flared sections near stopcocks were wrapped with glass wool. The reaction vessel, fitted with top-driven magnetic stirrer, has been described elsewhere.[20]

In a typical run the vessel was charged with 50 ml of chlorobenzene which was then degassed by means of several freeze–pump–thaw cycles. Oxygen-free nitrogen or helium was admitted to a pressure below 1 atm and the flask was placed into the constant-temperature oil bath. Stirring at 2000 rpm was begun and adjustments of the pressure were made until thermal equilibrium at one atmosphere was attained. Enough oxadiazoline to liberate about 40 ml of nitrogen, dissolved in about 1 ml of solvent, was injected through a septum by means of a syringe with a long needle. The mercury reservoir was adjusted manually to maintain atmospheric pressure while volume–time data were recorded until the volume became constant.

Rate Measurements by Infrared.—The intensity of the characteristic, isolated diazo absorption near 2040 cm^{-1} of the spectrum was measured with a Perkin-Elmer 521 instrument. Peak heights were converted to concentration figures through use of calibration curves obtained with chlorobenzene solutions prepared from pure diaryldiazomethanes. Cells were of NaCl spaced 0.1 mm.

Reaction vessels for the infrared-monitored decompositions were 20 × 200 mm test tubes. Chlorobenzene (5 ml) was pipeted into a tube which was then stoppered tightly and placed in the oil bath. When thermal equilibrium had been reached a known quantity of oxadiazoline in a little chlorobenzene was injected and the tube was shaken in the bath to mix the contents. Initial concentrations of oxadiazolines were about $8 \times 10^{-2} M$. Control experiments showed that solution temperature was within 0.5° of the bath temperature in 1 min from the time of injection.

Sampling was accomplished by removing 0.1-ml aliquots with a pipet and injecting these into ice-cold test tubes. The diazoalkane concentration was followed until it had dropped to about 10% of its maximum value, 20 to 30 points being taken.

A control experiment, in which phenyl isocyanate concentration was invariant, showed that the sampling technique did not lead to appreciable losses of solvent by evaporation.

Registry No.—**2a**, 21449-58-1; **2b**, 21449-56-9; **2c**, 21449-57-0; **2d**, 21449-59-2.

(20) J. Warkentin, *J. Chem. Educ.*, **43**, 265 (1966).

Diazocine Chemistry. VI. An Inquiry into the Aromaticity of 5,6-Dihydrodibenzo[*b*,*f*][1,2]diazocine

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The synthesis of dibenzo[*b*,*f*][1,2]diazocine (**1**) and its reduction to the 5,6-dihydrodibenzo[*b*,*f*][1,2]diazocine (**2**) is described. The spectral properties of the latter compound indicate that its central ring, because of the presence of 10 π electrons, is somewhat resonance-stabilized.

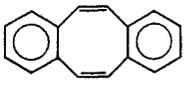
Our interest in the chemistry of nitrogen analogs of cyclooctatetraene[1] has led us to prepare dibenzo[*b*,*f*][1,2]diazocine (**1**) and the dihydro derivative **2**. The latter compound is of considerable interest, since it represents a potentially aromatic ring system which is isoelectronic with the dibenzo[*a*,*e*]cyclooctatetraene dianion.[2]

The reduction of *o*,*o*-dinitrobibenzyl with zinc and barium hydroxide afforded the 5,6,11,12-tetrahydrodibenzo[*b*,*f*][1,2]diazocine (**5**). The nmr spectrum (*cf.* Experimental Section) of this previously prepared[3] compound confirms its assigned structure (**5**). It should be mentioned that the methylene protons appear as a singlet, and consequently the central ring is not locked into a particular conformation.

The dihydro compound **5** is readily oxidized to the 11,12-dihydrodibenzo[*b*,*f*][1,2]diazocine (**6**),[3,4] whose structure is also confirmed by its nmr spectrum. The methylene protons now appear as an AB system, in agreement with expectation for a tub-shaped system such as is shown for this compound in Scheme I.[5]

In order to introduce the desired double bond at positions 11 to 12, the dihydro compound **6** was treated with N-bromosuccinimide to yield the monobromo dihydro derivative **7**. The nmr spectrum of this substance showed the anticipated ABX pattern due to the methine and methylene protons. This compound was readily dehydrohalogenated by treatment with potassium *t*-butoxide to afford the diazocine **1**. The structure proof of this compound, in addition to the elemental analysis, and its mass spectrometric molecular weight, rests upon the following observations.

