Finally, 4.5 g. of 2,4,6-collidine was recovered from the aqueous mother liquor.

Anal. of the carbinol. Calcd. for $C_{15}H_{17}ON$: C, 79.26; H, 7.54. Found: C, 78.62; H, 7.63.

Mercuric chloride–hydrochloride salt, m.p. 98–99° (reported[11] m.p. 99–100°); platinum tetrachloride–hydrochloride salt, m.p. 126–129°(reported[11] m.p. 125–130°); hydrochloride, m.p., 208–209° (reported[11] m.p. 209–211°).

Preparation of 2-styryl-4,6-dimethylpyridine. The collidylphenylcarbinol was dehydrated to the corresponding stilbazole by refluxing with an excess of acetic anhydride for 1 hr. The product was not purified but several derivatives were made. Mercuric chloride–hydrochloride salt, m.p. 231–232° (reported, m.p. 218–219°,[11] 220–222°[17]); picrate, m.p. 256° (reported, m.p. 240–241°,[11] 240–242°[17]); auric chloride-hydrochloride salt, m.p. 188–189° (reported, m.p. 189–191°,[11] 192–193°[17]).

The crude stilbazole was oxidized with potassium permanganate in acetone to 4,6-dimethylpicolinic acid. The product was purified by precipitation of the copper salt from aqueous solution and removal of the copper with hydrogen sulfide. After recrystallization from alcohol the acid melted at 157–158° (reported,[17] m.p. 155–156°); hydrazide, m.p. 74–75° (reported,[17] m.p. 77°).

The second fraction from the mercuric chloride purification was dehydrated with acetic anhydride. Several derivatives were made and their melting points and mixed melting points with the corresponding derivative of the 2-stilbazole are as follows: mercuric chloride-hydrochloride salt, m.p. 220–222° and 224–225°; platinum tetrachloride-hydrochloride salt, m.p. 241–242° and 242–243°; picrate, m.p. 242–244° and 249–250°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY]

Aromatic and Pseudoaromatic Nonbenzenoid Systems. II. Studies Directed toward the 1,2-Diaza-3,5,7-cyclooctatriene System[1,2]

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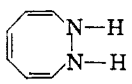
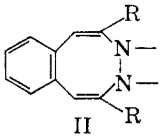
Molecular orbital calculations indicate a resonance energy of 2.99 β for 1,2-diaza-3,5,7-cyclooctatriene (I), and 4.76 β for the 5,6-benzo derivative (IIc). Compounds of structure IIIa and IIIb, which differ from derivatives of II only by the positions of double bonds, were synthesized. The failure of these derivatives of III to rearrange to the corresponding derivatives of II in the presence of a hydrogenation catalyst was noted. The calculated resonance energy of I, although large, is interpreted as being consistent with a lack of aromatic character in a ring system such as I.

According to the simple molecular orbital theory,[4,5] if cyclooctatetraene were planar it would have a significantly lower resonance energy than benzene (1.66 β *vs.* 2.00 β). In its simplest form the theory also predicts that a planar cyclooctatetraene would have a triplet ground state. Energy would be required to enlarge the interior natural angles of the tub form of cyclooctatetraene to force it into a planar configuration, and the resonance that could be gained is insufficient to bring this about. The molecule consequently exists in the tub form,[6,7] and has very little resonance energy.

From the molecular orbital point of view, 1,2-diaza-3,5,7-cyclooctatriene (I) is essentially a cyclooctatetraene containing 10 electrons. It therefore satisfies Hückel's rule ($4n+2$ π electrons)[8] and might be expected to be aromatic. It therefore seemed that the synthesis of such a system might be carried out, and more detailed molecular orbital calculations might be made and compared with experiment.

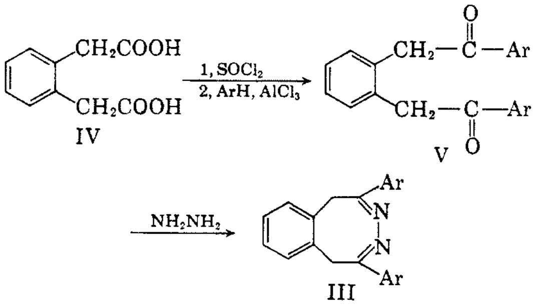


I



II

a. R = phenyl
b. R = 2,4-xylyl
c. R = H



IV V III

a. Ar = phenyl
b. Ar = 2,4-xylyl
c. Ar = H

The molecular orbital calculations were carried out for I with the usual assumptions[4,5]: (a) a planar system with exchange integrals all equal to β for adjacent atoms and zero otherwise, (b)

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[1] Paper I, N. L. Allinger and G. A. Youngdale, *Tetrahedron* Letters, No. 9, 10 (1959).

