anhydride was refluxed for 1 hr. The residue obtained upon concentrating the reaction mixture was triturated in 250 ml of 5% sodium bicarbonate solution, giving 14.3 g of the diacetyl derivative of **11a**, as light tan crystals.

An analytical sample had mp 237–241° after two recrystallizations from methylcyclohexane; uv, Figure 3; nmr δ 1.88 (s, 6 H, $COCH_3$), 6.35 (d of m, 2, two pyridine H), 6.90–8.20 (m, 12, H_α, H_β, H_γ, and remaining pyridine H with H_γ appearing as a singlet at 7.80; H_β, d, J = 9 Hz at 7.98; H_α, d, J = 9 Hz at 7.30); mass spectrum (70 eV) m/e 448 (M^+), 406, 370, 364, 328, 286.

Anal. Calcd for $C_{28}H_{20}N_2O_4$: C, 75.0; H, 4.5; N, 6.2. Found: C, 75.0; H, 4.9; N, 6.3.

The above product was deacetylated by heating a solution of it in 100 ml of 6 N hydrochloric acid for 0.5 hr at reflux temperature. The resulting crystalline dihydrochloride was isolated after concentrating the reaction mixture to dryness; its neutralization with 5% sodium bicarbonate solution gave 10.2 g (88%) of essentially pure (tlc) **11a** as fine yellow needles.

Registry No.—**5d**, 30309-81-0; **7**, 30309-82-1; **9**, 30309-83-2; **11a**, 26244-86-0; **11a** diacetyl derivative, 26244-85-9; **11b**, 30309-86-5; **11c**, 30309-87-6; **11d**, 30309-88-7; **11e**, 30309-89-8; **12**, 30259-90-6; **13** diacetyl derivative, 30309-90-1; **14**, 30259-91-7; **15** diacetyl derivative, 30309-91-2; 3,6-diacetylphenanthrene, 30309-92-3; 5-methyl-2-(1,3-dioxolan-2-yl)pyridine, 30309-93-4, 30309-94-5 (methoperchlorate); 3,10-dimethyl-4a,8a-diazoniapentaphene diperchlorate, 30309-95-6.

Acknowledgment.—We wish to thank Mr. D. P. Maier for supplying the mass spectral data and Dr. P. I. Rose for technical assistance in recording some of the nmr spectra and for helpful discussions regarding their interpretation.

Overcrowded Molecules. III. 13,14-Bis(2-pyridyl)pentaphene and Related Compounds

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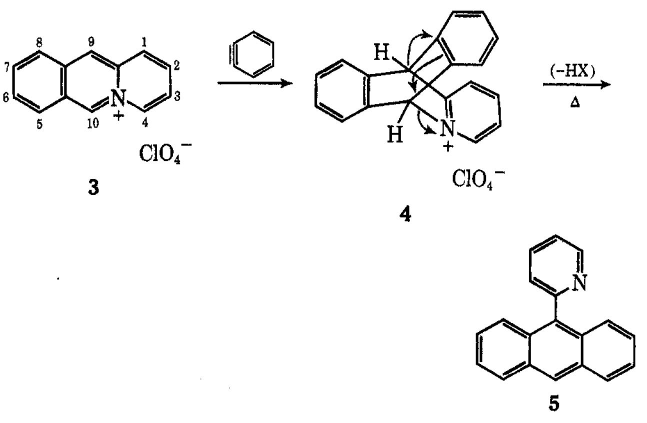
Received January 6, 1971

The reaction of benzyne with 4a-azoniaanthracene and 4a,8a- and 4a,12a-diazoniapentaphene salts produces, in good yields, azoniatriptycene-type adducts, which are thermolyzed in boiling acetic anhydride to 9-(2-pyridyl)-anthracene (**5**), 5,13- (**15**), and 13,14-bis(2-pyridyl)pentaphenes (**18**), respectively. The nmr spectrum of **19**, the bis-N-methyl quaternary salt of **15**, displays each of its N-methyl resonances as two sharp peaks of equal intensity up to 130°, indicative that both pyridine rings are suffering restricted rotation giving rise to a pair of geometric isomers. The nmr spectrum of the mono-N-methyl quaternary salt of **18** shows the presence of at least two of the four possible geometrical isomers; these, however, begin to interconvert at room temperature and are equilibrated above 80° ($\Delta F^{\ddagger} \sim 17$ kcal/mol). The bis-N-methyl quaternary salt of **18** shows its N-methyl absorptions as two singlets (2:1 area ratio) at 70°. The major peak is temperature independent, whereas the minor peak broadens as the temperature is lowered, finally separating into two singlets of equal area at 20°. These results are interpreted in terms of an unexpectedly facile pentaphene ring inversion accompanied by a synchronous rotation of both pyridines.

