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AROMATIC RESONANCE ENERGIES FROM EQUILIBRIUM DATA[1]

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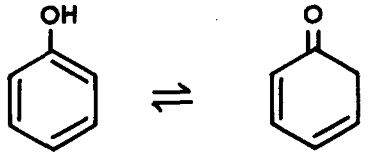
We recently[2] used tautomeric equilibria to estimate aromatic resonance energies for 2-pyridone and analogues. Resonance energies, or more precisely, resonance energy differences between two structures, are in principle quite generally available from equilibrium constants, provided the deduced $\Delta \underline{G}^{o}$ values can be converted into $\Delta \underline{H}^{o}$. We wish now to report the use of keto-enol, protonation, and pseudobase equilibria to deduce aromatic resonance energies for benzene, uracil, pyrrole, carbazole and isoquinoline.

Benzene. The resonance energy ($\underline{A}_{benzene}$) of the aromatic ring of phenol (1) is related to the resonance energy ($\underline{A}_{dienone}$) of 2, 4-cyclohexadienone (2) by Eq. 1 where $\Delta \underline{H}^{o}_{u}$ refers to the tautomeric equilibrium 1 $\rightleftharpoons$ 2 and $\Delta \underline{H}^{o}_{s}$ to the corresponding tautomeric equilibrium 3 $\rightleftharpoons$ 4. The treatment assumes that the enthalpy difference between 3 and 4 is a satisfactory approximation for the difference between the enthalpies of the hypothetical non-delocalised analogues of 1 and 2: for a justification see Ref. 3.

$$\underline{A}_{benzene} - \underline{A}_{dienone} = \Delta \underline{H}^{o}_{s} - \Delta \underline{H}^{o}_{u} \qquad (1)$$



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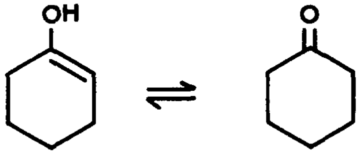

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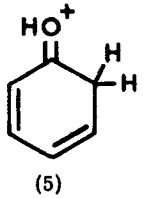

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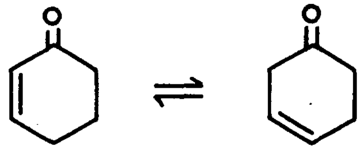


(6) (7)

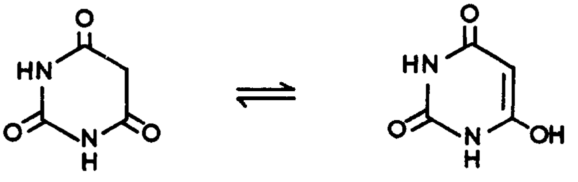
The cyclohexenol-cyclohexanone equilibrium 3 $\rightleftharpoons$ 4 has been measured directly[4] as 2.4×10^{5} and can be estimated from kinetic data[5] of ketone enolisation and enol ether hydrolysis as 2.0×10^{5}; these values indicate a $\Delta \underline{G}^{o}_{u}$ of -7.5 ± 0.5 kcal mole.$^{-1}$

The tautomeric equilibrium 1 $\rightleftharpoons$ 2 can be discussed in terms of protonation of each tautomer to the common cation 5. Phenol has a $\underline{H}_{o}$ of half protonation at the 4-position[6] of -7.04;[7]

however, this protonation probably follows the $\underline{H}_c$ and not the $\underline{H}_o$ acidity function[8] and the corresponding $p\underline{K}_a$ is therefore -11.3. The $p\underline{K}_a$ for protonation at the 2-position of phenol must be lower than this, as the 2-protonated species is not detected in the NMR spectrum; however, it will probably not be much lower as the kinetic acid-catalysed exchange rates of protons at the 2- and 4-positions are comparable (cf discussion in Ref. 9). We therefore take -12 ± 2 as the $p\underline{K}_a$ for protonation of phenol at the 2-position. The $p\underline{K}_a$ for cyclohexadienone (2) can be estimated as -2.5 ± 0.5 from the following data[10]: cyclohexanone, $p\underline{K}_a$ -5.6 by Arnett's calorimetric method[11] ($\underline{H}_o$ for half protonation -7.1[12]); 2-cyclohexenone $p\underline{K}_a$ -3.6 ($\underline{H}_A$ acidity function behaviour followed).[13] Hence, for the equilibrium 1 ⇌ 2, we estimate log $\underline{K}_T$ as 9.5 ± 2.5 corresponding to $\Delta \underline{G}^o$ of 13 ± 3 kcal mole^{-1}.

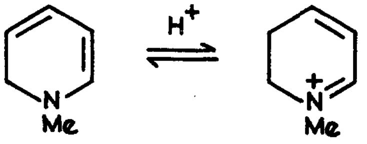
A detailed consideration of the conversion of $\Delta \underline{G}^o$ into $\Delta \underline{H}^o$ indicates[3] that for tautomeric equilibria $\Delta \underline{H}^o = (1.2 \pm 0.1)\,\Delta \underline{G}^o$. Hence from the difference between these two equilibria, we estimate $\Delta \underline{H}^o$ as 25 ± 5 kcal mole^{-1} for the difference in the resonance energies of 1 and 2. For the equilibrium 6 ⇌ 7,[14] $\Delta \underline{G}^o = 3.2$ kcal mole^{-1}: thus a value of 6 ± 1 kcal mole^{-1} seems appropriate for the resonance energy of cyclohexadienone. Hence, we obtain 31 ± 6 kcal mole^{-1} for the resonance energy of the benzene ring.

