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Tautomerism of Phenols—A Theoretical Study

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Keto-enol tautomerism in the polyacene series presents an interesting theroretical problem, since in the higher polyacene phenols the keto form is more stable, in contrast to the lower polyacene phenols where the enol form is more stable.[3] Although this displacement of equilibrium in the keto-enol tautomerism of phenols has been known for some time,[3] there are only a few theoretical studies, within the framework of the HMO theory, reported for these systems.[4]

Here we wish to report calculations of keto-enol tautomerism of the phenols based on Dewar's variant of the SCF π-MO method, which has been described in detail elsewhere.[5]

Theoretical Method

The location of a chemical equilibrium is determined by the variation of free energy (ΔF). Since free energy depends upon enthalpy and entropy, the equilibrium constant (K) can be expressed as a function of the variations of enthalpy (ΔH) and entropy (ΔS) of the compounds in the equilibrium:

$$-\boldsymbol{R}T\ln K = \Delta F = \Delta H - T\Delta S \qquad (1)$$

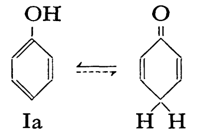
The entropy variation for a given reaction occurring in a series of related compounds under the same experimental conditions remains essentially constant and thus can be neglected.[6] Making the usual assumption[6,7] that the difference in the keto and enol forms is due to changes in the heats of atomization rather than the enthalpy of reaction, the equilibrium can be expressed as follows:

$$-\boldsymbol{R}T\ln K = \Delta H_a^{\mathrm{A}} - \Delta H_b^{\mathrm{B}} \qquad (2)$$

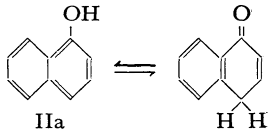
where ΔH_a^{A} and ΔH_a^{B} are the heats of atomization of the keto and enol form, respectively. Therefore, the position of equilibrium is determined essentially by the difference in the heats of atomization between the two tautomeric forms of phenols. The heats of stomization for the tautomeric forms in question can be calculated by Dewar's SCF π-MO (variable β)[4b] procedure.[4]

Results and Discussion

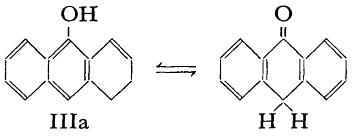
The systems studied are presented below.



Ia Ib



IIa IIb



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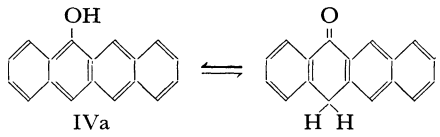

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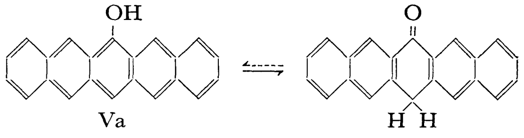

Va Vb

Table 1 lists the heats of atomization of tautomeric forms of phenols (A being phenol forms, B being

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[3] E. Clar, "Polycyclic Hydrocarbons," Vol. 1, Academic Press, New York (1964), p. 108.

[4] a) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York (1961), p. 250. b) B. Pullman and A. Pullman, Quantum Biochemistry, Interscience Publishers, New York (1963), p. 123.

[5] a) A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, **42**, 756 (1965). b) M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 685 (1965). c) M. J. S. Dewar and C. de Llano, *ibid.*, **91**, 789 (1969). d) M. J. S. Dewar and T. Morita, *ibid.*, **91**, 796 (1969). e) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York (1969).

[6] M. J. S. Dewar, *Advan. Chem. Phys.*, **8**, 65 (1965).

[7] a) M. J. S. Dewar and T. Morita, *J. Amer. Chem. Soc.*, **91**, 802 (1969). b) M. J. S. Dewar and N. Trinajstić, *Tetrahedron*, **25**, 4529 (1969).

Table 1. Heats of atomization of tautomeric forms of phenols

Tautomer A	ΔH_a^A (eV)	Tautomer B	ΔH_a^B (eV)	$\Delta H_a^A - \Delta H_a^B$ (kcal/mol)
Phenol (Ia)	-61.6675	Keto form (Ib)	-60.6913	-22.5
α-Naphthol (IIa)	-95.1193	Keto form (IIb)	-94.5830	-12.4
Anthranol (IIIa)	-128.4071	Anthranone (IIIb)	-128.4679	$+1.4$
Hydroxytetracene (IVa)	-161.6223	Tetracenone (IVb)	-161.9402	$+7.3$
Hydroxypentacene (Va)	-194.8007	Pentacenone (Vb)	-195.4114	$+14.5$

keto forms) and the differences in the heats of atomization between these forms. The obtained results appear to be in a good agreement with present experimental evidence.

