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Heat of Mixing for Binary Mixtures: Pyridine Derivatives+Benzene, and +Cyclohexane Systems

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The heat of mixing was measured for binary mixtures of pyridine derivatives (α-picoline, β-picoline, γ-picoline, and 2,6-lutidine) with benzene or cyclohexane at 25.0±0.01°C, and for a binary mixture of pyridine with benzene, or cyclohexane, at 30.0±0.01°C. The small values of the heat of mixing for pyridine derivatives-a benzene system were interpreted as an indication of strong specific interactions between pyridine derivatives and benzene. By treating the results in the manner described in a previous paper (*Bull. Chem. Soc. Japan*, **39**, 720 (1966)), the specific interaction energies of pyridine derivatives with benzene were estimated. The strengths of the molecular interaction energy were in the order: γ-picoline>pyridine>β-picoline>α-picoline> 2,6-lutidine; the order was discussed in terms of the molecular complexes.

Recently extensive studies of the formation of molecular compounds have been made by various techiques, but only a little information has been obtained by direct calorimetry measurements, which

seem to give the most reliable data on molecular interaction energy. In a previous paper,[1] we measured the heat of mixing for binary solutions and estimated the interaction energies of donor-accepter type complexes. Morcom *et al.* have measured the heat of mixing of pyridine derivatives+the carbon tetrachloride system and have discussed the specific interaction in terms of a possible donor-accepter interaction. In our experiment, we measured the heat of mixing for binary solutions of pyridine derivatives [pyridine (py), α-picoline (α-pi), β-picoline (β-pi), γ-picoline (γ-pi), and 2,6-lutidine (2,6-lut)]with benzene or cyclohexane. The small values of the heat of mixing for pyridine derivatives with benzene indicate the estimate of a specific interaction similar to that between pyridine derivatives and carbon tetrachloride. We will estimate the specific molecular energy between pyridine derivatives and benzene in a cyclohexane solution by using the enthalpy cycle, and will discuss the molecular interaction in terms of various types of molecular complexes.

Experimental

The calorimeter for measuring the heat of mixing was described in the previous paper,[1] but we made an improvement in the mixing cell. The mixing cell was made of glass instead of stainless steel, and its shape was similar to that used by Larkin and McGlashan[2] and by Amaya[3]. The experimental procedure was the same as before.

The technique of thermal compensation[1] was used for almost all the experiments. The pyridine was purified by a method described in the literature.[4] The methyl pyridines were supplied by the Tanabe Pharmaceutical Co., Ltd. All these samples except β-picoline were fractionally distilled over P_2O_5 and then under reduced pressure in a nitrogen atmosphere before use. The β-picoline was used without further purification, since no impurity was detected by gas chromatography.

The cyclohexane was treated with a concentrated sulfuric-nitric acid mixture, and then shaken with a

TABLE 1-1. HEAT OF MIXING FOR PYRIDINE + BENZENE AT 30.0°C

x_1	n_1 $\times 10^2$·mol	n_2 $\times 10^2$·mol	Q J	ΔH^M_{x2} J·mix^{-1}	ΔH_{x1} J·mol^{-1}
0.0665	0.1862	2.5091	0.41	15	219
0.1228	0.2567	1.8083	0.36	17	144
0.2862	0.5007	1.2482	0.30	17	59
0.4954	0.5838	0.5947	0.09	8	16
0.7705	1.3504	0.4022	0.20	12	15

1: pyridine 2: benznene

TABLE 1-2. HEAT OF MIXING FOR α-PICOLINE + BENZENE AT 25.0°C

x_1	n_1 $\times 10^2$·mol	n_2 $\times 10^2$·mol	Q J	ΔH^M_{x1} J·mix^{-1}	ΔH_{x1} J·mol^{-1}
0.1800	0.1330	0.6059	0.69	9.3	52.2
0.2293	0.2319	0.7774	0.16	15.4	67.2
0.3004	0.4050	0.9429	0.20	14.8	43.6
0.3830	0.2884	0.4647	0.17	22.6	59.0
0.5493	0.7463	0.3364	0.20	27.3	27.2
0.7412	0.4838	0.1689	0.16	23.9	32.2
0.7419	0.6647	0.2312	0.15	13.3	22.4
0.7999	0.8950	0.2238	0.15	13.3	16.7