(a) Its ultraviolet spectrum is closely similar to that of dibenzo[*a*,*e*]cyclooctatetraene (**3**).



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(b) The olefinic protons in compound **1** resonate within 0.01 ppm of those in dibenzo[*a*,*e*]cyclooctatetraene (δ 6.71).

(c) Electron bombardment causes the loss of N_2 from compound **1**.

The cited spectral data indicate that compound **1** has a geometry similar to that of the dibenzo[*a*,*e*]cyclooctatetraene (**3**).

Reduction of the diazocine **1** with zinc and barium hydroxide affords a dihydro derivative which has two readily replaceable (by deuterium exchange) hydrogens and a two-proton olefinic singlet at δ 6.50. Treatment of this dihydro derivative with methyl iodide in the presence of sodium bicarbonate affords a mixture of the monomethyl and dimethyl derivatives **8** and **9**.

The ultraviolet spectra of **1**, **2**, **5**, **8**, and **9** are shown in Figure 1.

A comparison of the ultraviolet spectra of the nonplanar diazocine derivative **1** and the tetrahydro deriva-

(1) (a) W. W. Paudler and A. G. Zeiler, *Chem. Commun.*, 1077 (1967); (b) *J. Org. Chem.*, **34**, 2138 (1969).

(2) T. J. Katz, M. Yoshida, and L. C. Siew, *J. Amer. Chem. Soc.*, **87**, 4516 (1965).

(3) H. Duval, *Bull. Soc. Chim. Fr.*, **7**, 727 (1910).

(4) J. R. Geigy, British Patent 940165; *Chem. Abstr.*, **61**, 1816 (1964).

(5) The ultraviolet spectrum of the dihydro derivative **6** has recently been compared with that of the *cis*- and *trans*-azobenzene, and it was concluded that compound **6** exists in the indicated tub form [F. Gerson, E. Heilbronner, A. VanVeen, and B. M. Wepster, *Helv. Chim. Acta*, **43**, 1889 (1960)].

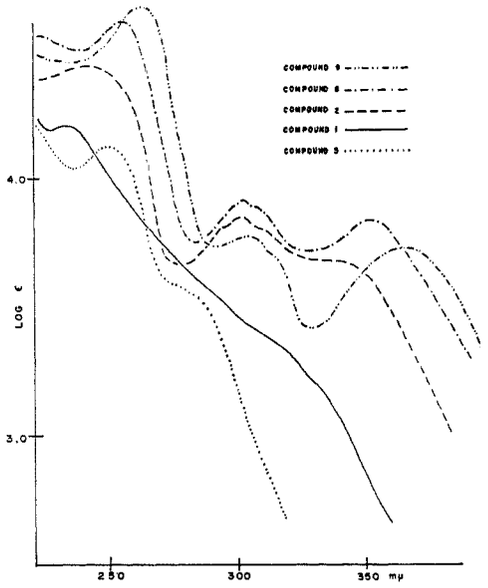
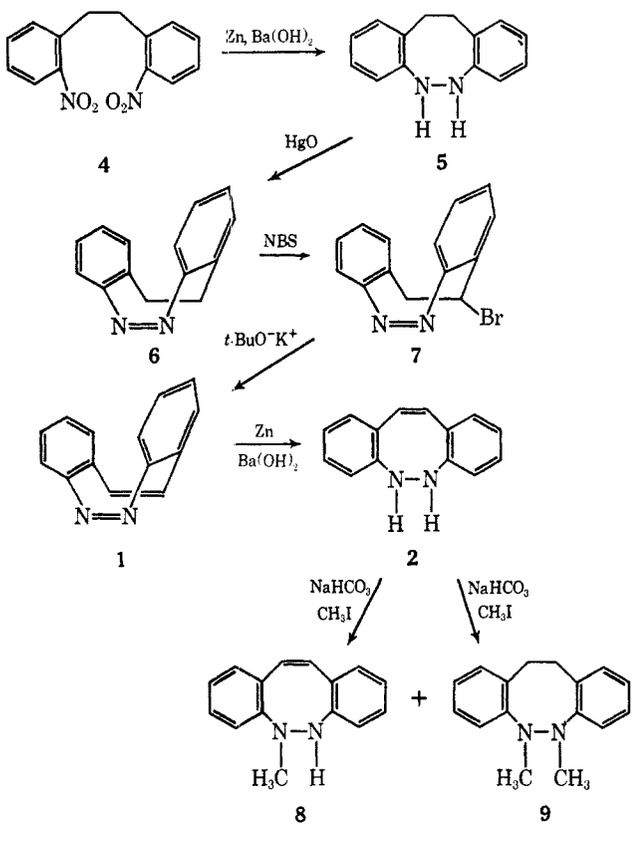