Previously it has been shown that, in marked contrast to the low order of reactivity that azonia polycyclic aromatic compounds display toward conventional electrophilic dienophiles, a variety of these compounds will readily undergo stereoselective 4 + 2 cycloadditions with nucleophilic olefins including enamines and ketene acetals to give adducts in high yields.[1] The ketene diethyl acetal adduct of 5-acetoxy-8-*tert*-butyl-4a-azoniaanthracene perchlorate and the bis adduct of 4a,8a-diazoniapentaphene diperchlorate have been particularly useful, serving as precursors to the interesting, highly overcrowded naphthalene **1**[2] and phenanthrene **2**,[3] respectively, *via* the synthesis shown in Scheme I.

Benzyne is considered to be an electrophilic reagent. Nevertheless, we have now found that it too will undergo cycloaddition efficiently with azonia polycyclics to afford azoniatriptycene-type adducts (**4**). Our interest in these types of compounds has been twofold. First, they serve as precursors to substituted anthracenes and related hydrocarbons in a synthesis to be described in a separate publication. Second, and relevant to this paper, is the discovery that their thermolysis usually leads to pyridyl-substituted polycyclic aromatic hydrocarbons, the simplest of these being 9-(2-pyridyl)anthracene (**5**). Exploitation of this reaction sequence as a new synthetic approach to overcrowded molecules has been profitably investigated in the synthesis of highly strained nonplanar, and therefore chiral, 13,14-bis(2-pyridyl)pentaphene. Manifestations of the ring strain and unusual geometry associated with this compound parallel those previously observed with 4,5-dipyridylphenanthrene **2** in several ways. One interesting and distinctive difference is discussed, related to conformational isomerism.



3

4

5

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[1] D. L. Fields, T. H. Regan, and J. C. Dignan, *J. Org. Chem.*, **33**, 390 (1968).

[2] D. L. Fields and T. H. Regan, *ibid.*, **36**, 2986 (1971).

[3] D. L. Fields and T. H. Regan, *ibid.*, **36**, 2991 (1971).

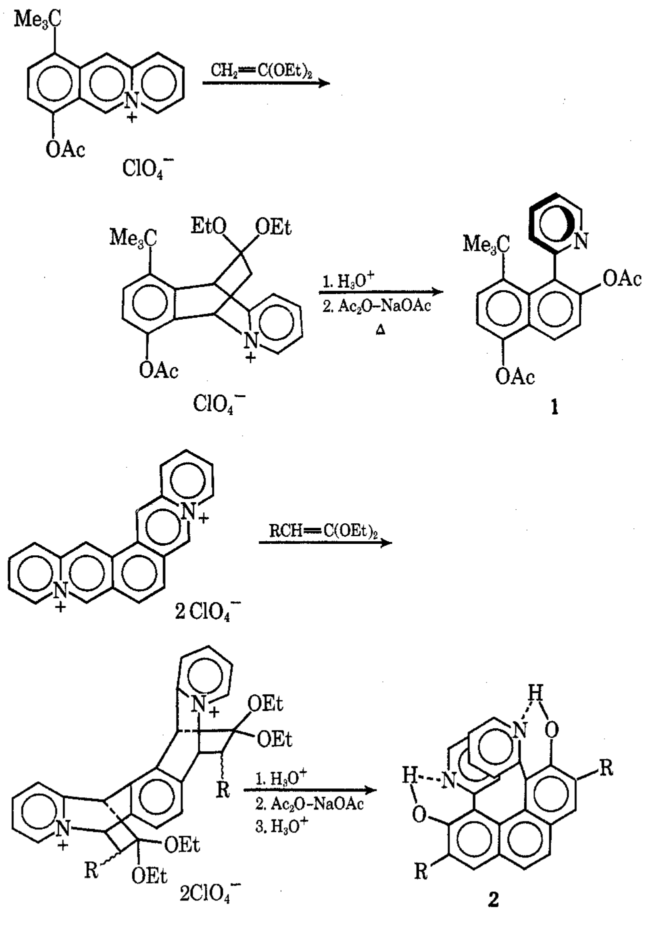
TABLE I

AZONIATRIPTYCENE PERCHLORATES (4)

No.	Starting azoniaanthracene (3)	Yield, %	Calcd, %			Found, %		
			C	H	N	C	H	N
4a	Unsubstituted[a]	78	64.1	3.9	3.9	64.2	4.1	3.9
4b	5,6-Diacetoxy-8-phenyl[b]	67	63.8	4.0	2.6	63.4	3.9	2.4
4c	5-Acetoxy-8-*tert*-butyl[c]	75	63.9	5.2	3.0	63.5	5.3	2.9
4d	5-Methyl[a]	75	65.0	4.3	3.7	64.8	4.4	3.7
4e	7-Methyl[a]	72	65.0	4.3	3.7	64.9	4.7	3.6
4f	9-Phenyl[d]	59	67.7	4.4	3.4	68.1	4.8	3.2
4g	5-Nitro[e]	55	56.8	3.2	8.8	56.5	3.2	8.7

[a] C. K. Bradsher and L. E. Beavers, *J. Amer. Chem. Soc.*, **77**, 4812 (1955). [b] D. L. Fields, J. B. Miller, and D. D. Reynolds, *J. Org. Chem.*, **30**, 252 (1965). [c] D. L. Fields and J. B. Miller, *J. Heterocycl. Chem.*, **7**, 91 (1970). [d] C. K. Bradsher and N. L. Yarrington, *J. Org. Chem.*, **28**, 78 (1963). [e] C. K. Bradsher and J. C. Parham, *J. Heterocycl. Chem.*, **1**, 30 (1964).

