Aromatic Azapentalenes. IV. Heats of Combustion of Monobenzo- and Dibenzo-1,3a,6,6a-tetraazapentalenes and Monobenzo- and Dibenzo-1,3a,4,6a-tetraazapentalenes. The Structure of Tetraazapentalenes

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Abstract: Precise heats of combustion and sublimation were determined for four derivatives of the recently synthesized 1,3a,6,6a- and 1,3a,4,6a-tetraazapentalene ring systems. The heats of formation referred to the gas phase in standard states were determined to be: dibenzo-1,3a,4,6a-tetraazapentalene (I), 142.8 ± 1.3 kcal/mole; dibenzo-1,3a,6,6a-tetraazapentalene (II), 132.1 ± 1.5 kcal/mole; monobenzo-1,3a,4,6a-tetraazapentalene (III), 136.4 ± 1.2 kcal/mole; and monobenzo-1,3a,6,6a-tetraazapentalene (IV), 128.2 ± 1.3 kcal/mole. From resonance energy considerations, these molecules appear aromatic in the usual thermodynamic sense. The aromaticity of the ten π-electron tetraazapentalene nuclei is discussed theoretically.

Previous papers in this series[1] have shown that dibenzo-1,3a,4,6a-tetraazapentalene (I), dibenzo-1,-3a,6,6a-tetraazapentalene (II), and their monobenzo analogs III and IV have chemical properties that indicate the ten π-electron tetraazapentalene nuclei are aromatic. In the present paper the results of measurements of the heats of combustion and sublimation of I–IV are given, and the structure and spectra of these compounds are discussed in more detail.
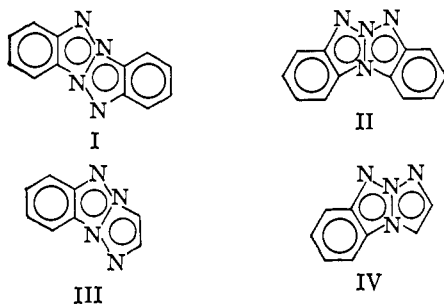
Experimental Section

A. Purification of Compounds. The compounds studied (I–IV) were purified by recrystallization from organic solvents and sublimation, and then by temperature–gradient sublimation. Infrared, ultraviolet, and mass spectral analyses were used to assay the final products, which were judged to be of high purity.

B. Heat of Combustion Measurements. The apparatus and procedures recommended by Jessup[2] were generally used with the following exceptions. The Mueller bridge was connected to a microvolt-indicating amplifier (both obtained from Leeds and Northrup Co.), and the latter was then connected to a recorder. Thus, the time of each of the different resistance settings at the "fast temperature change period" and the resistance measurements (to the fifth decimal place) during the initial and final periods were obtained from the chart of the recorder.

The calorimeter used was manufactured by Precision Scientific Co. (National Bureau of Standards Calorimeter Catalog No. 63090, Serial No. 10-R-4) and was calibrated by combustion of benzoic acid (National Bureau of Standards Sample No. 39i).

The energy equivalent of the calorimeter was 5022.0 cal in the interval 25.0–27.0° and was determined initially by an average of six combustions with a standard deviation of 0.016%. The calibration was checked periodically, but no significant change was detected during the measurements.

A Parr bomb (no. 1101 double valve) was used for the combustion; however, in order to permit mass spectral analysis of the final gas products of the combustion, a plain Hoke valve was used as the outlet valve.

The tetraazapentalenes I–IV were very difficult to burn. Small samples could be burned completely, but the temperature rise and the accuracy were insufficient. By using a sample of standard benzoic acid as binder (wt % of benzoic acid = 35%), it was possible to achieve complete combustion (confirmed by mass spectral analysis) of samples of adequate size. Both the benzoic acid and the tetraazapentalene were ground separately and weighed. The two were then thoroughly mixed and ground again in an agate mortar, and desired amounts of the mixture were removed and pelletized. The percentage composition of the pellet was assumed to be the same as the composition of the mixture before pelletizing.

A total of 1 ml of conductivity-grade water was introduced into the bomb with half the water placed in a platinum cup over the combustion crucible to ensure solution of all the nitrogen dioxide produced.[3] Mass spectrometry consistently showed the absence of NO_2 in the gas products.

In order to make sure that none of the nitrogen in the tetraazapentalenes was further oxidized to N_2O, NO, or other possible oxidation products of nitrogen, mass spectrometry was used to analyze the gas product from the combustion. No evidence of any other nitrogen compounds except N_2 in the final gas product was found.

The washings of the bomb were titrated with standard sodium hydroxide solution to determine the nitric acid formed, and this correction was used in the subsequent calculation of the heat of combustion. The final solution was then analyzed for nitrite ion, but none was ever detected.

