13)
C(14)
C(15)
C(16)
N(17)
C(18)
C(19)

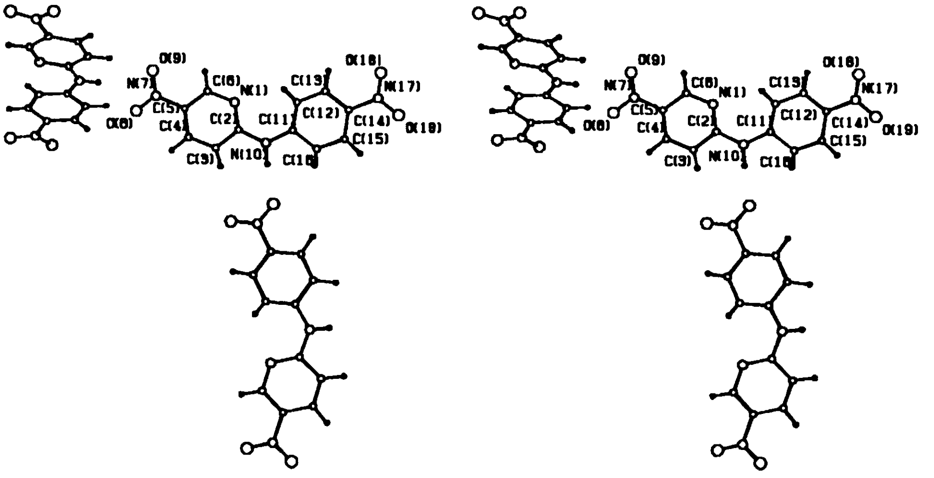
(1)


O(8)
N(7)
O(8)
C(4)
C(5)
C(6)
C(3)
C(2)
N(1)
N(10)
C(11)
C(12)
C(13)
C(14)
C(15)
C(16)

(6)


O(9)
N(7)
C(6)
N(1)
C(5)
O(8)
C(4)
C(2)
C(3)
C(11)
N(10)
C(13)
C(12)
Cl
C(14)
C(15)
C(16)

(7)



(11)

Figure 4. Stereoviews of molecules A and B, combined by intermolecular hydrogen bonds, in (1), (6), (7), and (11). Atom labellings are given for molecule A

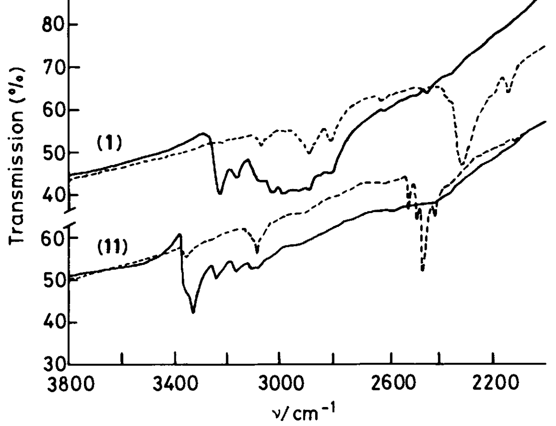


Figure 5. I.r. spectra of (1) and (11) (solid line) and their deuteriated compounds (broken line) mulled in perfluorocarbon solvents

the deuterium isotope frequency ratios ($\rho = \nu_{NH}/\nu_{ND}$). Typical spectra of the bands observed for (1) and (11) are shown in Figure 5. In the spectra of (1)—(6), the broad ν_{NH} bands with multiple submaxima which may be due to Fermi resonance perturbations and broad ν_{ND} bands are observed near 3 000 and 2 300 cm^{-1}, respectively, and their ρ values are in the region 1.28—1.30. However, those for (7)—(11) are observed at 3 380—3 310 and 2 470—2 400 cm^{-1}, which appear at higher wavenumbers compared with (1)—(6). Their ρ values fall in the region 1.35—1.38.

For AH ··· B intermolecular hydrogen bonds, relationships for ν_{AH} *versus* hydrogen-bond distance ($R_{A\cdots B}$) have been proposed for NH ··· N and NH ··· O systems in crystals.[26,27] These relationships can be applied to the NH ··· N system in (1) (ν_{NH} 2 980 cm^{-1}; $R_{N\cdots N}$ 2.984 and 3.018 Å) and (6) (ν_{NH} 3 020 cm^{-1}; $R_{N\cdots N}$ 2.996 and 3.074 Å) and to the NH ··· O system in (7) (ν_{NH} 3 352 cm^{-1}; $R_{N\cdots O}$ 3.090 and 3.168 Å) and (11) (ν_{NH} 3 328 cm^{-1}; $R_{N\cdots O}$ 2.957 Å and ν_{NH} 3 350 cm^{-1}; $R_{N\cdots O}$ 3.084 Å), respectively.

These results indicate that the intermolecular hydrogen-bonding systems in (2)—(5) are of the same type as those of (1) and (6) and those in (8)—(10) are of the same type as those of (7) and (11). Thus it was deduced that (1)—(6) with the electron-donating substituent take the *E*-form and (7)—(11) with the electron-withdrawing one take the *Z*-form.

This study showed that the linear relationship between the $\Delta G°$ value and the σ constant and the substituent effects on the conformational equilibrium ($E \leftrightarrows Z$) can be interpreted by a theoretical treatment using the CNDO/2 method. The information obtained should be useful for understanding the i.r. behaviour of analogous compounds and for examining conformational equilibria.

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