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2-BENZYLAMINO-4-BENZYLIMINO-2-PENTENE. EVIDENCE FOR ANOTHER NON-CLASSICAL AROMATIC SYSTEM INVOLVING π-ELECTRONIC INTERACTION THROUGH THE HYDROGEN BOND

Linneaus C. Dorman

Edgar C. Britton Research Laboratory
The Dow Chemical Company, Midland, Michigan

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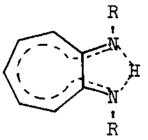
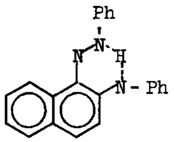
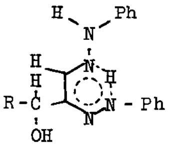
Recently, theoretical, chemical and physical evidence has been presented in support of three non-classical* aromatic systems, I[2], II[3] and III[4], involving π-electronic interaction or electron delocalization through the hydrogen bond.



I



II



III

Some of the evidence includes molecular orbital calculations, which when performed on II to determine the total π-electron energies, indicates that a π-electron interaction through the hydrogen bond probably exists, based on the total π-electron energies;[3] X-ray data showed that the six-membered chelate ring in III is essentially coplanar with the benzene rings and has bond angles around 120°;[4] n.m.r. and infrared data indicated equivalence of the ring protons of I and of the two nitrogen atoms and the dipole moment (1.24 D) is directed toward the ring. Hence, the aromatic character of I is best interpreted in terms of a ten π-electron system involving four formal double bonds (3 $>C=C<$ and 1 $>C=N/$) and the lone-pair electrons from one of the nitrogens.[2(c)]

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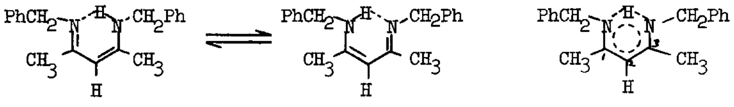
*In view of a recent definition[1] of <u>quasi</u>- and <u>pseudo</u>-aromatic compounds, the type of compounds under discussion here are termed non-classical aromatic as used by Benson and co-workers[2].

We now wish to present evidence for another non-classical aromatic system involving probable π-electronic interaction through the hydrogen bond, viz., 2-benzylamino-4-benzylimino-2-pentene, IV.

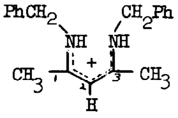


(a) (b) (c)

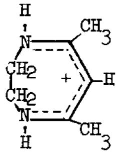
Tautomeric Forms Non-Classical Aromatic Form

IV

The principal evidence for non-classical aromatic character in IV is derived from n.m.r. data. The n.m.r. spectrum of IV ($CDCl_3$ solution, FIG. 1) shows only one sharp singlet for the two methyls, the two methylenes, and the two phenyl groups indicating their respective equivalence as well as equivalence of the nitrogens. The N-H proton is observed as a very shallow peak at -11.5 p.p.m., it is quite obvious at higher spectral amplitudes and disappears on deuteration. The large para-magnetic shift is indicative of a hydrogen-bonded chelate ring.[5] Although these observations are consistent with structure IV-c, they do not rule out a rapid tautomeric interconversion between forms IV-a and IV-b. When IV is protonated, the n.m.r. spectrum of the resulting cation, V ($CDCl_3$ solution, FIG. 2), shows that the methyl and vinyl protons (3-position) have been shifted downfield by 0.47 and 0.15 p.p.m., respectively



V



VI

relative to their positions in IV. These paramagnetic shifts are readily attributed to the increase in positive charge at the 1-, 2- and 3-positions. Similarly, it would also be expected that the methylenic hydrogens of V be