C. Vapor Pressure Measurements. The McLeod gauge method[4] was used to measure the vapor pressure of I–IV as a function of temperature. A 1-l. bulb was attached to the McLeod gauge through a 2-mm capillary which was about 4 in. in length. A cold trap was placed at the end of the capillary, and cold nitrogen was blown through the cold trap whose temperature was checked periodically by a thermocouple. Nitrogen was used as the inert gas in the system. A stainless steel wire soldered to a magnet was hung inside the tube above the cold trap. During the vapor pressure measurements at higher temperatures, the stainless steel wire could be moved up and down by an outside magnet to prevent the

(1) (a) R. A. Carboni, J. C. Kauer, J. E. Castle, and H. E. Simmons, *J. Am. Chem. Soc.*, **89**, 2618 (1967); (b) R. A. Carboni and J. C. Kauer, *ibid.*, **89**, in press; (c) J. C. Kauer and R. A. Carboni, *ibid.*, **89**, 2633 (1967).

(2) R. S. Jessup, National Bureau of Standards Monograph No. 7, U. S. Department of Commerce, Washington, D. C., Feb 26, 1960.

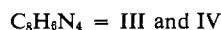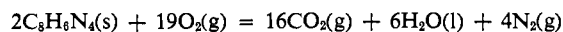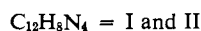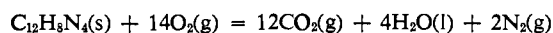(3) G. T. Armstrong and S. Marantz, *J. Phys. Chem.*, **64**, 1776 (1960).

(4) G. W. Thomson in "Technique of Organic Chemistry, Physical Methods," Part I, A. Weissberger, Ed., 3rd ed, Interscience Publishers, Inc., New York, N. Y., 1959, p 457.

capillary tube from becoming plugged. The reference temperature was 25° for the dibenzo derivatives I and II and 0° for the mono-benzo derivatives III and IV. At the reference temperature, the vapor pressure due to the sample studied was assumed to be negligibly small. Vapor pressures of the dibenzo derivatives were measured from 90 to 160° (or 170°) and of monobenzo derivatives from 50 to 100° (or 110°), both at 10° intervals. The apparatus was initially checked by measuring the vapor pressure of purified anthracene at 110, 120, and 130°, and the results agreed well with those reported in the literature.[5]

Results and Calculations

A. Heat of Combustion Results. The corrected temperature rise of a combustion run was computed by passing a least-squares straight line through the initial (0–6 min) and final (23–30 min) periods and computing numerically the appropriate integral. These computations were programmed for and carried out by an IBM 1620 computer.

As noted above, nitrogen dioxide was the only oxidation product of nitrogen detected in the combustion of the four tetraazapentalene derivatives; moreover, all the nitrogen dioxide formed was dissolved in the water, forming nitric acid. Thus, the combustion reactions of the compounds studied can be written as

$$C_{12}H_8N_4(s) + 14O_2(g) = 12CO_2(g) + 4H_2O(l) + 2N_2(g)$$

$$C_{12}H_8N_4 = \text{I and II}$$

$$2C_8H_6N_4(s) + 19O_2(g) = 16CO_2(g) + 6H_2O(l) + 4N_2(g)$$

$$C_8H_6N_4 = \text{III and IV}$$

The energy of combustion could be calculated on the basis of the above equations from the corrected temperature rise with appropriate corrections for the formation of nitric acid. Table I summarizes the results of the combustion experiments. The first and second columns represent the weights in air of sample and benzoic acid, respectively, and the third column (ΔE_t) gives the total energy of combustion for the bomb process calculated from the corrected temperature rise.

The values of q_1 and q_2 are corrections for the fuse and nitric acid, respectively. The sixth column gives the Washburn corrections,[6] and ΔE_B in the seventh column is the energy of combustion due to benzoic acid. The last column is the energy of combustion due to the sample and has been corrected to standard state, i.e.

$$-\Delta E_c° = (-\Delta E_t - q_1 - q_2 - q_3 + \Delta E_B)/M$$

The average value of $\Delta E_c°$ was corrected finally for buoyancy of air, and the uncertainty represents the standard deviation.

The standard state heats of combustion ($\Delta H_c°$) were calculated from the values of $-\Delta E_c°$ and the combustion reactions written above.[7] From the values of the heats of combustion (third column, Table II) and the heats of formation of water and carbon dioxide, the heats of formation [$\Delta H_f°(s)$] of the four tetraazapenta-

(5) F. S. Mortimer and R. V. Murphey, *Ind. Eng. Chem.*, 15, 1140 (1923); but see G. W. Sears and E. R. Hopke, *J. Am. Chem. Soc.*, 71, 1632 (1949).

