tracted with ether. The combined ether extracts were washed with brine, dried ($MgSO_4$), and evaporated with ether to give the epoxide mixture which was analyzed by vpc.[1] The results are summarized in Scheme I.

Registry No.—**1,** 13294-73-0; **2,** 7787-79-3; **4,** 7787-72-6; **5,** 7787-77-1; **7,** 7787-73-7; **8,** 7787-80-6.

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Nuclear Magnetic Resonance Analysis of 5,12*H*-Dibenzo[*b*,*e*]-1,3a,6,6a-tetraazapentalene

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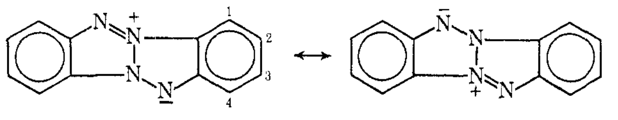
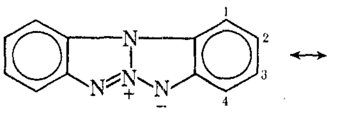
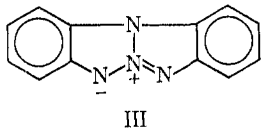
In an earlier paper,[1] the nmr spectrum of 5,6*H*-dibenzo[*b*,*f*]-1,3a,4,6a-tetraazapentalene (I) and two of its methyl derivatives was reported. In this paper, the analysis of the nmr of the isomeric 5,12*H*-dibenzo[*b*,*e*]-1,3a,6,6a-tetraazapentalene (II) is described.



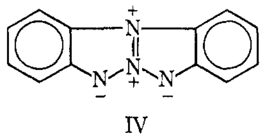
I



II



III



IV

Compound II was prepared by essentially the same procedure as has been reported by Carboni, *et al.*,[2] from 1-(2-azidophenyl)benzotriazole. The nmr spectrum of II was obtained in deuteriochloroform. The spectrum is shown in Figure 1. The experimental spectrum was matched with the calculated spectrum shown in Figure 1 using the LAOCN-3 program.[3] The calculated coupling constants and chemical shifts for II are tabulated in Table I. The data reported previously[1] for I are also tabulated in Table I for comparison purposes.

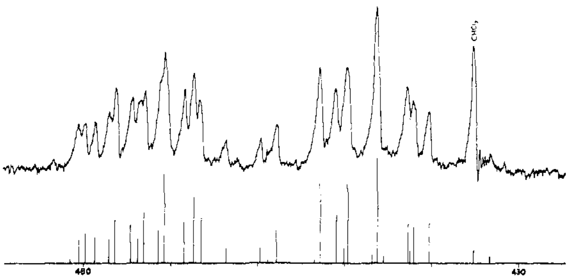


Figure 1.—Experimental and calculated spectra of 5,12*H*-dibenzo[*b*,*e*]-1,3a,6,6a-tetraazapentalene (II) in deuteriochloroform.

TABLE I

COUPLING CONSTANTS AND 60-MHz CHEMICAL SHIFTS

	Compd	
Chemical shifts[a]	I[b]	II
H_1	486.7	474.8
H_2	440.0	443.6
H_3	453.1	450.7
H_4	471.5	471.0
Coupling constants		
$J_{1,2}$	8.47	8.38
$J_{1,3}$	1.05	0.98
$J_{1,4}$	0.79	0.69
$J_{2,3}$	7.00	7.32
$J_{2,4}$	0.93	0.85
$J_{3,4}$	8.73	8.68

[a] Chemical shifts are in hertz downfield relative to internal tetramethylsilane. The values in this table were obtained by an iterative fitting using the LAOCN-3 program.[3] [b] Reference 1.

The coupling constants for both I and II are similar and of the order of magnitude expected for a normal benzenoid ring. The chemical shift of H_2 in each compound is furtherest upfield, a reflection of its location para to N-5, which carries a partial negative charge as seen in structures II–IV. H_4, which is ortho to N-5, is at nearly the same position in both I and II and in both cases is over 27 Hz downfield from H_2, a reflection of its closer proximity to the electronegative nitrogen. Apparently the inductive effect of the nitrogen in the ortho position decreases the effect of the partial negative charge on N-5 and results in the downfield shift. In both I and II, H_3 is located further downfield than H_2; however, in the II the difference between H_2 and H_3 is 7 cycles compared to 13 cycles in compound I. This result suggests that, whereas in compound I H_3 is located para to a nitrogen carrying a partial positive charge, in II the positive charge is much reduced; *i.e.*, structure IV contributes very little to the resonance hybrid. H_1 in compound II is 12 cps upfield compared to H_1 in compound I. This again suggests little contribution of structure IV to the resonance hybrid.

It is interesting to compare the observed chemical shifts of the protons in I and II with the molecular orbital calculations of Chia and Simmons.[4] In Figure 2 is shown a plot of the calculated electron densities *vs.* the observed chemical shifts. The chemical shifts of protons H_2 and H_3 in both I and II seem to correlate very well with the calculated electron densities. H_4 in both compounds falls nearly at the same point. This is not unexpected, since examination of structures I and II shows that in both H_4 has a similar electronic relationship to the nitrogens of the heterocyclic system. On the other hand H_1 in the compounds is in quite

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(1) J. H. Hall, J. G. Stephanie, and D. K. Nordstrom, *J. Org. Chem.*, **33**, 2951 (1968).