SCHEME I



Results and Discussion

Azoniatriptycenes (4).—While the triptycene synthesis developed by Friedman and Logullo,[4] involving the reaction of anthracene with benzyne generated from anthranilic acid, diazotized *in situ*, is suitable for converting azoniapolycyclics to azoniatriptycene-type adducts *per se*, this procedure was modified slightly to make it more compatible with our ionic starting materials. Thus, concurrent additions of acetonitrile solutions of approximately equimolar quantities (twofold excess) of anthranilic acid and isoamyl nitrite to a refluxing mixture of 0.1 mol of **3** in the same solvent is completed within 15 min, and the reaction mixture is worked up immediately. The isolation and purification of the desired product generally is easier than that encountered in the analogous triptycene preparation in that the azoniatriptycene salt can be precipitated by addition of ether, leaving the usual benzyne by-products in solution. Thus, a considerable excess of benzyne reagents can be used without unduly complicating the isolation–purification steps, thereby eliminating the usual product contamination by unreacted **3**. In Table I are listed azoniatriptycene perchlorates prepared in this manner. No attempt was made to optimize the reaction conditions and the reported yields generally represent the results of single experiments. Support for the structural assignment for these adducts was by elemental analysis, spectral evidence, and in several cases by their behavior upon thermolysis, as discussed later.

9-(2-Pyridyl)anthracenes.—To effect the conversion of an azoniatriptycene (**4**) to the corresponding 9-(2-pyridyl)anthracene, the adduct is heated in a high-boiling solvent such as acetic anhydride or diglyme, in the presence of sodium acetate, and the ensuing elimination reaction monitored by following the appearance and increase in the characteristic anthracene absorptions in the 320–390-nm region. Since aromatization to an anthracene provides a major driving force for this reaction, the facility with which the elimination occurs is influenced by the size of the R group on C_8; that is, the more bulky the C_8 substituent, the more destabilized the final product owing to adverse peri interaction with the 9-pyridyl group, and the less energetically favorable the reaction. This was borne out by qualitative observations made on the relative rates of anthracene formation starting with **4a**, **4b**, and **4c**, where R_8 = H, C_6H_5, and *tert*-C_4H_9, respectively (Scheme IIA). In refluxing acetic anhydride–sodium acetate the maximum concentrations of anthracenes **5** and **6** were formed within 5 min and 4 hr, respectively, and were isolated at the end of these periods in 86 and 62% yields. The 8-*tert*-butyl adduct **4c**, on the other hand, was recovered quantitatively after a 24-hr reaction period under the same conditions, was unchanged after 4 hr at 160° in diglyme, and slowly decomposed at 290° neat (10° above its melting point) with no indication of anthracene generation in the process.

After recognizing the relative inertness of **4c** to thermolysis, we also examined the 5-hydroxy derivative **8** (Scheme IIB) since the hydroxyl function could allow the formation of the much less sterically strained ketone **10**[5] as well as provide an alternate elimination route *via* ketomethine **9**. However, heating a mixture of **8** and sodium acetate in diglyme, varying