(6) (a) F. D. Rossini, "Experimental Thermochemistry," Interscience Publishers, Inc., New York, N. Y., 1956; (b) E. J. Prosen, National Bureau of Standards Report 1119, Washington, D. C., Aug 6, 1951.

(7) The authors are grateful to Professor J. L. Margrave and Miss Carla Barker who communicated privately to them their preliminary combustion results on compound I which were in substantial agreement with those reported here.

Table I. Energy of Combustion, 25°

M, g	M', g	$-\Delta E_t$	q_1	q_2	q_3	$-\Delta E_B$	$-\Delta E_c°$, cal/ g, air
		cal					
Dibenzo-1,3a,4,6a-tetraazapentalene (I)
0.83169	0.44593	8956.0	5.2	24.3	4.3	2817.5	7340.0
0.82623	0.44301	8898.9	5.2	23.2	4.3	2799.0	7343.2
0.83295	0.44661	8972.2	5.2	23.6	4.3	2821.8	7344.2
0.83355	0.44693	8974.2	5.2	25.6	4.3	2823.8	7336.5
0.83336	0.44683	8980.7	5.2	25.0	4.3	2823.1	7347.3
0.82148	0.47210	9050.2	5.2	24.3	4.3	2982.8	7344.7
						Av	7342.7

$$-\Delta E_c°(\text{I}) = 7337.6 \pm 4.4 \text{ cal/g, vac}$$

		Dibenzo-1,3a,6,6a-tetraazapentalene (II)
0.82084	0.45884	8950.2	5.2	28.3	4.3	2899.0	7325.8
0.81883	0.45772	8923.5	5.2	22.5	4.3	2891.9	7326.9
0.83620	0.44292	8955.6	5.2	24.2	4.3	2798.5	7322.9
0.82020	0.45809	8930.6	5.2	24.8	4.3	2894.3	7317.7
						Av	7323.3

$$-\Delta E_c°(\text{II}) = 6805.6 \pm 3.7 \text{ cal/g, vac}$$

		Monobenzo-1,3a,4,6a-tetraazapentalene (III)
0.94969	0.50462	9696.8	5.2	29.3	7.4	3188.3	6809.2
0.86309	0.48620	8995.1	5.2	28.2	7.4	3071.9	6815.5
0.86072	0.48568	8966.7	5.2	28.1	7.4	3068.6	6805.3
0.87789	0.47524	9022.3	5.2	28.0	7.4	3002.7	6810.6
						Av	6810.1

$$-\Delta E_c°(\text{III}) = 6805.6 \pm 3.7 \text{ cal/g, vac}$$

		Monobenzo-1,3a,6,6a-tetraazapentalene (IV)
0.86113	0.49117	8978.2	5.2	24.5	7.4	3103.3	6779.2
0.86356	0.48804	8975.9	5.2	27.9	7.4	3083.5	6776.4
0.86377	0.48816	8979.8	5.2	29.3	7.4	3084.3	6776.7
0.84640	0.50534	8964.6	5.2	28.2	7.4	3192.8	6770.8
						Av	6775.8

$$-\Delta E_c°(\text{IV}) = 6771.3 \pm 3.1 \text{ cal/g, vac}$$

lenes in solid form and standard state were derived and are reported in the last column of Table II.

The logarithm of the vapor pressures of the four compounds studied were plotted against the reciprocal of temperature. From the slopes of the straight lines obtained (Figure 1), it is possible to calculate the heats of sublimation at 298°K of these compounds. These values were also checked by the least-squares method and are listed in the fourth column of Table II; the uncertainty was also calculated by the least-squares method. No corrections were made for the variation of the heats of sublimation from the temperature range in which they were measured to 298°K. From the heats of sublimation and the heats of formation of the solid tetraazapentalene derivatives, it is possible to calculate the heats of formation referred to gaseous form in standard states. These are also listed in the last column of Table II.

As shown in Table II, the difference in heats of formation of I and II was found to be 10.7 kcal/mole, indicating that II is more stable than I. Similarly, IV was 8.2 kcal/mole more stable than III. These findings are in accord with theoretical considerations as discussed in the next sections.

