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N,N-DIMETHYLBENZO-1,6-DIHYDRO-1,6-DIAZOCINE. A 14π ELECTRON HETEROCYCLE.

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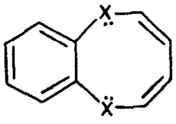
In the past several years considerable effort has been devoted to studying the criteria necessary for the existence of aromaticity. This work has resulted in the synthesis of numerous carbocyclic anions, cations, and neutral molecules,[2] all of which have displayed properties consistent with the original prediction made by E. Huckel.[3]

It was originally believed that the inclusion of heteroatoms only slightly perturbs the π-system, and Huckel's rule is valid for heterocyclic as well as carbocyclic molecules.[2] Although this extrapolation leads to the correct prediction that pyrrole should be aromatic, the criteria necessary for the existence of heteroaromaticity have not been completely defined experimentally.

Heterocycles of the type 1 contain 14π electrons and, if planar, they should be stabilized by cyclic delocalization. The oxygen derivative has been prepared and from an examination of its properties it was found to be non-aromatic.[4]

	X
Ia,	Ö
Ib,	N̈CH₃



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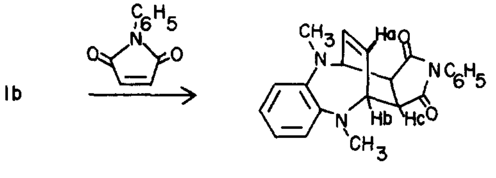
Dreiding molecular models indicate that a relatively unstrained conformer exists which places the two nitrogen atoms and the four carbon atoms of the eight-membered ring in one plane. Another plane intersecting the first plane contains the benzene ring and the two nitrogen atoms. The ultraviolet spectrum shows a long wavelength absorption at 348 nm (ϵ = 27,900). This is consistent with long wavelength previously reported for a similar conjugated bis-enamine.[12]

Diazocine 1b in contrast to cyclooctadiene is very reactive as a diene toward dienophiles. It reacts rapidly with N-phenylmalemide giving cycloadduct 5. This is consistent with the non-aromatic structure proposed. Structure 5 is based mainly on the nmr spectrum which shows: τ2.40-3.06 (m,9H,aromatics); 3.86-4.06 (m,2H,H_a); 5.91-6.10 (m,2H,H_b); 6.18 (broad singlet,2H,H_c) and 6.91(s,6H,N-CH_3).



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If 1b possessed additional stability due to cyclic delocalization of π electrons then it should be a relatively weak base. The pKa's of enamine 1b and amine 2 are 3.53 ± 0.13 and 4.83 ∓ 0.06 respectively.[13] The difference between enamine 1a and amine 2 is 1.30 pKa units and is consistent with the values normally observed for enamines and their secondary amine bases.[13] This result further substantiates the non-aromatic structure proposed for 1b.

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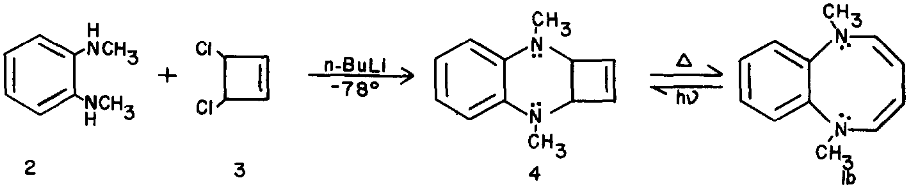
Because of its large electronegativity, oxygen is known to be a poor heteroatom for the construction of aromatic ring systems. For example, furan behaves as a diene in many of its reactions[5] and Anastassiou has recently observed that 1*H*-azonine is aromatic whereas the oxygen analog, oxonin, is not.[6] Apparently, any gain in resonance energy of these large ring oxygen heterocycles is not enough to overcome the strain energy of the planar structure. A previous attempt to prepare the nitrogen analog 1b has not been successful.[7]

For reasons mentioned in the above discussion, we were led to prepare the nitrogen derivative, 1b, and study is properties. We report the synthesis of the 14π electron heterocycle,N,N'-dimethyl-benzo-1,6-diazocine, and conclude from its physical properties that it is non-aromatic.

The key step in the synthesis of the 1b is the thermal ring opening of cyclobutene 4.[8] Cyclobutene 4 can readily be obtained by the reaction of N,N-dimethyl-*o*-phenylenediamine and *cis*-3,4-dichlorocyclobutene in the presence of *n*-butyl lithium.



The gas phase thermolysis of cyclobutene 4 at 285° produces the benzodiazocine 1b as the only detectable product. Irradiation of diazocine 1b results in the reformation of cyclobutene 4. The nmr spectrum of 1b shows the vinyl hydrogens as an AA' XX' pattern occurring at τ4.35 ($H_AH_{A'}$) and 5.62 ($H_XH_{X'}$). This spectrum could readily be analyzed[9] giving J_{AX} = 9.3 Hz and $J_{XX'}$ = 8.02 Hz. The chemical shifts of these hydrogens are typical of an enamine. In N-methyl-1,2-dihydropyridine[10] the α and β hydrogens occur at τ4.22 and 5.22 respectively. The vinyl hydrogens of 1b are upfield compared to the oxygen analog 1a The above data lead to the conclusion that 1b possesses no substantial diamagnetic ring current.

The small difference between J_{AX} and $J_{XX'}$ (1.28 Hz compared to 4.28 Hz for cyclohexadiene)[11] suggests considerable delocalization in the eight membered ring does occur.

1. Author to whom correspondence should be addressed.

2. See "Nonbenzenoid Aromatics," J. P. Snyder, Ed., Academic Press, New York and London, 1969, p IX; for a recent discussion of the literature in this field.

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b. *Z. Electrochem.*, **43**, 752 (1937); Although Huckel's rule is formally only applicable to monocycles the cross link in a *simple* polycyclic can be considered as a small perturbation and Huckel's rule can be applied to the peripherial electrons (see A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, 1962, p. 288).

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13. The pKa's were measured according to the method described by J. Stamuis, W. Maas and W. Wynberg (*J. Org. Chem.*, **30**, 2160 (1965)).