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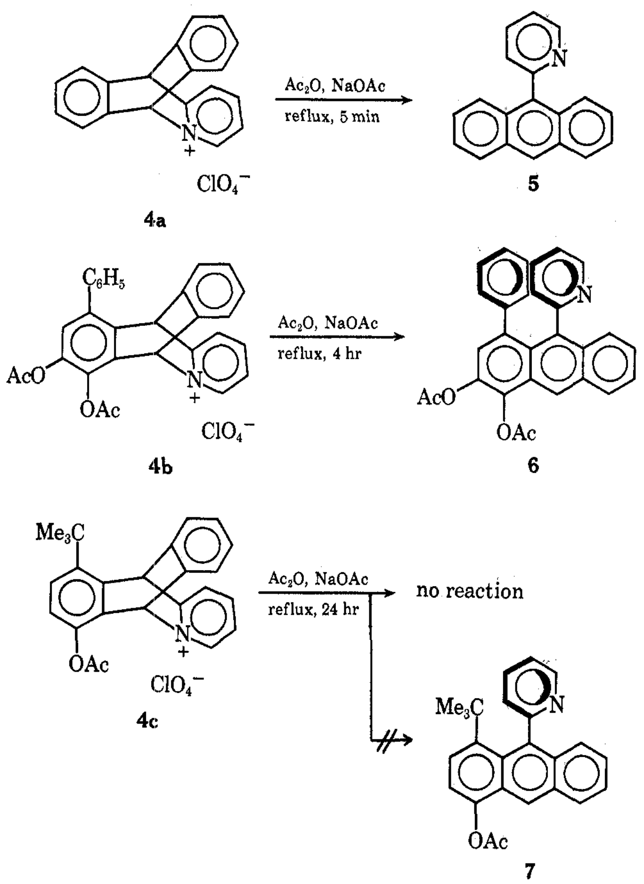
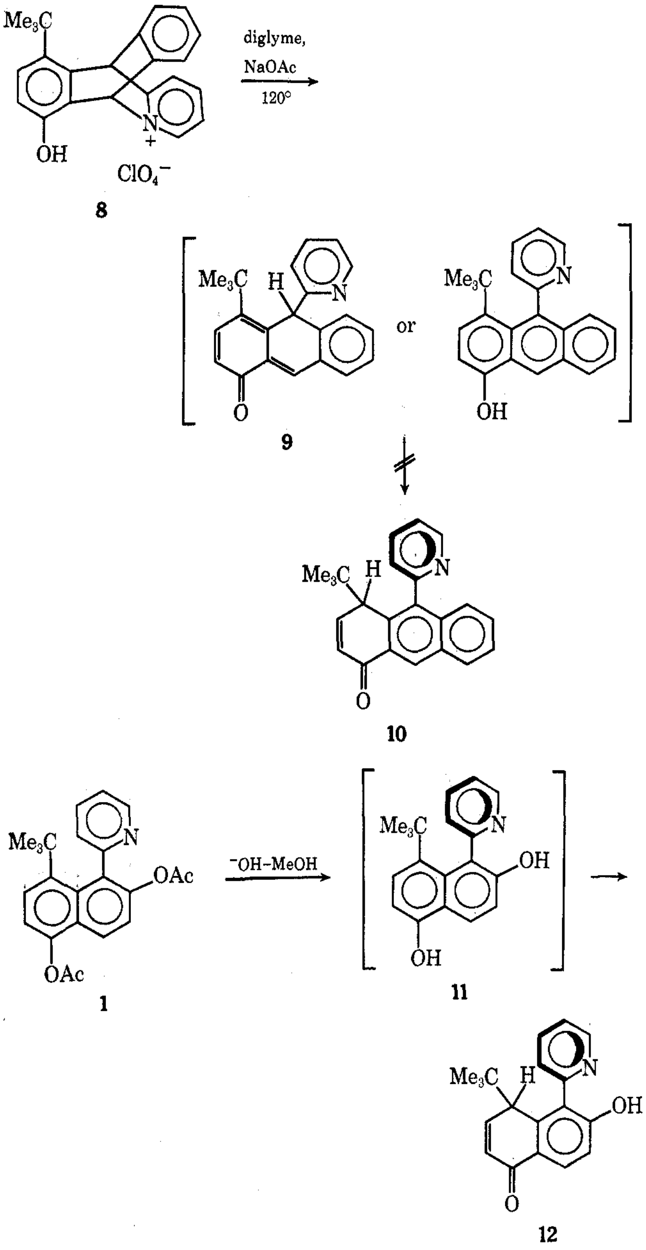
[4] L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, **85**, 1549 (1963).

[5] Naphthalenediol **11**, for example, avoids a similar peri interaction by existing exclusively in the tautomeric keto form, **12**; see ref 2.

SCHEME IIA

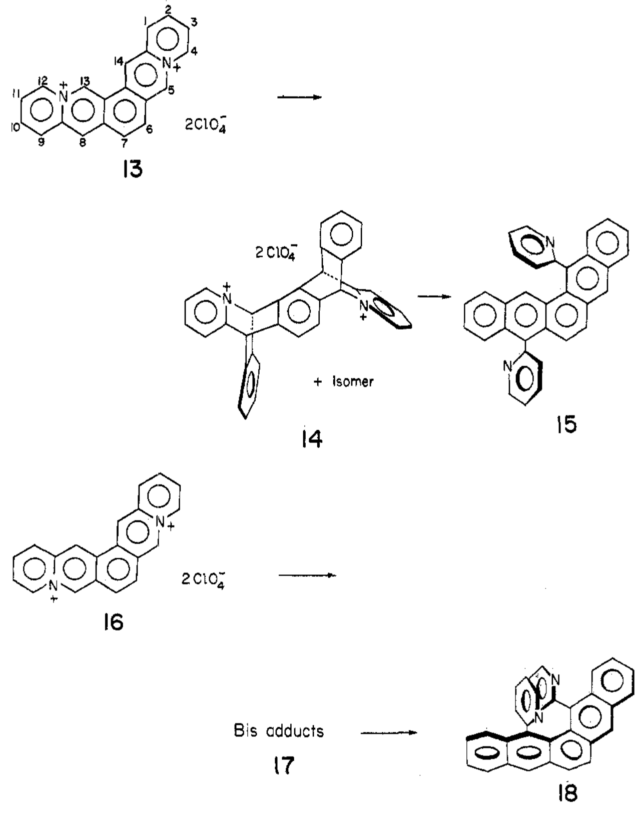


SCHEME IIB



the temperature and time, resulted only in the eventual nondescript decomposition of the starting material.