Discussion

Resonance Energies. The estimation of resonance energies is always fraught with uncertainties, and it is expected to be particularly so with molecules such as the tetraazapentalenes in which many formal struc-
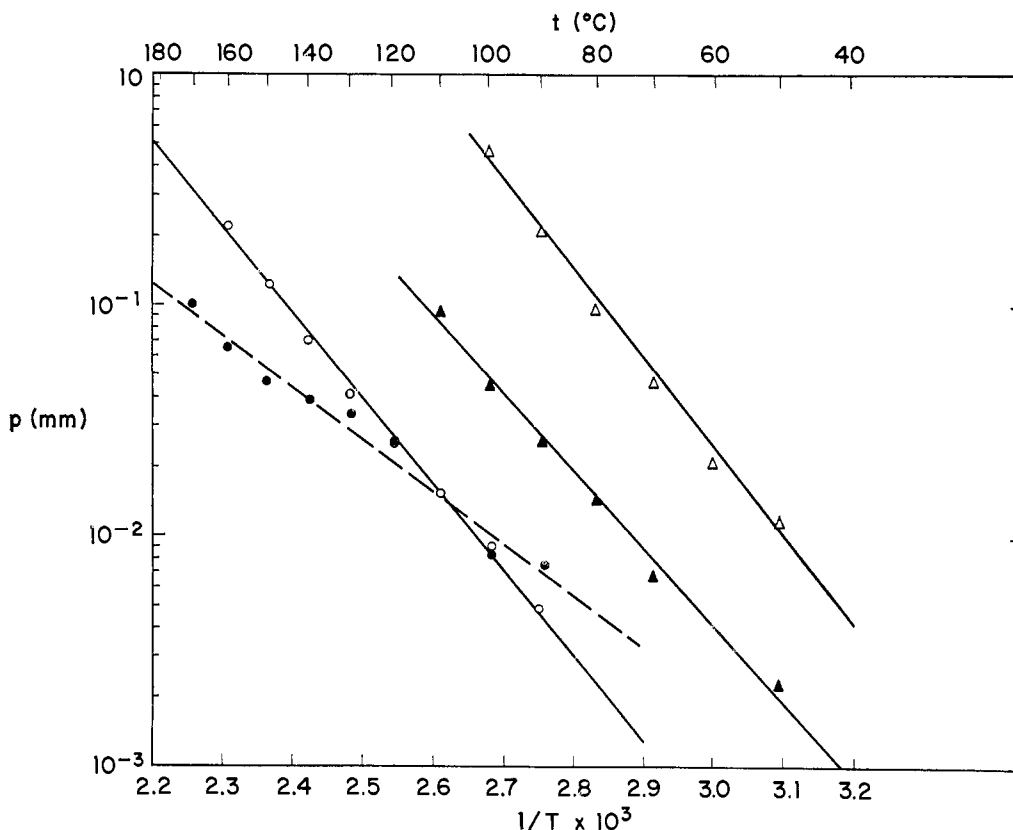
Figure 1. Temperature dependence of the vapor pressure of tetraazapentalenes: O, I; ●, II; △, III; ▲, IV.

tures contribute to the ground state.[1a] We have determined the empirical resonance energies of these compounds using two bases for the azapentalene nuclei: (1) the unique noncharge-separated structures V and

The heats of combustion were calculated according to the method of Klages as modified by Wheland.[8] For the calculation of series 1, a uniform value for the contribution to the heat of combustion of all N–N bonds

Table II. Heats of Combustion and Formation of Tetraazapentalenes

Compd	$-\Delta E_c^\circ$	ΔH_c°	ΔH_{sub}	ΔH_f°
		—————kcal/mole—————		
I(s)	1527.9 ± 0.9	-1527.9 ± 0.9	16.8 ± 0.4	126.0 ± 0.9
(g)				142.8 ± 1.3
II(s)	1523.9 ± 0.7	-1523.9 ± 0.7	10.1 ± 0.8	122.0 ± 0.7
(g)				132.1 ± 1.5
III(s)	1076.4 ± 0.6	-1075.8 ± 0.6	17.9 ± 0.7	118.5 ± 0.5
(g)				136.4 ± 1.2
IV(s)	1071.0 ± 0.5	-1070.4 ± 0.5	15.2 ± 0.7	113.0 ± 0.6
(g)				128.2 ± 1.3

VI, and (2) the charge-separated structures VII and VIII. The former structures emphasize that the ten π electron tetraazapentalene systems formally contain two
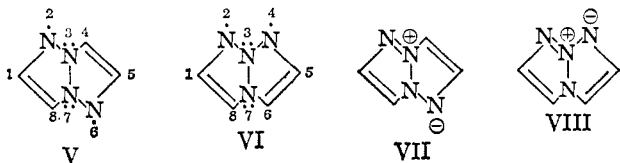
pyridine-like and two pyrrole-like nitrogen atoms. At first sight this seems to be a poor choice, since, e.g., VII has one more bond than V, and thus the empirical resonance energy might be overestimated when V is used as the basis. The energy of the extra bond is, however, largely offset by the large formal charge separation.