Figure 1.—Ultraviolet spectra of some 1,2-diazocine derivatives.

SCHEME I



tive **5** with that of the dihydro derivative **2** clearly shows the considerably enhanced conjugation existing in the latter compound. This enhanced conjugation can be satisfactorily explained by invoking the argument that the central ring in the dihydro compound is capable of transmitting conjugation effects fairly efficiently. This can occur if the ring is more planar than the tub-shaped diazocine ring. The driving force for this increased planarity may well be found in the enhanced stability of the central ring because of its "aromatic" character caused by the presence of 10 π electrons.

It is well known that the alkylation of a pyrrole-like nitrogen atom causes a decrease of the electronegativity of the nitrogen atom. This allows a more complete conjugation of the 2p orbital of this type of nitrogen atom with the remaining π system. For example, the ultraviolet absorption band of N-alkylpyrroles is 10 times as intense as that of pyrrole itself.

The ultraviolet spectrum of the monomethyl derivative **8** indicates that the same principle, although to a smaller extent, is applicable in this compound, namely, that the monomethyl derivative is somewhat more conjugated than the parent compound **2**.

The introduction of the second methyl group, to form the derivative **9**, introduces some slight steric repulsion, as is evidenced by the decreased absorption intensities of the long-wavelength bands. The increased conjugation of the 2p orbital of the "newly" alkylated nitrogen atom is reflected in the bathochromic shift of the longest wavelength band.

These spectral analyses indicate that we are dealing with an at least "partially planar" highly conjugated system in compound **2**.

It now remains to discuss the nmr spectra (*cf.* Experimental Section) of the various compounds. Reduction of the diazocine **1** to the dihydro derivative **2** causes a diamagnetic shift of the olefinic protons by 0.2 ppm. There is no significant additional change in the chemical shifts of these olefinic protons upon methylation of the nitrogen atoms to form compounds **8** and **9**, respectively. This shielding effect is, *a priori*, contrary to that expected for a system which has increased conjugation. However, it must be kept in mind that the reduction of the diazocine does, in fact, add two electrons to the ring system. If these are somewhat delocalized, the overall effect will be that of an increased charge on each of the carbon and nitrogen atoms of the dihydro derivative. Thus, the protons bonded to the carbon atoms will be more shielded. On the other hand, if the dihydro compound is "aromatic," it will be able to sustain a ring current. This ring current will cause the protons to become more deshielded. Depending upon which of these forces is stronger, the protons of the dihydro derivative will be either more shielded or more deshielded than the corresponding protons in the diazocine **1**.[6] Since the ultraviolet data indicate a certain amount of aromatic character of the dihydro derivative, it appears that the former process outweighs the latter in this instance.

The chemical shift of a proton bonded to nitrogen is subject to the electronegativity of the nitrogen atom. For example, an amine proton resonates at a more shielded position than does a proton bonded to a pyrrolelike nitrogen atom (this is true for dilute solutions where intermolecular hydrogen bonding effects are minimized).