The experimental evidence can be summarized as follows; there is no indication in literature that phenol (Ia) exists to any appreciable extent in the keto form (Ib), the equilibrium being heavily located on the phenol form. However, the keto form (Ib) is apparently quite stable when substituents are attached to the ring;[8] the substituents may stabilize this form considerably. Naphthol (IIa) shows some reactions which point to existence of keto form (IIb), but here again as in the case of phenol only the substituted keto form (IIb) is stable enough to be isolated.[9] In anthracene series the keto form (IIIb) is in a slightly more stable form in the equilibrium. The equilibrium anthranol (IIIa) $\rightleftharpoons$ anthranone (IIIb) has been fairly thoroughly investigated recently by Löber[10] and Baba and Takemura[11] using spectrometric methods (absorption and fluorescence spectrometry). The equilibrium was found[11] to be solvent dependent and the enthalpy change indicated a slight displacement of the equilibrium to the keto form (IIIb) in the less polar solvents ($_{293}\Delta H = 2.6$ kcal/mol in benzene; $_{293}\Delta H = 3.3$ kcal/mol in isooctane).[11] The anthranol/anthranone equilibrium can be pushed on the anthranol side by adding basic substances.[13] This has been used for the preparation of anthranol from anthranone.[12,13] However, even pure anthranol is not stable and after some time a chemical equilibrium sets up between these two tautomers.[14] Tetracenone is a stable species and well known.[15] It can be transformed into hydroxytetracene (IVa) only in an alcoholic alkali solution.[15] There is no evidence, so far, that pentacenone (Vb) can be enolized to hydroxypentacene (Va),[3,16] although the pure keto form (Vb) has been isolated and studied.[16,17]

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8) *i. e.* H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962); V. Ershov, A. A. Volod'kin and G. N. Bogdanov, *Uspekhi himii*, **32**, 1954 (1963); W. Ried and E. Torok, *Liebigs Ann. Chem.*, **687**, 232 (1965); B. Miller, *Tetrahedron Lett.*, **1964**, 3527; *ibid.*, **1965**, 1727; G. Legler and B. Quiring, *Tetrahedron*, **23**, 2683 (1967).

9) *i. e.* R. T. Arnold, J. S. Buckley, Jr., and J. Richter, *J. Amer. Chem. Soc.*, **69**, 2322; (1947); H. E. Zimmerman, R. C. Hahn, H. Morrison and M. C. Wani, *ibid.*, **87**, 1138 (1965); J. W. Huffman and T. W. Bethea, *J. Org. Chem.*, **30**, 2956 (1965); V. D. Shteingarts, G. G. Jakobson and N. N. Vorozhtsov, Jr., *Doklady Akad. Nauk SSSR*, **170**, 1348 (1966); L. H. Klemm, J. Shabatai and P. R. Taylor, *J. Org. Chem.*, **33**, 1480, 1489 (1968); P. B. D. de la Mare and H. Suzuki, *J. Chem. Soc.*, *C*, **1968**, 648.

10) G. Löber, *Acta Chim Acad. Sci. Hung.*, **40**, 9 (1964); *Z. Wiss. Phot. Photophys. Photochem.*, **59**, 20 (1965); *Z. Phys. Chem.* (Frankfurt), **54**, 73 (1967).

11) H. Baba and T. Takemura, This Bulletin, **37**, 1241 (1964); *Tetrahedron*, **24**, 4779, 5311 (1968).

12) K. H. Mayer, *Liebigs Ann. Chem.*, **397**, 37 (1911); K. H. Mayer and A. Sander, *ibid.*, **396**, 133 (1913); *ibid.*, **420**, 113 (1920).

13) Anthranol has been obtained from anthranone also by the irradiation of the degassed ether solution by a light flash (S. Kanamaru and S. Nagakura, This Bulletin, **39**, 1355 (1966).

14) Y. Bonsho and K. Nukada, This Bulletin, **33**, 579 (1960).

15) L. F. Fieser, *J. Amer. Chem. Soc.*, **53**, 2329 (1931); E. de B. Barnett and R. A. Lowry, *Ber.*, **65B**, 1649 (1932); C. Dufraisse and H. Vayson de pradenne, Festhr. Arthur Stoll 1957, 701.

16) E. Clar, *Chem. Ber.*, **82**, 495 (1949).

17) W. H. Mills and M. Mills, *J. Chem. Soc.*, **1912**, 2194; C. Marshalk, *Bull. Soc. Chim. Fr.*, **1937**, 1381, 1547.