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THE SYNTHESIS OF 1-METHYL-2:3,6:7-DIBENZO-1,4,5-TRIAZA-CYCLOHEPTA-2,6-DIENE[1]

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SINCE the application of the simple molecular orbital theory to aromatic compounds by Hückel[3] the method has been used extensively to calculate resonance energies of conjugated systems, and the energies so found have been in exceedingly good agreement with experimental values. The ability of the theory to yield accurate predictions of aromaticity has been dramatically demonstrated in the cases of the tropylium[4] and cyclopropenium[5] ions, but there appears to be only one authentic report[6] of a monocyclic conjugated system containing $(4n + 2)$ π-electrons for which $n > 1$. The resonance energy in this latter system has not yet been reported, and no experimental evidence for aromaticity was cited.

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[1] Supported in part by a research grant from the National Science Foundation.

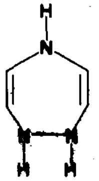
[2] National Science Foundation Predoctoral Fellow, 1956-1959.

[3] E. Hückel, Z. Physik **70**, 204 (1931).

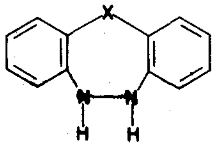
[4] W. von E. Doering and L. H. Knox, J. Amer. Chem. Soc. **76**, 3203 (1954).

[5] R. Breslow and C. Yuan, J. Amer. Chem. Soc. **80**, 5991 (1958).

[6] F. Sondheimer and R. Wolovsky, J. Amer. Chem. Soc. **81**, 1771 (1959).



I



II

X=a, $-N-CH_3$
b, $-O-$
c, $-S-$
d, $-CH_2-$

Structure I is a monocyclic system which contains ten π-electrons and is capable of planarity without undue strain. The resonance energy of the planar system, calculated with all the usual approximations[3,7] and taking the value[7] of the nitrogen Coulomb integral as 0.5β, is 2.47β. The dibenzo derivative (IIa) was similarly found to have a resonance energy of 6.34β, or 2.34β above that of the two benzene rings.[8]

Derivatives of I, which represents a heretofore completely unknown type of potentially aromatic system,[9] have now been synthesized. The compounds prepared were IIa, IIb, and IIc. As a model compound lacking the essential features required for a large resonance energy, IId was

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[7] C. A. Coulson, Valence p. 238. Oxford Press, London (1952).

[8] The molecular orbital calculations for I, II and related structures were carried out be matrix diagonalization utilizing an IBM 650 computer, and the details will be presented in the full publication.

[9] Compounds containing this ring system were reported by P. C. Guha and M. K. De, Quart. J. Indian Chem. Soc. **3**, 41 (1926). The substances described by these authors were prepared by improbable reactions, were not properly characterized, and do not have the characteristic properties which have been found in the present work. It is exceedingly unlikely that any of them actually contain the 10 π-electron ring system in question. The earlier claim of a synthesis of IIc has been retracted H. H. Szmant and Y. L. Chow, J. Amer. Chem. Soc. **79**, 5584 (1957) .

also prepared. The synthetic procedures used were similar in each case. N-methyl-2,2'-dinitro-diphenylamine was reduced to the cyclic azo compound (1-methyl-2:3,6:7-dibenzo-1,4,5-triaza-cyclohepta-2,4,6-triene) as red needles in 21% yield using lithium aluminum hydride in tetrahydrofuran (Found: C, 74.53; H, 5.59; N, 20.01). The azo compound absorbed two moles of hydrogen upon catalytic reduction, and yielded 2,2'-diaminodiphenylmethylamine (III) m.p. 88°. When the azo compound was reduced with Raney nickel and hydrazine,[10] IIa (1-methyl-2:3,6:7-dibenzo-1,4,5-triazacyclohepta-2,6-diene) was isolated in 91% yield, as a colorless crystalline solid, m.p. 93.5-95°. Found: C, 73.91; H, 6.18; N, 19.93, mol. wt. (Rast) 219. The compound absorbed one mole of hydrogen upon catalytic reduction and yielded the amine III. Upon oxidation with mercuric oxide, IIa was converted back to the azo compound. Compounds IIb, c, and d were prepared by analogous series of reactions. All of the hydrazo compounds[11] show bands in the infrared at 3.0 and 3.1μ. Compound IIa reacted irreversibly with dilute acid, (reminiscent of pyrrole) which prevented pK measurements.

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[10] S. Hornsby and W. L. Peacock, *Chem. & Ind.* 858 (1958).

[11] Crystallographic studies of these compounds by the X-ray method have been undertaken by Professor K. N. Trueblood, University of California at Los Angeles.