A comparison of the "amine-proton" chemical shifts of the tetrahydro compound **5** and that of the dihydro derivative **2** clearly shows the more "acidic" nature of the latter protons.[7]

(6) At this point it should be mentioned that there is no change in the chemical shifts of the olefinic protons of cyclooctatetraene when it is converted into the "aromatic" dianion [T. J. Katz, *J. Amer. Chem. Soc.*, **82**, 3784 (1960)].

(7) A detailed study of NH nmr absorptions in 10-π-electron systems has been reported [N. L. Allinger and G. A. Youngdale, *ibid.*, **84**, 1020 (1962)].

All of these accumulated data are in favor of the existence of a somewhat resonance-stabilized 10-π-electron central ring in 5,6-dihydrodibenzo[*b*,*f*][1,2]diazocine (**2**).[8,9]

Experimental Section[10]

5,6,11,12-Tetrahydrodibenzo[*b*,*f*][1,2]diazocine (5).—The following procedure is a modification of that described by Duval.[3] To a refluxing solution of 30 g (0.118 mol) of *o*,*o*-dinitrobibenzyl in 2 l. of refluxing ethanol was added a solution of 65 g of barium hydroxide octahydrate in 500 ml of hot water. Zinc powder (60 g) was added over a period of 15 min with vigorous stirring, and refluxing was continued for an additional 4 hr. The reaction mixture was cooled to room temperature, and Dry Ice (*ca.* 20 g) was added in small portions. The resulting suspension was filtered and the filtrate was evaporated to dryness. The residue was dissolved in ether and the ether solution was washed with water, dried over anhydrous potassium carbonate, and evaporated to dryness to leave an orange solid. This solid was recrystallized from carbon tetrachloride to afford 15 g (60%) of compound **5**: mp 151–152° (lit.[3] mp 151°); nmr ($CDCl_3$) δ 6.98 (m, 6), 6.60 (m, 2), 5.33 (s, 2, NH), and 3.18 (s, 4).

11,12-Dihydrodibenzo[*b*,*f*][1,2]diazocine (6).—To a solution of 2.10 g (0.01 mol) of compound **5** in 150 ml of refluxing ethanol was added 5 g of yellow mercuric oxide. The suspension was stirred and refluxed for 5 hr and filtered, and the solvent was removed by vacuum evaporation. The remaining orange residue was recrystallized from cyclohexane to yield 1.80 g (87%) of compound **6**: mp 112–113° (lit.[3] mp 112.5°); nmr ($CDCl_3$) δ 6.89 (m, 8), 2.92 (H_A), and 2.74 (H_B) (AB, 4, J = 12 cps).

11-Bromo-11,12-dihydrodibenzo[*b*,*f*][1,2]diazocine (7).—A solution of 1.5 g (7.1 mmol) of compound **6** in 120 ml of carbon tetrachloride was stirred and refluxed for 12 hr with 1.5 g of N-bromosuccinimide (NBS). The reaction mixture was cooled and filtered, and the filtrate was evaporated to dryness. The resulting dark residue was extracted with 100 ml of boiling cyclohexane. The extract was decolorized with charcoal and the filtrate was evaporated to dryness to afford 1.1 g (54%) of crude compound **7**. An analytical sample was obtained by recrystallization from cyclohexane: mp 105–106° dec; nmr ($CDCl_3$) δ 7.12 (m, 8), 5.22 (H_X), 3.43 (H_A), and 3.13 (H_B) (ABX, 3, J_{AX} = 8.5 cps, J_{BX} = 12 cps, J_{AB} = 14 cps); mass spectrum mol wt 287 (calcd mol wt 287).

Anal. Calcd for $C_{14}H_{11}N_2Br$: C, 58.55; H, 3.86; N, 9.75. Found: C, 58.79; H, 3.82; N, 9.97.