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

[3] National Science Foundation Predoctoral Fellow, 1956–59.

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[6] O. Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.* **27,** 1311 (1957).

[7] H. D. Springall, T. R. White, and R. C. Cass, *Trans. Faraday Soc.*, **50,** 815 (1954).

[8] Ref. 5, p. 145.

Coulomb integrals of α for carbon and $\alpha + 0.5\ \beta$ for nitrogen, and (c) neglecting overlap. The energy levels are given in Table I. The total π energy was found to be 10.99 β, and the resonance energy (relative to a single Kekule form) is 2.99 β.

For synthetic reasons, a study of the system II appeared to offer certain advantages. The calculations were therefore repeated for IIc. The total π energy found for this compound was 16.76 β, and this yields a resonance energy of 4.76 β. Since a benzene ring has a calculated resonance energy of 2.0 β, the additional resonance of the system (2.76 β) is a measure of the resonance of the heterocyclic ring, and differs little from the value calculated for the monocyclic compound. The energy levels are listed in Table I.

TABLE I

ENERGY LEVELS FOR THE 1,2-DIAZA-3,5,7-CYCLOOCTATRIENES

I	IIc
−1.917	−2.269
−1.384	−1.589
−1.193	−1.494
+0.104	−1.135
+0.150	−0.894
+1.460	0.000
+1.590	+0.244
+2.190	+0.949
	+1.316
	+1.544
	+2.000
	+2.329

A value for β of about 20 kcal./mole is generally accepted,[9] and would yield delocalization energies of 59.8 and 55.2 kcal./mole for the planar systems I and the heterocyclic ring of IIc respectively. From the appropriate bending frequency of ethylene[10] the energy required to distort the bond angles sufficiently to flatten out the tub can be calculated to be 31.5 kcal./mole. Clearly then, simple theory predicts planar systems will be more stable than the tub forms by 28.3 and 23.7 kcal./mole respectively for both I and II. It is possible to improve the values of the exchange and overlap integrals without too much labor,[4,5] but such improvements appear to have negligible effect on the total calculated energies and on the conclusions as to the presence or absence of aromaticity in other cases studied.[11] Electron correlation and configuration interaction are more difficult to treat,[12] and might be rather important here because of the relatively high electron density. No attempt has been made to pursue the theoretical calculations beyond this point, however, for reasons given below.

Compound IIIa, an isomer of IIa, was first prepared as outlined on the flow sheet. The known *o*-phenylenediacetic acid was converted *via* the acid chloride to diketone VIIa. This compound was allowed to react with hydrazine under high dilution conditions,[13] and gave IIIa in low yield. The structure of IIIa was established by analysis and molecular weight, and by the absence of any N—H stretching absorption in the infrared spectrum.

If the isomerization of an imine to a vinyl amine is endothermic by 3–6 kcal./mole, which are the values found for enolization of ketones,[14] the planar structure IIc would appear to be at least 11.7 kcal./mole more stable than the nonplanar IIIc, and it would appear that the reaction IIIc→IIc should proceed. However, prolonged treatment of IIIa with palladium-on-charcoal in refluxing xylene brought about no isomerization. There appeared therefore to be a conflict between the predicted and observed results. For simplification, the effect of the aromatic substituents had been ignored in the calculations. Since these substituents were conjugated with the azine system, the possibility existed that this conjugation tended to stabilize the azine arrangement and to prevent the isomerization. It is well known that the two rings in biphenyl can be forced from co-planarity by the presence of *ortho*-groups, and therefore the synthesis of IIIb was undertaken. This synthesis paralleled the earlier one, although the cyclization step had to be modified somewhat to obtain the desired product. It was found that IIIb was similarly reluctant to isomerize to the desired form (IIb).