Bis(2-pyridyl)pentaphenes.—Based on the known sites of cycloaddition of ketene diethyl acetal to 4a,12a- and 4a,8a-diazoniapentaphene diperchlorates,[1,3] benzyne should cycloadd twice in each case, across the 5,14 and 8,13 positions, to give a mixture of two isomers resulting from attack by the second benzyne from the same or the opposite side of the pentaphene ring. Thermolysis of bis adducts **14** and **17**, regardless of their stereochemistry, should, and in fact did, give pentaphenes **15** and **18**, respectively.



As an example of the rather simple synthetic technique required, crude amorphous adduct **14**, isolated following treatment of **13** in the usual way with a threefold molar excess of benzyne reagents, was neither purified nor characterized other than to establish the absence of unreacted **13** (by uv), but was heated for 2 hr in refluxing acetic anhydride in the presence of sodium acetate. Florisil chromatography of the syrup obtained after removing solvent and neutralizing the residue with aqueous sodium carbonate solution gave the desired crystalline **15** in 26% overall yield. The structural assignments of it and its bis-*N*-methyl perchlorate derivative (**19**) were supported by elemental analyses and by the spectral evidence cited below.

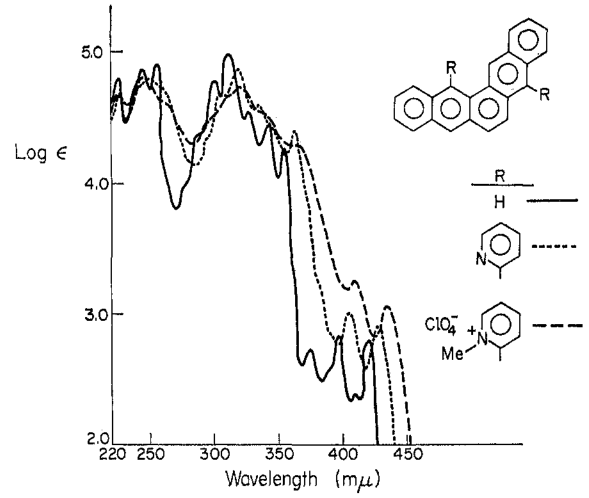


Figure 1.—Ultraviolet spectra of **15**, **19**, and pentaphene.

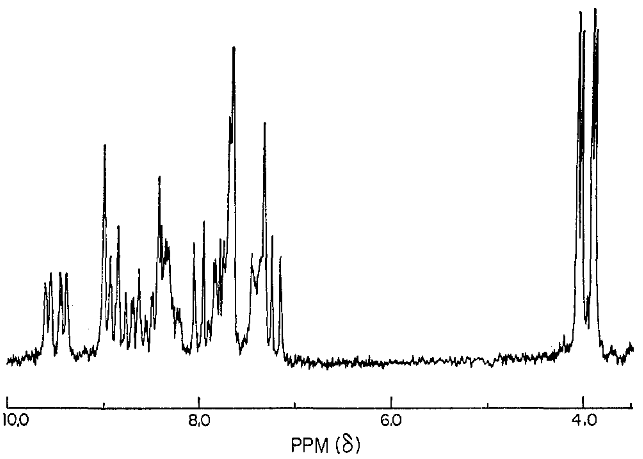
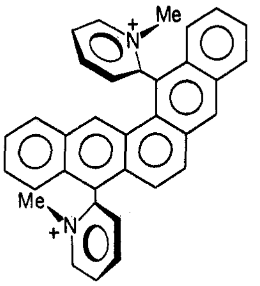


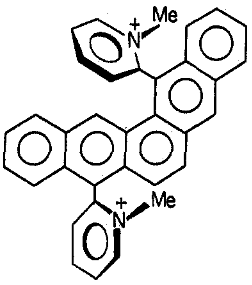
Figure 2.—*Nmr spectrum of pentaphene* **19a,b**.

The two important peaks in the mass spectrum of **15** occur at *m/e* 432 (100%) M$^+$ and 431 (92%). A comparison of the ultraviolet spectra of **15**, **19**, and pentaphene itself (Figure 1) shows them to be very similar, in keeping with the expectation that, owing to potential steric interaction with the 7,9- and 1,13-pentaphene hydrogens, the pyridines are nonplanar with respect to the pentaphene moiety and thus do not significantly perturb the pentaphene chromophore.

The presence of the methyl groups found in bispyridinium salt **19** greatly accentuates the degree of interaction with these same pentaphene hydrogens, and should further discourage rotational freedom of both pyridines. An examination of the aliphatic region in the nmr spectrum of **19** is quite informative on this point (Figure 2), showing each of the methyls as a pair of sharp singlets up to at least 130° with no hint of peak coalescence. This indicates that, at least on the nmr time scale, **19** is actually a mixture of two noninterconverting geometric isomers, **19a** and **19b**. It is not known whether parent **15** also exists in two analogously stable isomeric forms.