Dibenzo[*b*,*f*][1,2]diazocine (1).—To 1.1 g (3.8 mmol) of crude compound **7** was added an excess of potassium *t*-butoxide in 150 ml of *t*-butyl alcohol. The mixture was warmed on a steam bath for 15 min, poured into 300 ml of water, and extracted with ether. The ether extract was washed with water, dried over anhydrous potassium carbonate, and evaporated to dryness. Recrystallization of the residue from 20 ml of ethanol afforded yellow crystals (313 mg, 39%) of compound **1**: mp 135–138°; nmr ($CDCl_3$) δ 7.06 (m, 8) and 6.70 (s, 2); mass spectrum *m*/*e* (rel intensity) 206 (100), 178 (23), 154 (44), 149 (74).

Anal. Calcd for $C_{14}H_{10}N_2$: C, 81.52; H, 4.88; N, 13.58. Found: C, 81.79; H, 5.03; N, 13.60.

5,6-Dihydrodibenzo[*b*,*f*][1,2]diazocine (2).—A solution of 206 mg (1 mmol) of compound **1** and 0.5 g of barium hydroxide octahydrate in 50 ml of refluxing ethanol was treated with 0.5 g of powdered zinc. After refluxing for a few minutes, the solution became colorless and heating was discontinued. Dry Ice (*ca.* 5 g) was added in small portions and the resulting suspension was filtered. The filtrate was evaporated to 20 ml and cooled to 0° to afford white crystals (82 mg, 40%) of compound **2**: mp 168–169° dec; nmr ($CDCl_3$) δ 7.22 (m, 2), 7.04 (m, 4), 6.68 (m, 2), 6.50 (s, 2), and 6.07 (s, 2, NH); mass spectrum mol wt 208 (calcd mol wt 208).

Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.73; H, 5.81; N, 13.45. Found: C, 80.46; H, 5.82; N, 13.38.

5-Methyl- and 5,6-Dimethyldibenzo[*b*,*f*][1,2]diazocine (8 and 9).—A mixture of 205 mg (1 mmol) of compound **2**, 5 g of sodium bicarbonate, 25 ml of methanol, and an excess of methyl iodide was stirred at room temperature for 5 days. The mixture was filtered and the filtrate was evaporated to dryness to afford a brown residue. Column chromatography of this material on Grade III alumina afforded, upon elution with benzene, two pure compounds. These compounds, **8** and **9**, were treated as follows.

Compound **9** (62 mg, 26%) was recrystallized from cyclohexane: mp 149–151°; nmr ($CDCl_3$) δ 7.06 (m, 8), 6.44 (s, 2), and 2.69 (s, 6).

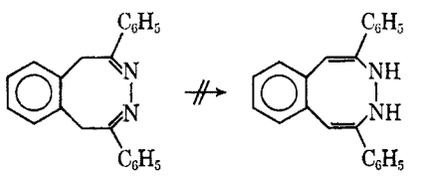
Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.31; H, 6.82; N, 11.85. Found: C, 81.32; H, 6.88; N, 11.90.

Compound **8** (113 mg, 51%) was recrystallized from ethanol: mp 157–158°; nmr ($CDCl_3$) δ 7.04 (m, 8), 6.50 (s, 2), 4.83 (s, 1, NH), and 2.98 (s, 3).

Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.04; H, 6.34; N, 12.60. Found: C, 81.12; H, 6.92; N, 12.58.

Registry No.—**1**, 21372-41-8; **2**, 21363-72-4; **5**, 2225-55-0; **6**, 21372-42-9; **7**, 21372-43-0; **8**, 21363-74-6; **9**, 21363-75-7.

(8) It is of interest to point out that attempts to isomerize compound **10** to compound **11** are reported to have failed [N. L. Allinger and G. A. Youngdale, *J. Org. Chem.*, **25**, 1509 (1960)].



10 **11**

(9) Compounds such as **2** have recently been predicted to be nonaromatic from molecular orbital theory [M. E. Volpin, *Russ. Chem. Rev.*, **29**, 153 (1960)].

(10) The nmr spectra were obtained with a Varian HA-100 spectrometer. The purity of the compounds was ascertained by thin layer chromatography (silica gel G). The mass spectra were determined with an Hitachi Perkin-Elmer RMU-6E mass spectrometer. Elemental analyses were done by Mrs. W. Decker of this department.