

EMPIRICAL RESONANCE ENERGIES FOR BENZENE AND PYRIDINE

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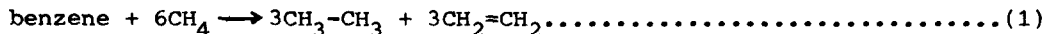
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Summary: Empirical resonance energies are calculated for benzene and pyridine from both experimental  $\Delta H_f^\circ$  data and from total molecular energies obtained using the 6-31G\* basis set, as the energy change for three distinct types of reaction. The results show that the aromatic stabilization of pyridine and benzene is essentially the same.

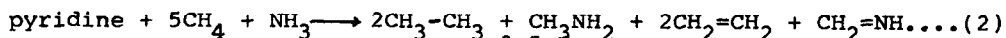
It has been suggested that since the enhanced stability of aromatic molecules is due to the  $\pi$ -electrons, and because the nitrogen atom in a six-membered heteroaromatic ring attracts electrons from this layer, pyridine should be less stable than benzene and this loss of stability should be reflected in a smaller empirical resonance energy.<sup>1,2</sup> The purpose of this study is to ascertain whether the values obtained using current  $\Delta H_f^\circ$  data and values of  $\Delta E_\pi$  calculated ab initio using the 6-31G\* basis set with full geometry optimization support this conclusion, and to enquire into the meaning of such energy difference.

Empirical resonance energies obtained from thermochemical data, no matter by what procedure, are tantamount to the evaluation of  $\Delta H^\circ$  for certain reactions involving the aromatic molecule and other specified molecules whose bonding energy serves as the reference.<sup>3</sup> The procedures utilizing increments in heats of combustion, increments in heats of formation, or bond energy terms, are equivalent to evaluating  $\Delta H^\circ$  in the case of benzene for reactions of the type



where  $\text{CH}_4$ ,  $\text{CH}_3\text{-CH}_3$  and  $\text{CH}_2=\text{CH}_2$  are the reference molecules.

The corresponding reaction for pyridine<sup>4</sup> is

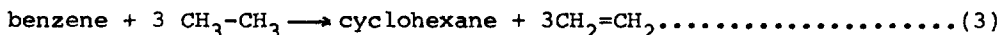


But, as pointed out in previous papers,<sup>3,5,6</sup> the  $\Delta H^\circ$  values for these isodesmic bond separation reactions<sup>7</sup> are made up in part from contributions due to changes in the number and type of C/C and C/N bonds, and changes in the number of hydrogen atoms bonded to the carbon atoms with C(3) and C(4) connectivity and the nitrogen atoms with N(2) and N(3) connectivity. Hence the magnitude of the  $\Delta H^\circ$  values cannot be taken simply as an assessment of the enhanced stability.

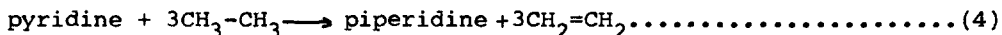
The procedures introduced by Kistiakowsky et al.<sup>8</sup> and by Dewar and Schmeising<sup>9</sup>, namely taking the difference between the hydrogenation heat for the aromatic molecules and the heat of hydrogenation for the appropriate number of cyclohexene or ethylene molecules respectively, are equivalent, in the case of benzene for example, to the evaluation of  $\Delta H^\circ$  for the reactions



and

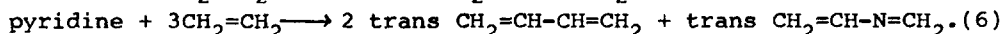
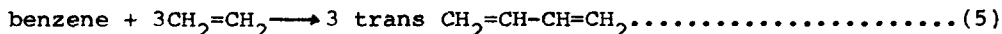


For pyridine<sup>4</sup> the reaction corresponding to (3) is



But reactions of this type are also mismatched with respect to the bonding criteria referred to above<sup>3,5,6</sup>, and hence extraneous energy changes again contribute to the  $\Delta H^\circ$  values.

A procedure in which these bonding criteria are met involves the use, for example, of ethylene and the appropriate conjugated diene(s) as the reference molecules,<sup>4,5,10</sup> e.g.