Uracil. Using a similar approach the aromatic resonance energy of uracil ($\underline{A}_{uracil}$), ie. the extra stabilisation of the molecule over the hypothetic structure in which the C_5-C_6 bond is not conjugated with the remainder of the molecule, is obtained from the difference in $\Delta \underline{H}^o$ for the equilibrium 3 ⇌ 4 and that for barbituric acid 8 ⇌ 9. For barbituric acid, the trioxo form (8) is favoured by $\Delta \underline{G}^o = 2.6$.[15] Together with the data quoted above for 3 ⇌ 4, and placing $\Delta \underline{H}^o = (1.2 \pm 0.1)\,\Delta \underline{G}^o$, this gives a value of 5 ± 2 kcal mole^{-1} for the resonance energy difference between 8 and 9. $\underline{A}_{uracil}$ will be larger than this in view of the extra conjugation of the third carbonyl group in structure 8.



(8) (9)

Pyrrole. The low basicity of pyrrole at the ring carbon atoms ($p\underline{K}_a$ of protonation of 1-methylpyrrole -2.9 and ca -5.1[16] at the α- and β-position, respectively) is due to the loss of resonance energy on protonation. Thus dieneamines 10 and 11 possess $p\underline{K}_a$ values of ca 9.5[17] and 7.4[17] respectively for protonation to cations comparable π-electronically with the cations derived from α and β protonation of 1-methylpyrrole. The differences of 12.4 and 12.5 between the $p\underline{K}_a$ values of these dienamines and the corresponding $p\underline{K}_a$ values for 1-methylpyrrole protonation can be converted[3] into $\Delta\Delta \underline{H}^o$ values of 20 ± 4 and 21 ± 4 kcal mole.$^{-1}$ The resonance energy of 11 has been estimated as ca 6 kcal mole^{-1}, hence $\underline{A}_{\text{pyrrole}}$ = 27 ± 4 kcal mole.$^{-1}$* The p$\underline{K}_{\underline{a}}$ value for the protonation of pyrrole in the 1-position has been estimated[19] as ca -10: although the uncertainty is considerable, this also leads to a similar value for the aromaticity of pyrrole.[18]



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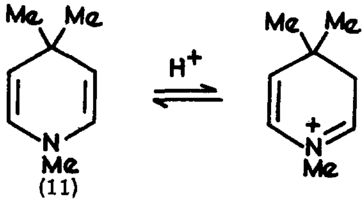
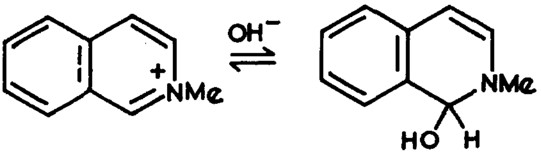


(11)

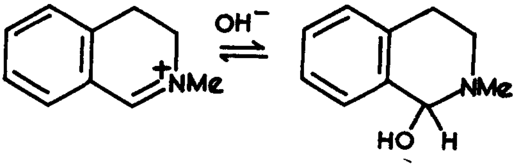
Carbazole. From the p$\underline{K}_{\underline{a}}$ of carbazole ca -6[19] and dibenzoquinuclidine +4.46[20] the $\Delta \underline{H}^{o}$ difference between their resonance energies is deduced as 17 ± 3 kcal mole.$^{-1}$ The resonance energy of benzene reported above is 31 ± 6 kcal mole^{-1}, hence $\underline{A}_{\text{carbazole}}$ = 79 ± 9 kcal mole.$^{-1}$

Isoquinoline. The p$\underline{K}_{\underline{a}}$ values for the equilibria 12 ⇌ 13 and 14 ⇌ 15 were measured as 16.29 and 10.75 respectively. This corresponds to a $\Delta \underline{H}^{o}$ difference of 9.2 kcal mole.$^{-1}$ Equation 2 follows where the terms x and y are the differences in resonance energies between 13 and benzene and 14 and benzene respectively.

$$\underline{A}_{\text{isoquinoline}} = \underline{A}_{\text{benzene}} + 9.2 + x + y \qquad (2)$$



(12) (13)



(14) (15)

The resonance energy, as deduced from thermochemical data of ethyl vinyl ether is 3.6 kcal mole^{-1} and the value for styrene less that of benzene is about 2:[21] assuming values of 6 ± 2 and 2 ± 1 for x and y respectively, we obtain a value for $\underline{A}_{\text{isoquinoline}}$ of 48 ± 9 kcal mole.$^{-1}$

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*During the preparation of this paper D. Lloyd and D. R. Marshall [Chem. Ind. 335 (1972)] reported results of a similar approach. We report our results here because we use different models, different p$\underline{K}_{\underline{a}}$' data and obtain different values for resonance energies.

[1] Part III of series Aromaticity and Tautomerism. For part II see M. J. Cook, A. R. Katritzky, P. Linda and R. D. Tack, submitted to *J. C. S. Perkin II*

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