was determined from the heat of combustion of gaseous hydrazine ($\Delta H_c^\circ = -154.99$ kcal/mole)[9] and was found to be λ(N–N) = 33.0 kcal/mole. The heats of combustion of both I and II were found to be -1666.4 kcal/mole. The resonance energies are then E_R(I) = 121.7 kcal/ mole and E_R(II) = 132.4 kcal/mole. For series 2, the N=N bond contribution determined by Coates and Sutton[10] was employed, λ(N=N) = 34.2 kcal/mole, giving a heat of combustion of -1667.6 kcal/mole for both I and II. The resonance energies were thus determined to be E_R(I) = 122.9 kcal/mole and E_R(II) = 133.6 kcal/mole. The agreement between the two esti-

(8) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp 88–89.
(9) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, Washington, D. C., 1952.
(10) G. E. Coates and L. E. Sutton, J. Chem. Soc., 1187 (1948).

mates is very good. Because the models for I and II are virtually equivalent with regard to kinds of bonds, the experimental heats of formation reflect the resonance energies directly.

It is seen that the more angular-shaped molecule II is some 10.7 kcal/mole stable than the linear-shaped I. This behavior is typically that of pure benzenoid hydrocarbons where the analogs of I and II, naphthacene and chrysene, respectively, have resonance energies[8] as shown. Here the angular hydrocarbon is more stable

E_R=110.0 kcal /mole E_R=116.5 kcal /mole
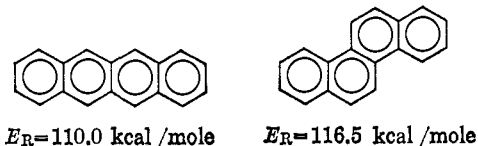
than the linear by 6.5 kcal/mole. It is interesting to note that the resonance energies of I and II are larger than those of their isoelectronic hydrocarbon counterparts.

If we consider that each benzene ring in I and II contributes roughly 36.0 kcal/mole to the resonance energy, then the contributions of the 1,3a,4,6a- and 1,3a,6,6a-tetraazapentalene nuclei in I and II, respectively, are roughly 49.7 (50.9) and 60.4 (61.6) kcal/mole for the series 1 and 2, respectively. The naphthalene-like nuclei of naphthacene and chrysene contribute 38.0 and 44.5 kcal/mole, respectively, to the resonance on this basis.

Calculations using similar models for the monobenzo derivatives III and IV give theoretical heats of combustion of −1178.4 kcal/mole for series 1 and −1179.6 kcal/mole for series 2. The empirical resonance energies are E_R(III) = 84.7 (85.9) kcal/mole and E_R(IV) = 92.8 (94.0) kcal/mole. The contributions of the tetraazapentalene nuclei are then 48.7 and 56.8 kcal/mole, respectively, in rough agreement with the values derived from the dibenzo derivatives.

Electronic Structure of Tetraazapentalenes. The relationship between the structure of the tetraazapentalenes and the valence isomerization ($e.g.$, Z → Z') which destroys aromaticity was discussed in paper I.[1a] HMO
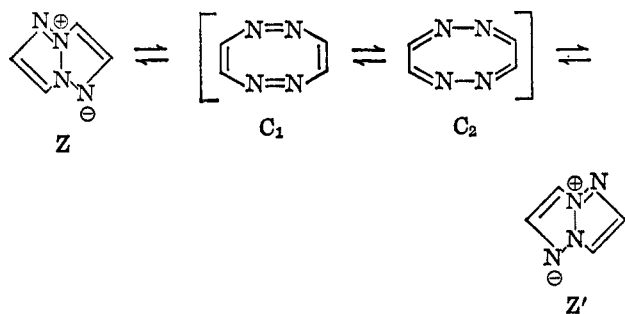
theory predicts that the delocalization energy per π electron is larger in pentalene dianion than in a fictitious planar cyclooctatetraene, and the same situation prevails for the nitrogen analogs.

Hückel calculations were carried out for Z, C_1, and C_2 employing the reasonable parameters[11] $\alpha_N = \alpha_C + 1.5\beta$ (pyrrole-like), $\alpha_N = \alpha_C + \beta$ (pyridine-like), and setting all $\beta = \beta_{CC}$. If we base the delocalization energy of the tetraazapentalene on one covalent structure such as Z, then the results in Table III are obtained.