It seems difficult to escape the conclusion that in this case the simple molecular orbital theory appears to fail to predict that which is experimentally found. Other apparent failures of the theory in predicting aromaticity have been reported in the past.[15] It may be noted, however, that although the predicted resonance energy of I (2.99 β) appears large relative to that of benzene (2.00 β), when other effects are taken into account, the predicted isomerization energy for IIIc→IIc amounts to only 12 kcal./mole, so that a lack of aromaticity in II cannot be considered alarming. Since the simple form of the molecular orbital theory appears to suffer from some basic difficulties

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(9) Ref. 5, p. 669. The quantity referred to as β in the present work is called γ by Wheland.

(10) The value 0.8×10^{-11} ergs/radian^2 has been used for the force constant for reasons outlined by F. H. Westheimer in M. S. Newman's *Steric Effects in Organic Chemistry*, John Wiley and Sons, Inc., New York, 1956, p. 537.

(11) B. Pullman and A. Pullman in *Les Theories Electroniques de la Chimie Organique*, Masson et Cie, Editeurs, Libraires de l'Academie de Medecine 120, Boulevard Saint-Germain, Paris VI^e, 1952, p. 226.

(12) D. P. Craig, *J. Chem. Soc.*, 3175 (1951).

(13) C. G. Overberger and M. Lapkin, *J. Am. Chem. Soc.*, **77**, 4651 (1955).

(14) G. Schwarzenbach and C. Wittwer, *Helv. Chim. Acta*, **30**, 669 (1947).

(15) W. von E. Doering, Paper Presented at the Sixteenth National Organic Chemistry Symposium, Seattle, Wash., June, 1959.

which are at present the subject of considerable discussion,[16] it does not seem profitable to pursue this matter further at the present time.

EXPERIMENTAL

o-Phenylenediacetic acid (IV). A mixture of *o*-phenylenediacetonitrile,[17] 70 g., and 700 ml. of 6*N* hydrochloric acid was refluxed until a homogeneous solution was obtained. Five hundred milliliters of the solution was then distilled, and the remaining solution was cooled. The solid which separated was filtered and recrystallized from water to give 81 g. (93%) of product in the form of colorless needles, m.p. 149–150° (lit.,[18] m.p. 149–150°).

o-Phenylenediacetophenone (Va). Ten grams of diacid IV were converted to the corresponding acid chloride by heating at 70° with 15.3 g. of thionyl chloride for 6 hr. The excess thionyl chloride was then removed under reduced pressure and the acid chloride was dissolved in 30 ml. of benzene. The resulting solution was added over 30 min. to a stirred mixture of 16 g. of anhydrous aluminum chloride in 80 ml. of benzene. Stirring was continued for 2 hr. and the mixture was then poured onto a mixture of ice and hydrochloric acid. The aqueous layer was separated and extracted with benzene. The combined benzene layers were washed with dilute sodium carbonate solution, and then with water. The benzene solution was then concentrated to a volume of 100 ml., and deposited colorless crystals upon cooling. Two recrystallizations from benzene gave the diketone as needles, wt. 11.9 g. (74%), m.p. 181.5–182°.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.02; H, 5.77. Found: C, 84.30; H, 5.84.

2-Phenyl-3-benzoylindene. In another run, which was carried out in essentially an identical manner to that described, the isolation procedure gave a viscous black residue instead of the desired product. Distillation gave 40% yield of a material, b.p. 240–290° (4 mm.), which partially solidified. Upon recrystallization from dioxane the compound was obtained as colorless plates, m.p. 164–165°. The infrared spectrum showed absorption at 6.02 μ.

Anal. Calcd. for $C_{22}H_{16}O$; C, 89.14; H, 5.44. Found: C, 88.92; H, 5.46.