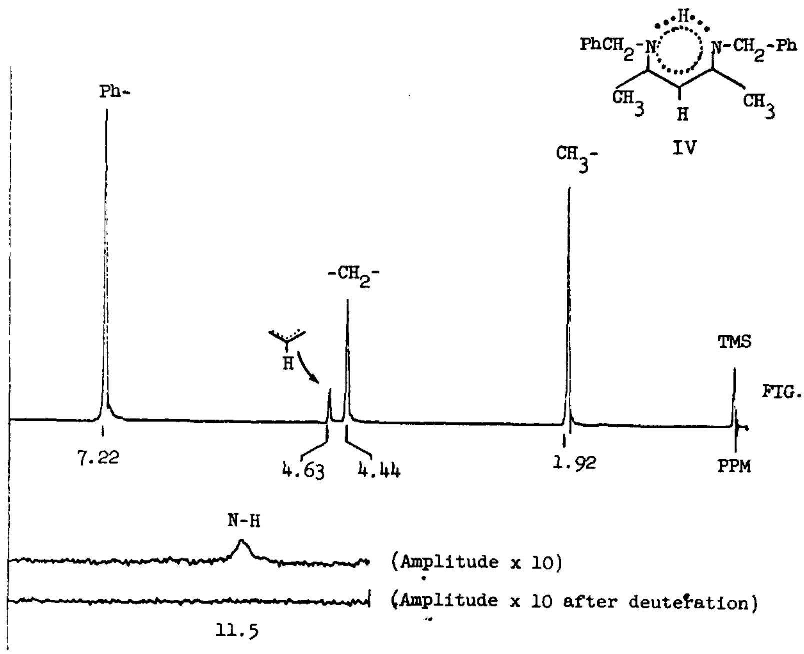


FIG. 1

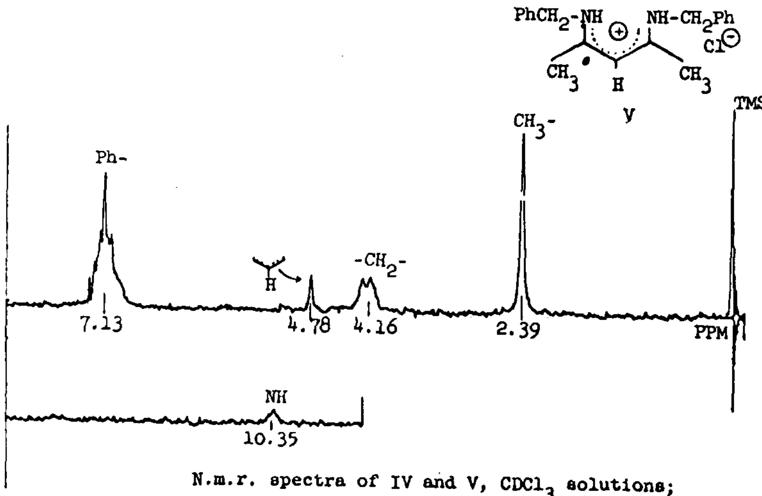


FIG. 2

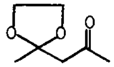
N.m.r. spectra of IV and V, $CDCl_3$ solutions; Varian A-60 (60 Mc/sec.) spectrophotometer.

shifted downfield because of the increase in positive charge on the adjacent nitrogens. Instead, the methylenic peak of cation V (split into a doublet by N-H) is shifted upfield by 0.28 p.p.m. Apparently, the methylenic hydrogens are more deshielded in the free base IV than in the cation V. This greater deshielding of $-CH_2-$ in the free base is best interpreted in terms of the non-classical aromatic structure IV-c in which ring currents result by virtue of electron delocalization or π-electronic interaction through the hydrogen bond. As in the other examples, II-III, the π-electron system involves two formal double bonds and the lone-pair electrons on one of the nitrogens. The general n.m.r. spectral patterns observed for IV and V in deuterochloroform as well as the relative differences in the chemical shifts of their respective peaks were also observed in methylene chloride solution, i.e., Δ p.p.m. (IV-V): (CH_3), -0.52, ($>$-H), -0.22, (CH_2), +0.22, (Ph), ca. +0.01, (H), +0.77.

Ultraviolet data are also in accord with structure IV-c for the free base. The free base has $\lambda_{max}^{MeOH} = 322$ mμ, $\log \epsilon = 4.60$, whereas the cation has $\lambda_{max}^{MeOH} = 321$, $\log \epsilon = 4.62$. If the base had a classical acyclic conjugated system, then its λ_{max} might be expected to appear at a shorter wavelength such that a bathochromic shift would result on protonation.[6] In addition, the cation would also be expected to absorb at a higher wavelength than the base because of its greater symmetry assuming the base to have a classical structure like IV-(a or b) in which the N-H bond length would probably differ from the N---H length. The fact that the base absorbs at about the same place as the cation is support for structure IV-c which depicts a symmetrical, closed conjugated system by virtue of π-electronic interaction through the hydrogen bond.

Ironically, cationic systems like V have been termed quasi-aromatic[1] on the basis of their high stability[7] and ability to undergo electrophilic substitution reactions as exemplified by the 2,3-dihydro-5,7-dimethyl-1,4-diazapine cation, VI[8]. Base IV is stable for about six months when stored in a desiccator shielded from diffuse light. Light appears to accelerate the decomposition, this appears to be a general property of these kinds of compounds[9]. We intend to study other physical and chemical properties of IV.

Base IV was prepared by a reaction that appears not to have been previously described in the literature. Heating 4-ethylenedioxy-2-pentanone* with a small excess of benzylamine on the steam bath for ca. 40 min. followed by trituration with a little methanol gave IV (44%), white needles, m.p. 83-84° (hexane). Anal. Calcd. $C_{19}H_{22}N_2$: C, 81.97; H, 7.97; N, 10.06; mol. wt., 278. Found: C, 82.12; H, 8.05; N, 9.78; mol. wt., 271; infrared, $\lambda_{max}^{CCl_4/CS_2}$, 3.26, 3.31, 6.68, 6.89, 9.42, 9.8, 13.74, 14.43 ($PhCH_2$-), 6.18, 6.42 (double bonds), 7.26 (CH_3-)μ. The N-H absorption starts at ca. 3.0 and ends at ca. 4.0μ, appears to be weak, shallow and largely masked by C-H vibration bands. Identity of the N-H absorption was confirmed by the spectrum of the N-D derivative. The weak shallow absorption band absorbing between ca. 3-4μ disappeared and a new band appeared at 4.41μ attributable to N-D.

 $+ \ 2\ PhCH_2NH_2 \longrightarrow$ IV

Treatment of IV with ethereal HCl gives V, m.p. 166.5-168° ($CHCl_3$-Et_2O). Anal. Calcd. for $C_{19}H_{23}ClN_2$: C, 72.48; H, 7.36; N, 8.90; Cl, 11.26. Found: C, 72.60; H, 7.28; N, 8.82; Cl, 11.11.

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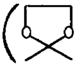
* Prepared from acetylacetone and ethylene glycol, p-toluenesulfonic acid catalyst, benzene solution under azeotropic removal of water. Best distillation fraction contained 90% product, 6.3% diketal, and 3.7% glycol monoacetate[10]; g.l.c. sample, $\lambda_{max}^{CCl_4}$ = 5.82 (), 9.44 ()μ

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