1: α-picolihe 2: benzene

TABLE 1-3. HEAT OF MIXING FOR β-PICOLINE + BENZENE AT 25.0°C

x_1	n_1 $\times 10^2$·mol	n_2 $\times 10^2$·mol	Q J	ΔH^M_{x1} J·mix^{-1}	ΔH_{x1} J·mol^{-1}
0.1836	0.1863	0.8284	−0.14	−14.2	−77.7
0.2982	0.2474	0.2557	−0.13	−15.5	−52.0
0.5548	0.4482	0.3596	−0.04	−4.5	−8.2
0.6675	0.6033	0.3004	0.04	4.7	7.1
0.7182	0.6540	0.2557	0.10	11.4	15.8
0.8118	0.7249	0.1681	0.05	69.5	5.6

1: β-picoline 2: benzene

TABLE 1-4. HEAT OF MIXING FOR γ-PICOLINE + BENZENE AT 25.0°C

x_1	n_1 $\times 10^2$·mol	n_2 $\times 10^2$·mol	Q J	ΔH^M_{x1} J·mix^{-1}	ΔH_{x1} J·mol^{-1}
0.1184	0.1105	0.8212	0.09	10	77
0.2342	0.2246	0.7341	0.12	12	53
0.4831	0.4475	0.4788	0.15	16	34

1: γ-picoline 2: benzene

TABLE 1-5. HEAT OF MIXING FOR 2,6-LUTIDINE + BENZENE AT 25.0°C

x_1	n_1 $\times 10^2$·mol	n_2 $\times 10^2$·mol	Q J	ΔH^M_{x1} $\times 10^{-2}$· J·mix^{-1}	ΔH_{x1} $\times 10^{-2}$· J·mol^{-1}
0.1061	0.0917	0.7732	0.22	0.26	0.24
0.1402	0.1273	0.7806	0.30	0.33	0.23
0.1505	0.1823	0.9538	0.40	0.35	0.22
0.2915	0.3300	0.8023	0.53	0.47	0.16
0.3289	0.3531	0.7204	0.61	0.56	0.19
0.3951	0.3232	0.4949	0.50	0.58	0.15
0.4637	0.4247	0.4912	0.55	0.60	0.13
0.6713	0.6858	0.3357	0.44	0.43	0.06

1: 2,6-lutidine 2: benzene

1) S. Murakami and R. Fujishiro, This Bulletin, **39**, 720 (1966); M. Takami, S. Murakami and R. Fujishiro, *ibid.*, **38**, 291 (1965).

2) J. A. Larkin and M. L. McGlashan, *J. Chem. Soc.*, **1961**, 3425.

3) K. Amaya, This Bulletin, **34**, 1287 (1961).

4) D. G. Leis and B. C. Currans, *J. Am. Chem. Soc.*, **67**, 79 (1945).

Table 1-6. Heat of mixing for pyridine + cyclohexane at 30.0°C

x_1	n_1 $\times 10^2$·mol	n_2 $\times 10^2$·mol	Q J	ΔH^M_{x1} $\times 10^{-3}$. J·mix^{-1}	ΔH_{x1} $\times 10^{-3}$. J·mol^{-1}
*0.0491	0.1880	3.6444	14.98	0.39	7.97
*0.0689	0.2128	2.8772	15.55	0.50	7.30
*0.0812	0.2392	2.7084	17.33	0.59	7.24
0.0852	0.2190	2.3503	14.34	0.56	6.55
0.1067	0.2030	1.6990	12.32	0.65	6.07
*0.1474	0.1880	1.0874	11.05	0.87	5.88
*0.2434	0.2905	0.9027	15.15	1.27	5.21
*0.2374	0.2852	0.9161	14.01	1.17	4.91
0.3065	0.4284	0.9692	17.43	1.25	4.07
0.3233	0.5064	1.0598	20.82	1.33	4.11
0.4786	0.6116	0.6663	18.51	1.45	3.03
0.5942	0.6597	0.4505	14.70	1.32	2.22
0.6627	1.0823	0.5509	20.18	1.24	1.86
0.8011	1.4351	0.3563	15.40	0.86	1.07