(11) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 135.
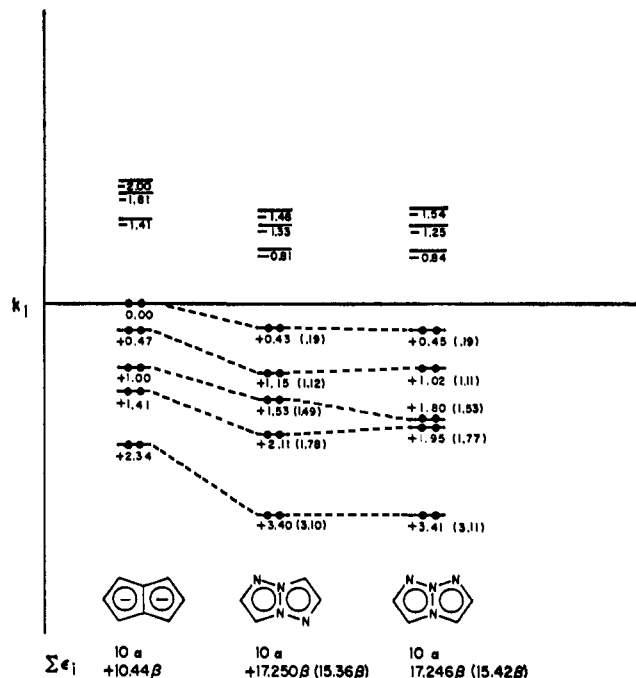

Figure 2. Energy level diagrams, $\epsilon_i = \alpha + k_i\beta$.

It is evident that the azapentalene structure is highly stabilized by electron delocalization on the basis of the delocalization energy per π electron, compared to either eight-membered ring structure. Since the latter structures would most likely exist in tub conformations, these values are also included, and it is seen that the azine form C_2 is slightly preferred over the azo form C_1.

Table III. Energies of Z, C_1, and C_2

	Total energy	Delocalization energy, β^{-1}	Delocalization energy/π electron
Z	$10\alpha + 17.250\beta$	4.421	0.44
C_1 (planar)	$8\alpha + 14.314\beta$	2.314	0.29
C_1 (tub form)	$8\alpha + 12.000\beta$	~0	~0
C_2 (planar)	$8\alpha + 14.314\beta$	1.369	0.17
C_2 (tub form)	$8\alpha + 12.944\beta$	~0	~0

The chemical reaction C_1 (or C_2) → Z involves the change of two nitrogen atoms from the valence state ($tr^2trtr\pi$) to ($trtrtr\pi^2$). This energy which amounts to 6.2 ev[12] must be less than the gain in π-delocalization energy plus the energy of the new N–N σ bond for this reaction to proceed. Therefore, since E_a(N–N) ~ 2.6 ev, then E_π(Z) − E_π(C_1) = $2\alpha + 5.25\beta$ must be greater than 3.6 ev. Any reasonable estimate of the integrals involved assures us that this is indeed so, and we conclude that the process C_1 (or C_2) → Z will be exothermic. Similar conclusions can be drawn about the tetraazapentalene nucleus in III.

Molecular orbitals were calculated for T, the nucleus of III, using the same integral values, and the energy level diagrams in Figure 2 compare Z, T, and pentalene dianion. First, it is to be noted that all bonding levels are displaced to lower energies as expected, when nitro-

(12) J. Hinze and H. H. Jaffé, $J. Am. Chem. Soc.$, **84**, 540 (1962).

T
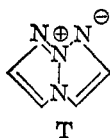
gen is introduced into the nucleus of pentalene dianion. Second, it is clear that the *position of the nitrogen atoms has very little effect on the energy levels or the total energy*. This kind of behavior would be expected if the tetraazapentalene nucleus is aromatic and its π electrons highly delocalized. The bond orders and charge distribution of Z and T are also very similar, in further confirmation of this conclusion (Table IV).

Table IV. Bond Orders and Charge Densities of Z and T

Z   T

		Bond orders	
12	0.421	12	0.443
23	0.514	34	0.581
34	0.739	45	0.751
45	0.588	56	0.491
26	0.433	26	0.435
		Charge densities	
1,5	1.497	1,3	1.490
2,6	1.447	2	1.436
		6	1.454
3,7	1.080	5,7	1.082
4,8	0.976	4,8	0.983

These crude calculations are sufficient for our purpose of explaining the aromaticity of the tetraazapentalenes. The results suggest that Z and T are close in energy, and similar calculations on I and II show that the mono- and dibenzo derivatives have delocalization energies that do not depend much on the location of the nitrogen atoms. More accurate calculations indicate that II is slightly more stable than I, and this conclusion is in accord with precise thermodynamic data.

A better estimate of the energy levels of the azapentalenes can be made by considering their structures more closely. In an HMO calculation some means must be found for estimating the parameters, since a given nitrogen atom occurs successively in various valence states depending on the canonical structures. In the 1,3a,6,6a system there are 12 resonance structures like VII which are nonexcited in the Pauling sense. Presumably, most of these make significant contributions to the ground state, and monoexcited structures such as
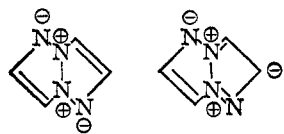

will contribute to a lesser extent.