3,8-Diphenyl-1,2-diaza-5,6-benzo-2,5,8-cyclooctatriene (IIIa). The procedure used was adapted from that described by Overberger and Lapkin[13] for a similar cyclization. A warm solution of 6.28 g. of the diketone (V) in 110 ml. of dimethylformamide was mixed with a warm solution of 2.26 g. of hydrazine hydrobromide in 70 ml. of dimethylformamide. The resulting solution was allowed to stand for 2 days, and then was diluted with 400 ml. of absolute ethanol and added to 1500 ml. of absolute ethanol containing 60 ml. of pyridine under high dilution conditions over a period of 24 hr. The resulting mixture was then heated under reflux for 3 days, and concentrated under vacuum to a volume of 300 ml. This solution was poured into ice water. The yellow solid which separated was collected, wt. 6 g. A portion of this material was recrystallized twice from aqueous acetone and furnished large pale yellow needles, m.p. 157.5–158.5°, and a small amount of small golden plates, m.p. 244–244.5°, which were not further investigated. Recrystallization of the large needles from acetone gave colorless plates, m.p. 157.5–158.5°. The infrared spectrum showed absorption at 6.2, 6.3, 6.65, and 6.85 μ, quite like the absorption shown by benzalazine. No N—H absorption was evident. The ultraviolet spectrum showed a maximum at 267 mμ with ε 28,200 (95% ethanol).

Anal. Calcd. for $C_{22}H_{18}N_2$: C, 85.10; H, 5.84; N, 9.03; mol. wt., 310. Found: C, 85.10; H, 5.92; N, 9.26; mol. wt., 307 (Rast).

Attempted isomerization of IIIa to IIa. A mixture of 0.1 g. of IIIa and 0.1 g. of 5% palladium-on-carbon in 25 ml. of xylene was heated under reflux for 48 hr. The solution was filtered and the xylene was evaporated. The residue was identified as IIIa by melting point, mixed melting point, and ultraviolet spectrum. No other compound was found.

o-Xylylene di(2,4-xylyl) ketone (Vb). The Friedel-Crafts reaction was carried out in a manner similar to that described for the synthesis of Va. The product, after two recrystallizations from petroleum ether, was obtained in 35% yield, m.p. 81–82°.

Anal. Calcd. for $C_{26}H_{26}O_2$: C, 84.29; H, 7.07. Found: C, 84.17; H, 6.87.

3,8-Di(2,4-xylyl)-1,2-diaza-5,6-benzo-2,5,8-cyclooctatriene (IIIb). The procedure was adopted from that described by van der Zanden and DeVries.[19] A solution of 18 g. of potassium acetate in 68 ml. of boiling alcohol was added to a hot solution of 9 g. of hydrazine dihydrochloride in 32 ml. of water and 45 ml. of alcohol. After cooling the reaction mixture, the solution was filtered and added to a suspension of 10 g. of Vb in 320 ml. of alcohol. The mixture was heated under reflux for 6 hr. One half of the alcohol was distilled, and the remaining solution was diluted with water and extracted with ether. The ether solution was washed and dried, and the ether was evaporated. The residue was a brown semisolid, wt. 10 g. Three grams of this material was dissolved in 10 ml. of benzene and adsorbed on 100 g. of neutral alumina. Elution of the column with 3:2 hexane-ether gave pale yellow crystals which were recrystallized from ether-hexane, m.p. 156–157.5°, wt. 0.43 g. (14%). For analysis a sample was recrystallized and gave colorless needles, m.p. 158–159°. The ultraviolet spectrum showed a maximum at 260 mμ, ε 19,200 (95% ethanol). The infrared spectrum showed no bands in the N—H or C=O regions.

Anal. Calcd. for $C_{26}H_{26}N_2$: C, 85.21; H, 7.15; N, 7.65; mol. wt. 366. Found: C, 84.97; H, 6.89; N, 7.46; mol. wt., 384 (Rast).

Attempted isomerization of 3,8-di-(2,4-xylyl)-1,2-diaza-5,6-benzo-2,5,8-cyclooctatriene (IIIb). A mixture of 0.1 g. of V and 0.1 g. of 5% palladium-on-charcoal in 25 ml. of xylene was heated under reflux for 18 hr. Filtration and removal of the solvent gave good recovery of V, identified by melting point and mixed melting point. No other product was found.

Molecular orbital calculations. In each case the matrix was formulated from the integrals in the usual way[4] and diagonalized with the aid of an IBM 650 computer using a standard matrix diagonalization program. The total π energies and resonance energies were calculated from the eigen values in each case in the usual way. Since the physical systems of interest if they existed, would very likely be nonplanar, calculations of electron densities, bond orders, and free valence did not seem meaningful, and were not carried out.

DETROIT 2, MICH.

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