* measured at 35.0°C
1: pyridine 2: cyclohexane

Table 1-7. Heat of mixing for α-picoline + cyclohexane at 25.0°C

x_1	n_1 $\times 10^2$·mol	n_2 $\times 10^2$·mol	Q J	ΔH^M_{x1} $\times 10^{-3}$. J·mix^{-1}	ΔH_{x1} $\times 10^{-3}$. J·mol^{-1}
*0.0658	0.0452	0.6168	2.78	0.41	6.16
*0.0848	0.0571	0.4867	3.47	0.52	6.08
*0.1163	0.1112	0.8445	4.73	0.63	5.39
0.1754	0.1600	0.7523	7.55	0.83	4.72
0.2380	0.2088	0.6686	9.08	1.03	4.35
0.2671	0.2226	0.6106	9.20	1.10	4.14
0.3902	0.3735	0.5835	11.97	1.25	3.21
0.5312	0.4978	0.4386	11.50	1.23	2.31
0.6734	0.5520	0.2676	12.55	1.03	1.53
0.7693	0.6079	0.1822	6.38	0.81	1.05

* calculated from heat of dilution
1: α-picoline 2: cyclohexane

Table 1-8. Heat of mixing for β-picoline + cyclohexane at 25.0°C

x_1	n_1 $\times 10^2$·mol	n_2 $\times 10^2$·mol	Q J	ΔH^M_{x1} $\times 10^{-3}$. J·mix^{-1}	ΔH_{x1} $\times 10^{-3}$. J·mol^{-1}
*0.0444	0.0282	0.5629	2.11	0.31	6.98
0.1081	0.0733	0.6774	4.44	0.66	6.06
0.1983	0.1865	0.9407	9.22	0.98	4.94
0.2841	0.2262	0.5699	9.35	1.17	4.13
0.3873	0.3953	0.6252	13.57	1.32	3.43
0.4340	0.3821	0.4982	11.78	1.33	3.08
0.5125	0.3985	0.3790	10.14	1.30	2.54
0.7326	0.4193	0.5723	5.51	0.96	1.31
0.7878	0.6579	0.1772	6.79	0.81	1.03

* calculated from heat of dilution
1: β-picoline 2: cyclohexane

Table 1-9. Heat of mixing for γ-picoline + cyclohexane at 25.0°C

x_1	n_1 $\times 10^2$·mol	n_2 $\times 10^2$·mol	Q J	ΔH^M_{x1} $\times 10^{-3}$. J·mix^{-1}	ΔH_{x1} $\times 10^{-3}$. J·mol^{-1}
0.1420	0.1556	0.9403	8.92	0.81	5.73
0.1550	0.1407	0.7570	8.12	0.89	5.77
0.2419	0.2202	0.6273	10.39	1.23	4.72
0.4777	0.5413	0.5917	15.74	1.39	2.91

1: γ-picoline 2: cyclohexane

Table 1 -10. Heat of mixing for 2,6-lutidine + cyclohexane at 25.0°C

x_1	n_1 $\times 10^2$·mol	n_2 $\times 10^2$·mol	Q J	ΔH^M_{x1} $\times 10^{-3}$. J·mix^{-1}	ΔH_{x1} $\times 10^{-3}$. J·mol^{-1}
0.0843	0.0846	0.9186	4.19	0.42	4.94
0.1062	0.0880	0.7404	4.79	0.54	5.04
0.1651	0.1555	0.7869	6.12	0.65	3.93
0.2041	0.1624	0.6334	5.71	0.72	3.51
0.2930	0.2348	0.7666	6.54	0.82	2.78
0.3941	0.5892	0.3570	6.01	1.02	2.59
0.4043	0.4786	0.7053	12.49	1.06	2.61
0.4721	0.3406	0.3808	7.36	1.02	2.16
0.7307	0.4076	0.1502	3.84	0.69	0.94
0.8104	0.6832	0.1598	4.50	0.53	0.66

1: 2,6-lutidine 2: cyclohexane

Table 1-11. Heat of mixing for benzene + cyclohexane at 30°C

x_1	n_1 $\times 10^2$·mol	n_2 $\times 10^2$·mol	Q J	ΔH^M_{x1} $\times 10^{-3}$. J·mix^{-1}	ΔH_{x1} $\times 10^{-3}$. J·mol^{-1}
0.0614	0.1633	2.4968	4.73	0.18	2.90
0.1472	0.2367	1.3710	5.93	0.37	2.51
0.3878	0.5861	0.9250	10.34	0.68	1.76

1: benzene, 2: cyclohexane

sodium hydroxide aqueous solution and with distilled water. Then it was twice passed through about 1 m silica gel column. The benzene was shaken with concentrated sulfuric acid, a sodium hydroxide aqeuous solution, and distilled water. The cyclohexane and benzene were shaken with mercury and distilled over metal sodium respectively. Gas-chromatographic analysis showed only a single peak for each sample.