We estimate the HMO coulomb (h) and resonance (k) parameters in the following way. For each nitrogen in a fixed position a factor was determined that corresponds to the number of times it occurs as a pyridine, pyrrole, quaternary, and amide type. The usual Hückel

parameters suggested by Streitwieser[11] were then weighted by these factors to determine an average parameter for each nitrogen. The monoexcited structures were taken into account the same way, but weighted only one-tenth relative to the nonexcited. The β's were determined similarly. In this manner, valence-bond structures were used to estimate the molecular orbital parameters. For our purpose, the systems are numbered as in V and VI. The resulting one-electron parameters are

V	VI
$h_2 = +0.383$	$h_2 = +0.388$
$h_3 = +1.733$	$h_3 = h_7 = +1.747$
$k_{23} = k_{37} = k_{34} = +0.80$	$k_{23} = k_{37} = k_{67} = +0.80$
$k_{12} = k_{45} = +1.00$	$k_{12} = k_{56} = +1.00$

The energy levels are given in parentheses in Table IV, and it is thought that these results are close to self-consistent values. The total energies of the dibenzo derivatives are $E(\mathrm{I}) = 18\alpha + 26.904\beta$, $E(\mathrm{II}) = 18\alpha + 27.002\beta$ and of the monobenzo derivatives, $E(\mathrm{III}) = 14\alpha + 21.152\beta$, $E(\mathrm{IV}) = 14\alpha + 21.210\beta$. The corresponding delocalization energies based on the non-charge-separated structures are $E_\mathrm{D}(\mathrm{I}) = 7.905\beta$, $E_\mathrm{D}(\mathrm{II}) = 8.004\beta$, $E_\mathrm{D}(\mathrm{III}) = 6.151\beta$, and $E_\mathrm{D}(\mathrm{IV}) = 6.213\beta$. Isomer II is predicted to be more stable than I, and similarly IV more stable than III, in accord with the experimental heats of formation. It is expected that the difference in delocalization energies, *e.g.*, $E_\mathrm{D}(\mathrm{II}) - E_\mathrm{D}(\mathrm{I})$, should be proportional to the difference in heats of formation. Thus, $8.004\beta - 7.905\beta = 10.7$ kcal/mole, or β(empirical) $= 108.1$ kcal/mole. It is calculated for the monobenzo derivatives than $E_\mathrm{D}(\mathrm{IV}) - E_\mathrm{D}(\mathrm{III}) = 0.062\beta = 6.7$ kcal/mole, while the experimental value is 8.2 kcal/mole, in satisfactory agreement.

Charge distributions were calculated for I–IV, and the results are shown below. If electrophilic substitution in these molecules parallels electron density in the

I

II

III

IV
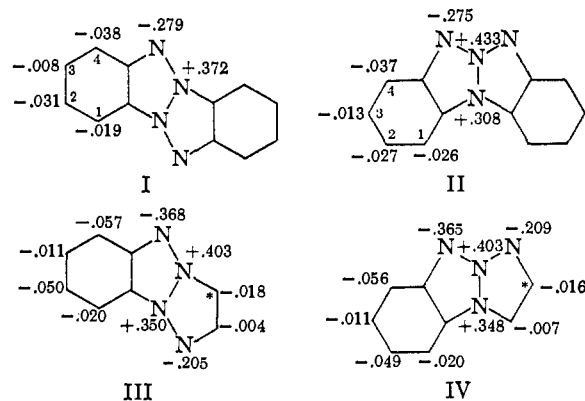
ground state, then the 2 and 4 positions in the benzene rings of I and II should be preferentially nitrated, chlorinated, etc., and this seems to be the case.[1b,c] Electrophilic attack in the tetraazapentalene nucleus is predicted to occur preferentially at the positions marked by asterisks in III and IV, and substitution products[1b,c] are believed to have these structures. It is interesting to note that HMO calculations employing the usual parameters[11] for these charge-separated structures give charge distributions that make the benzene rings assume small net positive charges and predict incorrect orientation for electrophilic substitution. Experi-

mentally, I and II are nitrated, for example, more readily than benzene, an observation in accord with the more nearly self-consistent calculations.

The bond orders of the N–N central bonds in the tetraazapentalene nuclei have the values ρ_{NN} = 0.300 (I), 0.285 (II), 0.300 (III), 0.297 (IV). The bond orders of the C–C central bonds in pentalene dianion and naphthalene are ρ_{CC} = 0.531 (PA), 0.518 (N), and the buildup of density in the central bond region is characteristic of normal aromatic structures. The appreciable bond orders of the tetraazapentalenes in this region further support the conclusion that these molecules are truly aromatic.