(2) R. A. Carboni, J. C. Kauer, J. E. Castle, and H. E. Simmons, *J. Amer. Chem. Soc.*, **89**, 2618 (1967).

(3) A. A. Bothner-By and S. Castellano, *J. Chem. Phys.*, **41**, 3863 (1964).

(4) Y. T. Chia and H. E. Simmons, *J. Amer. Chem. Soc.*, **89**, 2638 (1967).

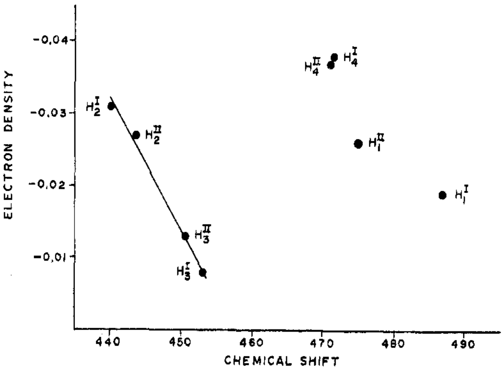

Figure 2.—Chemical shifts of protons in I and II *vs.* calculated electron densities. Electron densities are from ref 4 and the chemical shifts for I from ref 1.

different environments and there is observed a large chemical shift difference as well as a calculated electron density difference.

On the basis of the chemical shift data and transition state considerations,[5] one would predict a large preference for electrophilic aromatic substitution at H_2 with a much smaller reactivity at H_4 for each of these compounds. On the basis of the electron density calculations, one might expect the 2 and 4 positions to be about equally reactive or with a slight preference for the 4 position. Nitration, chlorination, bromination, and chlorosulfonation of I has been reported to give substitution at the 2 position.[5] Substitution at the 4 position is observed after positions 2 and 8 have been substituted. Although II has been nitrated and chlorosulfonated, the position of substitution has not been established.[6] These results suggest that the calculated electron densities at H_4 are too high relative to those at H_2.

Experimental Section

The nmr spectrum of II was taken in deuteriochloroform using a Varian A-56/60 spectrometer. The peak positions were determined relative to TMS by use of the side-band technique immediately preceding and immediately following the spectral scan. The initial peak assignments were based on similarities between the spectrum of II and the published spectrum of I.[1] The exact chemical shifts and couplings constants were calculated using the LAOCN-3 program.[3] In plotting the computed spectrum in Figure 1, lines closer together than 0.2 Hz were added together, since such lines would not normally be resolved.

5,12*H*-Dibenzo[*b*,*e*]-1,3a,6,6a-tetraazapentalene (II).—In 2 ml of decalin was placed 52.1 mg (0.221 mmol) of 1-(2-azidophenyl)benzotriazole.[2] The mixture was first warmed to dissolve the solid and then heated slowly up to the boiling point of the decalin. After 5 min of refluxing, the solution was cooled to room temperature. The needles which precipitated were filtered and washed thoroughly with petroleum ether, yield 26.5 mg (58%), mp 251–252° (lit.[2] 255°).

Registry No.—II, 2055-55-2.

Acknowledgment. –The author is indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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(5) R. A. Carboni, J. C. Kauer, W. R. Hatchard, and R. J. Harder, *J. Amer. Chem. Soc.*, **89**, 2626 (1967).

(6) J. C. Kauer and R. A. Carboni, *ibid.*, **89**, 2633 (1967).

Thermolysis of 3,3′,5,5′-Tetraphenyldiphenoquinone

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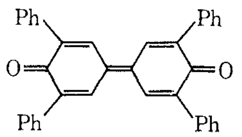
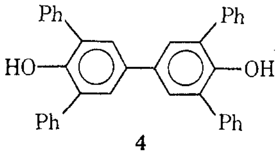
When 3,3′,5,5′-tetraphenyldiphenoquinone **1**[1] is



1

heated above its melting point, the melt which initially is an intense red color gradually fades and becomes almost colorless. Thin layer chromatography on silica gel using xylene as eluent shows the presence of three compounds, **2**, **3**, and **4**, with R_f values of 1, 0.7, and 0.5, respectively. By comparison with an authentic sample, **4** was identified as 2,2′,6,6′-tetraphenyl-*p*,*p*′-biphenol.



4

Superposition of the infrared spectra (in CS_2) of **2** and **4** gives a spectrum that is essentially identical with that of **3**. This is shown in Table I which lists the principal absorption bands of the three compounds. Furthermore, the molar extinction coefficients of all the major bands of **3** are approximately one-half of the corresponding bands in **2** or **4**. The infrared spectrum of 2,6-diphenylphenol (**5**)[1] also shows a doublet at 685 and 695 cm^{-1} indicating the two phenyl groups are not equivalent.

TABLE I

PRINCIPAL INFRARED ABSORPTION BANDS (IN CM^{-1})

2			1188			772	745	691	
3	3538	1225	1188	1120	867	772	745	700, 691	565
4	3538	1225		1120	872	772		700, 691	571

The spectrum of **2** is exceptionally simple. The strong C–O stretching absorption at 1188 cm^{-1}, which is also present in **3**, is also found in 4-phenyldibenzofuran (**6**, ν 1184 cm^{-1}) and dibenzofuran (**7**, ν 1195 cm^{-1}). The former also has a strong absorption at 691 cm^{-1}.

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[1] J. Plesek, *Collect. Czech. Chem. Commun.*, **21**, 375 (1956).