Results and Discussion

The results obtained for eleven systems are given in Tables 1-1—1-11, where x_i and n_i ($i=1$ or 2) are the mole fraction and the number of the mole of the i component, respectively. Q is the quantity of heat produced during the mixing process, while ΔH_{x_i} and $\Delta H^M_{x_i}$ are the heats of mixing per mole of the 1 component and per mole of the mixture

respectively. For the mixtures with lower mole fractions, the heat of mixing was measured by diluting a solution, the heat of mixing of which was known from a previous run, with the other component. In eleven systems, for pyridine+cyclohexane or +benzene, and benzene+cyclohexane systems, the heat of mixing was measured at 30.0°C, while for the other systems it was measured at 25.0°C. The heat of mixing for benzene with cyclohexane agrees with that of the literature.[5] Our results for the pyridine+benzene system were endothermic over the whole concentration range, though they were almost zero; Amaya[3,6] found that this system at 25.0°C changed from endothermic to exothermic in the neighborhood of an equimolar composition, though the absolute values will be very small. The heat of mixing at 30°C, $\Delta H^{M}_{x_i}(30°C)$, is related to that at 25°C, $\Delta H^{M}_{x_i}(25°C)$, as follows: $\Delta H^{M}_{x_i}(30°C) = \Delta H^{M}_{x_i}(25°C) + (30-25)C^{E}_{p}$, where C^{E}_{p} is the excess heat capacity. According to Morcom and Travers,[7] C^{E}_{p} for the pyridine-benzene system is positive. Therefore, our data seem to be consistent with those obtained by Amaya.

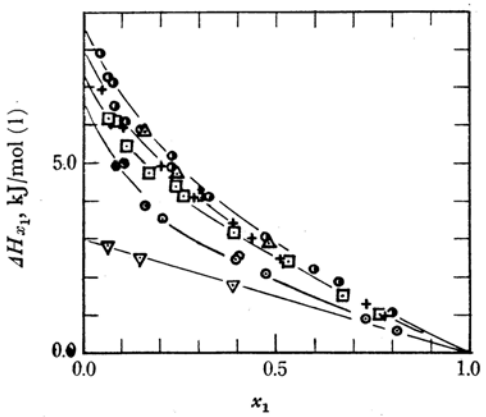

Fig. 1. Heat of mixing for pyridine derivative with cyclohexane.
◐ pyridine, ⊡ α-picoline, + β-picoline, △ γ-picoline, ⊙ 2,6-lutidine, and ▽ benzene with cyclohexane

The experimental data for ΔH_{x_i} have been plotted against the mole fraction in Figs. 1 and 2. By smoothing and extrapolating the curves to an infinite dilution for each system, we can obtain the heat of mixing per mole of the pyridine derivatives at an infinite dilution ($\lim_{x_i \to 0} \Delta H_{x_i}$). These values are given in Table 2.

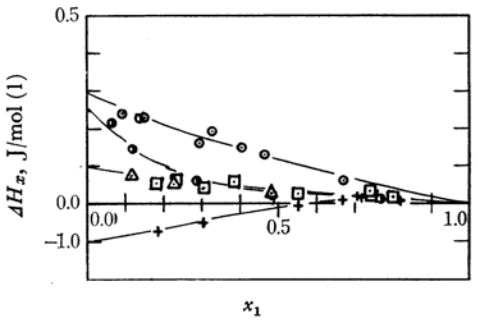

Fig. 2. Heat of mixing for pyrine derivative with benzene.
◐ pyridine, ⊡ α-picoline, + β-picoline, △ γ-picoline, and ⊙ 2,6-lutidine with benzene

TABLE 2. HEAT OF MIXING AT INFINITE DILUTION

	in benzene: ΔH_c kJ·mol^{-1}	in cyclohexane: ΔH_a kJ·mol^{-1}
Pyridine	0.3	8.5
α-Picoline	0.1	7.3
β-Picoline	−0.1	7.9
γ-Picoline	0.1	8.5
2,6-Lutidine	0.3	6.5
Benzene		3.0 (: ΔH_b)