The ultraviolet spectra of I and II are complicated but are not unlike those expected for fully aromatic structures.[1a] In naphthalene, which contains ten π electrons, the three lowest observed singlet states correspond to states predicted by Pariser–Parr theory (employing all singly excited configurations)[13,14] which occur at 4.19 ($^1B_{3u}$), 4.48 ($^1B_{2u}$), and 5.92 ev ($^1B_{3u}$), and only transition to the latter two are allowed. The B_{2u} state is largely derived from the configuration V_{56}, obtained by promoting an electron from MO 5 to MO 6. The two B_{3u} states are obtained mostly from mixing of V_{57} and V_{46} which interact strongly because their energies are degenerate. Although $E(V_{56}) < E(V_{57}) = E(V_{46})$, the mixing depresses one of the resulting B_{3u} states so that it actually occurs below the B_{2u} state.

The isoelectronic pentalene dianion shows two strong absorptions in the ultraviolet region[15] which agree with the spectrum calculated by Pariser–Parr configuration interaction theory.[16] The three lowest singlets corresponding to those observed for naphthalene are predicted to occur at 4.57 ($^1B_{2u}$), 5.12 ($^1B_{3u}$), and 7.11 ev ($^1B_{3u}$), and here all three are allowed. The states of same symmetry are formed primarily from the same configurations as in naphthalene, but the nonalternant character of the molecular orbitals precludes the strong degenerate mixing of V_{46} and V_{57}. Thus, the B_{2u} state is the lowest, in accord with the observation that $E(V_{56}) < E(V_{57})$ or $E(V_{46})$. In pentalene dianion, the high-energy B_{3u} state occurs in the vacuum ultraviolet and has not yet been identified.

Three similar absorptions are expected to occur in the tetraazapentalenes Z and T. Inspection of Figure 2 shows that on going from pentalene dianion to Z, V_{56} decreases strongly in energy, V_{57} decreases only slightly, and V_{46} increases slightly. On going to T, V_{56} decreases less strongly than in Z, V_{57} decreases more strongly, and V_{46} decreases slightly. When two benzene rings are fused on Z and T to form I and II, the characteristic properties of the states in question are anticipated to be largely preserved.

Although the assignments for the spectra of I and II are yet unknown, it is reasonable that the three regions of absorption in them correlate with the three lowest energy configurations discussed above. From Table I in paper I we see that the two longest wavelength regions of I are indeed red shifted with respect to the aromatic hydrocarbon analog chrysene, and the highest energy absorption is blue shifted, as predicted. Also, in accord with expectation, the long-wavelength absorption of II is blue shifted with respect to that of I and occurs actually at about the same place as that in chrysene. The next two bands in II, however, are also blue shifted with respect to those in I. This crude picture is satisfying and is all we might have hoped for using such poor molecular orbitals as a basis and neglecting electron repulsion effects.

(13) R. Pariser, *J. Chem. Phys.*, 24, 250 (1956).
(14) H. E. Simmons, *ibid.*, 40, 3554 (1964).
(15) T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.*, 84, 865 (1962).
(16) H. E. Simmons, unpublished results.

Aromatic Azapentalenes. V. 1,1'- and 1,2'-Bibenzotriazoles and Their Conversion to Dibenzotetraazapentalenes

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Abstract: The syntheses, physical properties, and structural assignments for 1,1'-bibenzotriazole (4a) and 1,2'-bibenzotriazole (8) are described. Both 4a and 8 lose nitrogen on heating to give dibenzo-1,3a,4,6a-tetraazapentalene (1) and dibenzo-1,3a,6,6a-tetraazapentalene (2), respectively.

In earlier papers in this series,[1,2] the synthesis of dibenzo-1,3a,4,6a-tetraazapentalene (1) by thermal or photochemical decomposition of o,o'-diazidoazobenzene was described. This interesting heteroaromatic system has now been prepared by an alternative route,

(1) R. A. Carboni and J. E. Castle, *J. Am. Chem. Soc.*, 84, 2453 (1962).
(2) R. A. Carboni, J. C. Kauer, J. E. Castle, and H. E. Simmons, *ibid.*, 89, 2618 (1967).

i.e., through controlled thermal decomposition of 1,1'-bibenzotriazole (4). A similar thermolysis occurs with the isomeric 1,2'-bibenzotriazole (8) to form the corresponding dibenzo-1,3a,6,6a-tetraazapentalene (2).[2] This paper discusses the synthesis, proof of structure, and decomposition of the hexaaza compounds 4 and 8.

1,1'-Bibenzotriazole. The hexaaza derivative 4 was prepared in good yield from tetraazotized o,o'-diamino-