19a

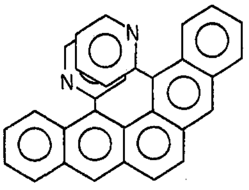


19b

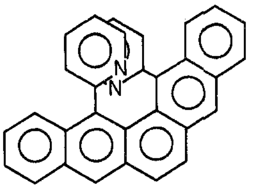
The synthetic procedure just described proved equally applicable to converting diazoniapentaphene **16** to dipyridylpentaphene **18**. The overcrowding found in this compound is probably quite similar to that being experienced by the 4,5-bis(2-pyridyl)-phenanthrene-3,6-diols (**2**),[3] a class of compounds we have studied previously in some detail. For example, we know by a single-crystal X-ray analysis[6] that **2** (R = Br) is distorted from a planar configuration (see Figure 3). The two pyridines have a stair-step relationship to one another, are almost parallel, and are extremely close, having a nonbonded intramolecular contact of 2.81 Å. In all likelihood **18** will be similarly distorted, and, indeed, abnormalities we have noted in some of the spectral properties of **2** as a result of overcrowding are equally evident for **18**.

Its mass spectrum shows *m/e* 432 (14%) M$^+$, 431 (0.3%), and 354 (100%) M − pyridyl. The predominant and unusual loss of a pyridyl group, an insignificant fragmentation (5%) in the less strained isomeric **15**, is also the major mass spectral fragmentation path taken by **2**, and is attributed in both instances to a drive toward strain relief. Likewise, perturbations in the π system of **18** owing to overcrowding are prominently displayed in its uv spectrum (Figure 4) in the form of bathochromic and hyperchromic shifts and loss of fine structure in the long-wave absorptions when compared with the spectrum of **15** (Figure 2). The uv spectrum of **2** was previously characterized by analogous spectral shifts.[3]

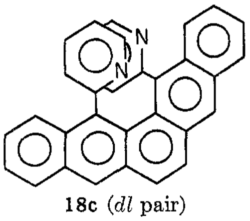
There is one interesting dissimilarity in these two types of compounds. In the di-ring-opening reactions leading to **2** and **18**, we had assumed earlier that once aromatization to the phenanthrene or pentaphene was complete, the pyridines would suffer restricted rotation, thus giving rise to three possible geometrical isomers differing solely in the conformational relationship of the pyridines to one another, *i.e.*, **18a–c**. In our study of **2**, only one of these types of isomers was recognized, that one having both pyridine nitrogens oriented toward their respective neighboring hydroxyls, thus permitting intramolecular hydrogen bonding to prevail.



18a (*dl* pair)



18b (*dl* pair)



18c (*dl* pair)

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(6) D. L. Smith and E. K. Barrett, *Acta Crystallogr., Sect. B*, **27**, 419 (1971).

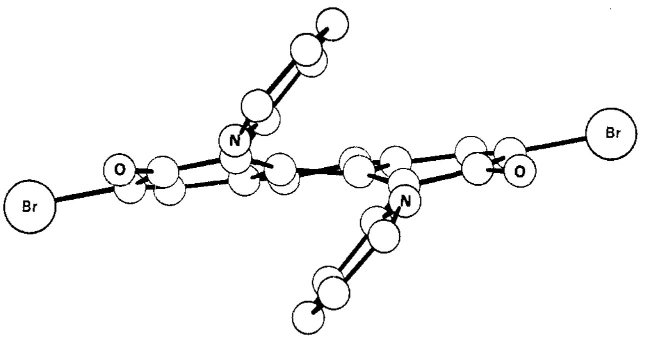
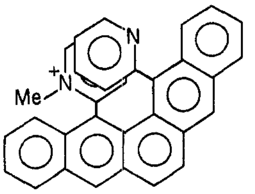


Figure 3.—View of **2** (R = Br) along the twofold symmetry axis.

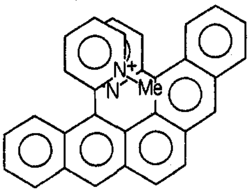
However, in the thermolysis of **17** to produce **18**, there is no obvious influence which would similarly dictate the orientation of the pyridines prior to complete aromatization. Therefore it would be reasonable to expect **18** to be a mixture of the three diastereoisomers shown.

In hope of shedding light on this possibility through nmr techniques, both mono- and bis-*N*-methylpyridinium derivatives were prepared. The mono derivative **20** was formed quantitatively by allowing a solution of **18** in methyl iodide to stand at room temperature for 6 hr. Prolonged treatment (18 hr) at reflux temperature (42°) failed to effect the alkylation of the second pyridine, reflecting the fact that the bis derivative must necessarily have two positive charges very close to one another. Bisquaternary salt 21 was obtained in good yield, but only by using much more drastic conditions, *i.e.*, boiling methyl *p*-toluenesulfonate.