The values of $\lim_{x_i \to 0} \Delta H_{x_i}$ correspond to the energy changes from the pure pyridine derivatives state to that in which each pyridine derivative molecule is surrounded by a large amount of the solvent medium. As may be seen in Table 2, the values of $\lim_{x_i \to 0} \Delta H_{x_i}$ in benzene are cosiderably smaller than the corresponding values in cyclohexane. This may suggest that a pyridine derivative molecule exists more stably in a benzene solution, by making a specific interaction or by forming a complex with a benzene molecule, than in a cyclohexane solution. The possibility of such a complex formation is supported by the NMR[8] measurements for the pyridine-benzene system. Further, according to Ott *et al.*,[9] the positive excess heat capacity in the binary mixture shows the existence of a specific interaction, or the formation of a complex between the solvent and solute molecules, and the pyridine-benzene solution is a system in which the excess heat capacity is positive.

In order to estimate the interaction energy between a pyridine derivative and benzene molecules, we carried out a treatment described in the

5) A. E. P. Watson, I. A. McLure, J. E. Bennet and G. C. Benson, *J. Phys. Chem.*, **69**, 2753 (1965).
6) H. Loiseleur, J. C. Merlin and R. A. Paris, *J. Chim. Phys.*, **62**, 1380 (1965).
7) K. W. Morcom and D. N. Travers, *Trans. Faraday Soc.*, **62**, 2063 (1966).
8) J. N. Murrel and V. M. S. Gill, *ibid.*, **61**, 402 (1965).
9) J. R. Goates, R. J. Sullivan and J. Bevan. Ott, *J. Phys. Chem.*, **63**, 589 (1959); L. R. McKinnon and A. G. Williamson, *Aust. J. Chem.*, **17**, 1374 (1964).

previous paper.[1] In the enthalpy cycle shown in Fig. 3, ΔH_a is the energy of breaking up all the interaction between pure pyridine deriatives by adding a large quantity of cyclohexane; ΔH_b is equal to the value of $\lim_{x_i \to 0} \Delta H_{x_i}$ for the benzene-cyclohexane system, and ΔH_c is the energy change produced by the dilution of pure pyridine derivative with x mol of benzene, where $x \gg 1$: these enthalpy changes were also measured in the present work. ΔH_d consists of two parts; one is equal to $(x+1) \cdot \Delta H_b$, while the other is due to the enthalpy change from the state in which pyridine-benzene associated complexes are surrounded by benzene to that in which they are surrounded by cyclohexane. The latter part of ΔH_d may be put at zero, or even neglected because the two media have almost equal dielectric constants and the dipole stabilization energies of a complex in the two media are considered to be nearly equal.[10]

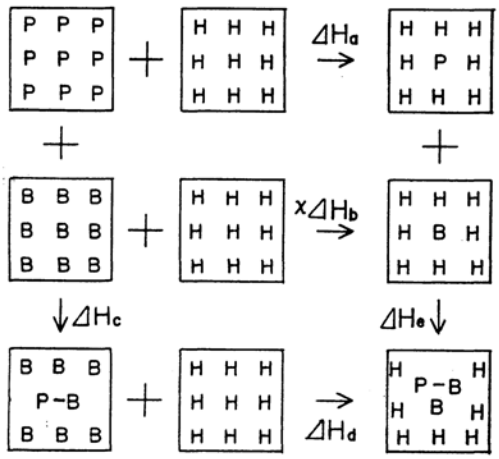

Fig. 3. Enthalpy cycle.[1]

The energies of the specific interaction between a pyridine derivative and benzene in the cyclohexane solution thus obtained from the enthalpy cycle:

$$\Delta H_e = \Delta H_c + \Delta H_d - \Delta H_a - \Delta H_b$$

are tablated in Table 3. Morcom *et al.*[7] measured the heats of mixing for the binary mixtures of carbon tetrachloride with pyridine derivatives; they found that there exists a specific interaction between carbon tetrahcloride and a pyridine derivative. Using their data,[7,11] and following the method of treatment described above, we calculated the specific interaction energies between pyridine derivatives and cabon tetrachloride; they are listed in Table 3. The strength of the specific interaction between

Table 3. The strength of the specific interaction for pyridine derivative with benzene, or carbon tetrachloride

	Benzene kJ·mol^{-1}	CCl_4 [7,11] kJ·mol^{-1}
Pyridine	−5.2	−7.4
α-Picoline	−4.2	−7.5
β-Picoline	−5.1	
γ-Picoline	−5.4	−8.3
2,6-Lutidine	−3.2	−7.2

pyridine derivatives and benzene in cyclohexane is in the order of; γ-pi$>$py$>\beta$-pi$>\alpha$-pi$>$2,6-lut, while the specific interactions between pyridine derivatives and carbon tetrachloride in cyclohexane solutions are in the order: γ-pi$>\alpha$-pi$\simeq$py$\simeq$2,6-lut.