In these homodesmotic reactions the empirical resonance energy of the aromatic molecule is, in effect, evaluated relative to whatever the resonance energy may be for the diene(s), but this can be allowed for to a considerable extent by using the 90°-rotamer(s) as reference.<sup>6</sup>

Empirical resonance energies for benzene and pyridine evaluated as the energies for reactions (1)-(6) are listed in the Table. For a rigorous comparison heat capacity and zero-point energy corrections would have to be made,<sup>5,7</sup> but in any case close agreement between the experimental and ab initio values is not to be expected in view of basis set truncation effects and the neglect of correlation energy. What is significant in the present context is

Table. Empirical Resonance Energies (kcal mol<sup>-1</sup>)

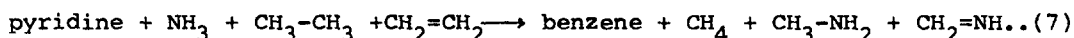
	$\Delta H_{298}^{\circ}$ (expt.) <sup>a</sup>	$\Delta E_{\pi}$ (calc.) <sup>b</sup>
<u>Isodesmic Bond Separation</u> <sup>7</sup>		
1. benzene + 6CH <sub>4</sub> → 3CH <sub>3</sub> -CH <sub>3</sub> + 3CH <sub>2</sub> =CH <sub>2</sub>	64.1 ± 1.7	58.2
2. pyridine + 5CH <sub>4</sub> + NH <sub>3</sub> → 2CH <sub>3</sub> -CH <sub>3</sub> + CH <sub>3</sub> NH <sub>2</sub> + 2CH <sub>2</sub> =CH <sub>2</sub> + CH <sub>2</sub> =NH	65.5 ± 1.6 <sup>c</sup>	60.7
<u>Reduction by Ethane</u> <sup>9</sup>		
3. benzene + 3CH <sub>3</sub> -CH <sub>3</sub> → cyclohexane + 3CH <sub>2</sub> =CH <sub>2</sub>	48.4 ± 1.2	-
4. pyridine + 3CH <sub>3</sub> -CH <sub>3</sub> → piperidine + 3CH <sub>2</sub> =CH <sub>2</sub>	52.2 ± 1.7	-
<u>Homodesmotic Group Separation</u> <sup>4,5,10</sup>		
5. benzene + 3CH <sub>2</sub> =CH <sub>2</sub> → 3 trans CH <sub>2</sub> =CH-CH=CH <sub>2</sub>	21.6 ± 1.5	24.8
6. pyridine + 3CH <sub>2</sub> =CH <sub>2</sub> → 2 trans CH <sub>2</sub> =CH-CH=CH <sub>2</sub> + trans CH <sub>2</sub> =CH-N=CH <sub>2</sub>	-	25.4

a.  $\Delta H_{298}^{\circ}$  values calculated from  $\Delta H_f^{\circ}$  data.<sup>11</sup>

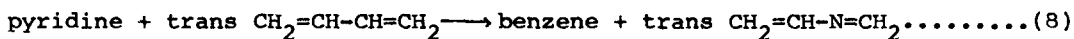
b.  $E_{\pi}$  values calculated using the GAUSSIAN 82 program and the 6-31G\*(5D) basis set with full geometry optimization.

c. Using an estimate of +20.0 kcal mol<sup>-1</sup> for  $\Delta H_f^{\circ}(\text{CH}_2=\text{NH})$ <sup>12</sup>; the uncertainty of ±1.6 kcal mol<sup>-1</sup> does not include any allowance for the uncertainty in this  $\Delta H_f^{\circ}$  value.

that the values for pyridine are consistently greater, and thus do not bear out the expectation that electron withdrawal by the nitrogen should lead to a smaller empirical resonance energy. Be that as it may, whatever the difference is, it cannot be attributed solely to the benzene and pyridine since the empirical resonance energies themselves are not uniquely a property of the aromatic molecule. The differences amount to  $\Delta H^{\circ}$  for composite reactions in which there is an interchange of structural features between the aromatic molecules and the aliphatic reference molecules, i.e. for reactions (1) and (2),



and for reactions (5) and (6),



The finding that  $\Delta E_T$  is so small for reaction (8), less than 1 kcal mol<sup>-1</sup>, shows the effect of substituting =N- for =CH- to be almost identical in benzene and the aliphatic diene.

Acknowledgement. We gratefully acknowledge the generous grant of computer time provided by the Computer Center of the Philadelphia College of Textiles and Science.

#### References and Notes

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2. Values reported in the older literature overlap, and thus leave the question open : e.g. for benzene 35.9, 36, 36.0, 36.0, 36.4, 37 and 41 kcal mol<sup>-1</sup>, and for pyridine 21, 22, 23.0, 27.2, 27.9, 31, 32, 35, 37.3, 43 and 43 kcal mol<sup>-1</sup>, see K. Schofield, "Hetero-Aromatic Nitrogen Compounds", Plenum Press, N. Y., 1967, chap. 2, Table 2.1.
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(Received in USA 28 May 1985)