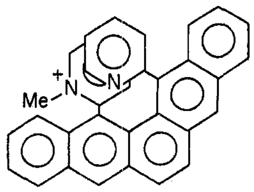
Considering first the monopyridinium derivatives, if one assumes 18 to be a mixture of **a**, **b**, and **c** isomers, then their mono-N-methylation could give a total of four diastereoisomers, **20a–d** (each as a *dl* pair), wherein **18a** and **18b** yield **20a** and **20b**, respectively, while **18c** gives both **20c** and **20d**. *A priori*, the chemical shifts of the methyls of **20a** and **20c** should be sufficiently different from those of **20b** and **20d** to make the two pairs distinguishable even though the methyl environments of **20a** and **20c**, or **20b** and **20d**, are similar enough to probably make their respective chemical shifts coincidental.



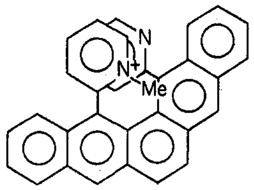
20a (*dl* pair)



20b (*dl* pair)



20c (*dl* pair)



20d (*dl* pair)

In the nmr spectrum of **20** dissolved in DMSO-d_6–CD$_3$CN (1:1 v/v) the line shape of the methyl resonance was found to be a function of temperature (Figure 5). At 5° two distinct peaks at δ 2.89 and 3.01 were seen, which are due to conformers **20a,c** and **20b,d**. As the temperature was raised, the two lines coalesced and became a sharp singlet above 80°. A line-shape analysis[7a] of the methyl signal of **20** dissolved in a mixture of DMSO-d_6–acetone-d_6 (3:7 v/v) yielded a free energy of activation of 16.6 ± 0.1 kcal at 30° and a $\Delta H^{\ddagger}$ of 10.0 ± 0.1 kcal.[7b] Changing the solvent to hexafluoroacetone increased the temperature at which coalescence occurs to ~45°.

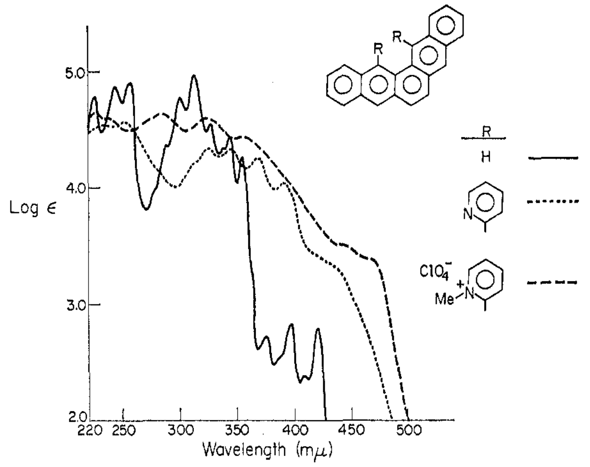
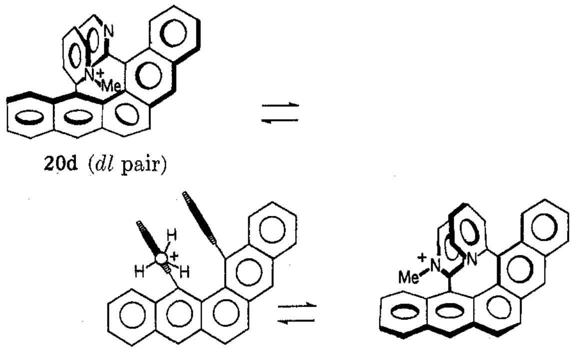


Figure 4.—Ultraviolet spectra of **18**, **21**, and pentaphene.

The only reasonable explanation for these results is that our original assumption that the pyridines are locked into a rigid conformation is incorrect. Instead it appears that at room temperature, the twisted pentaphene is undergoing ring inversion accompanied by a *synchronous* rotation of both pyridines so that **20a** and **20b** are interconverting as are **20c** and **20d** (for example, eq 1).



20d (*dl* pair)

20c (*dl* pair)

(1)

At elevated temperatures the two types of *N*-methyls are interchanging environments sufficiently rapidly by this process so that the resulting spectrum shows a single sharp line. The ring inversion is slowed as the temperature is lowered to the point where the two types of unequally populated conformers can be observed.

Further support for this rationale comes from examination of the nmr spectrum of the bis-*N*-methylpyridinium derivative **21**. For the bis-*N*-methyl-

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(7) (a) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Amer. Chem. Soc.*, **88**, 3185 (1966); J. Jonas, A. Allerhand, and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 3396 (1965). (b) On the basis of the above figures one can estimate a value of $\Delta S^{\ddagger}$ that is ~−20 ± 10 eu. However, there was no attempt made to estimate the size of the temperature dependent part of $\Delta H^{\ddagger}$ which may be fairly large: G. Govil and H. J. Bernstein, *ibid.*, **48**, 285 (1968).