A pyridine molecule has nonbonding lone pair electrons and π-electrons; these n- and π-electrons may be expected to play an important role in complex formation with other molecules. Therefore, the complex formation between pyridine derivatives and benzene may be considered to take place between n- or π-electrons in pyridine derivatives and between π-electrons in benzene. First, we will take up the n–π complex formation. The strength of the complex formation depends upon the ease with which n-electron can be released, and is measured by the pK_a value.[12] According to the pK_a value in Table 4, the strengths of the complexes

Table 4. The values of pK_a[12] and heat of reaction[13] for pyridine derivative with BF_3, $\frac{1}{2}B_2H_6$, and CH_3SO_3H

	pK_a	BF_3 kcal·mol^{-1}	$\frac{1}{2}B_2H_6$ kcal·mol^{-1}	CH_3SO_3H kcal·mol^{-1}
Pyridine	6.75	−17.5	−16.3	−19.5
γ-Picoline	6.02			
β-Picoline	5.68			
α-Picoline	5.97	−23.0	−17.2	−18.3
2,6-Lutidine	5.14	−25.0	−17.9	−17.1

will be in the following order: 2,6-lut$>\alpha$-pi$>\gamma$-pi$>\beta$-pi$>$py. In fact, the measurement[13] of the heats of reaction of pyridine derivatives with CH_3SO_3H shows that the absolute values of the heat of reaction increase with the pK_a value of pyridines, in accordance with the order mentioned above. However, our data obtained for the specific interaction of pyridine derivatives with benzene result in the opposite order except for γ-picoline. This inversion is not particularly surprising, however, since it has been known that

10) H. Fröhlich, "The Theory of Dielectrics," Clarendon Press, Oxford (1949), p. 49.
11) J. S. Rowlinson, "Liquid and Liquid Mxiture," Butterworths, London (1959), p. 153.
12) L. Sacconi, P. Paoletti and M. Ciampolinl, *J. Am. Chem. Soc.*, **82**, 3828 (1960).
13) C. T. Mortimer, "Reaction Heat and Bond Strength," Pergamon Press, London (1963), p. 111.

because of the steric hindrance of the methyl group of 2,6-lutidine or α-picoline, the heat of the reaction[10] of the pyridine derivative with BF_3, or $(1/2)B_2H_6$ is in the order of: py$>\alpha$-pi$>$2,6-lut.

Thus, it seems that the methyl group of 2,6-lutidine or α-picoline offers steric hindrance to the approach of the benzene molecule; this results in a corresponding decrease in the strength of the molecular interaction. We can qualitatively explain our result in terms of the n–π interaction. On the other hand, in the pyridine derivative-carbon tetrachloride systems we can find only a small change in the strength of the molecular interaction, as shown in Table 3. This may be illustrated as follows. Provided that the carbon tetrachloride molecule interacts with the nitrogen of the pyridine derivative, we know that the carbon tetrachloride molecule is not sterically interfered with so much as the benzene molecule by the methyl group of the pyridine derivative. The strengths of the interaction of pyridine, α-picoline, and 2,6-lutidine with carbon tetrachloride are nearly equal to each other as a result of the cancellation of the inductive effect of the electron-releasing by the methyl group and the effect of the steric hindrance.

On the other hand, the molecular interaction of the π-electrons of the pyridine derivative with the π-electron of the benzene molecule can be shown to be highly plausible. Comparing the ionization potential, or the electron affinity of the pyridine derivatives with that of benzene, it seems reasonable to regard the benzene molecule as a donor. In this case, it seems that the strengths of the interaction are in the order of: py$>\beta$-pi$>$ α-pi$>\gamma$-pi$>$2,6-lut. Our results show the same trend except for γ-pi.

Then, it seems reasonable to explain the specific interaction of pyridine derivatives with benzene in terms of a n–π interaction. On the basis of a thermochemical study alone, however, it can not be decided whether the specific interaction of pyridine derivatives with benzene is an n–π or π–π interaction.