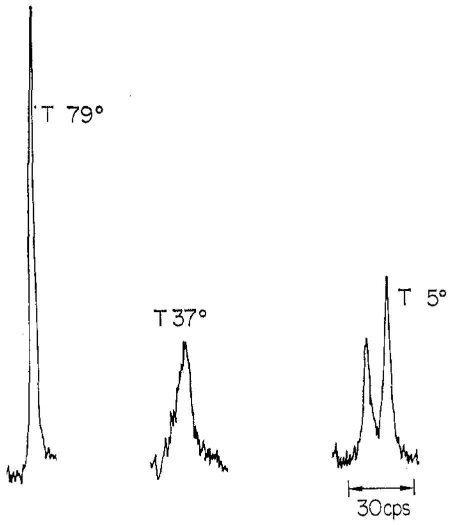


Figure 5.—The temperature dependence of the N–CH_3 resonances of pentaphenes **20a–d** (100 MHz).

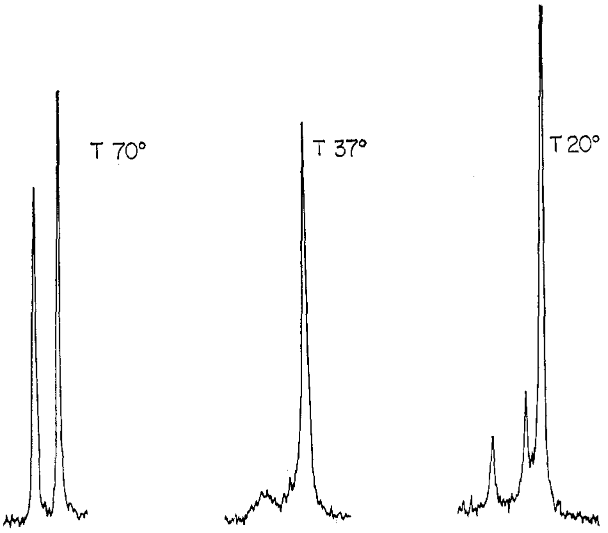
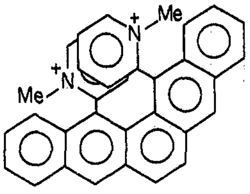
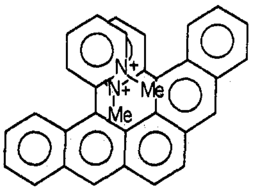


Figure 6.—The N–CH_3 resonances of pentaphenes **21a–c** at different temperatures.

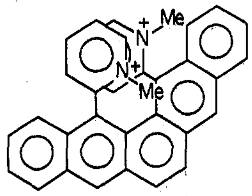
pyridinium derivative there are three diastereoisomers possible, **21a**, **21b**, and **21c**, each again existing as a *dl* pair. Isomers **21a** and **21b**, each have a twofold axis of symmetry, making their respective methyls magnetically equivalent. If our interpretation of the ring inversion with synchronous pyridyl rotation is correct, they will equilibrate in solution, allowing one isomer, that one having the largest N^+–N^+ charge separation, to strongly dominate, and its *N*-methyl absorption would be observed as a temperature-independent singlet. The preferred conformer would probably be **21b**, based on analogy with the known distances found in **2** by X-ray analysis. On the other hand, ring inversion of **21c** simply results in an equilibration of its two enantiomeric forms with no net ground-state energy change, and its nmr spectrum should reveal this fact by a temperature dependency. The nmr results (Figure 6) are completely consistent with this concept. At 70°, the methyls are observed as two sharp singlets having an area ratio of 2:1. The major peak (**21b**) was temperature independent, whereas the lesser singlet (**20c**) broadened upon cooling and at 20° appeared as two singlets (area ratio ~1:1).



21a (*dl* pair)



21b (*dl* pair)



21c (*dl* pair)

One of the intriguing aspects of these results comes from the realization that ring inversion involves a *planar* pentaphene transition-state conformation which must still accommodate a 2.8–3.0-Å separation between the two pyridine rings. The strain energy of such a conformer must be extraordinarily high owing to large distortions of bond angles (up to 30° each), particularly those associated with the bonds attaching the pentaphene to the pyridines and to H_1 and H_{12}. However, the free energy barrier for ring inversion, at least for the mono-*N*-methyl derivatives, is less than 17 kcal/mol. Since this value represents the difference in energy between the lowest energy ground state and the planar transition state, it serves to emphasize the high energy of the ground state caused by steric strain.

Experimental Section

Melting points (uncorrected) were determined on a Thomas-Hoover apparatus. Ultraviolet absorption spectra were recorded on a Cary Model 14 spectrophotometer. Infrared spectra were obtained with a Perkin-Elmer Infracord spectrometer. The mass spectral data were obtained using a CEC 21-110B mass spectrometer, with the samples analyzed *via* the direct inlet system. Nmr spectra were determined with either a Varian A-60 or HA-100 instrument. Chemical shifts are recorded as parts per million to lower field from TMS (δ = 0), followed by (in parenthesis) multiplicity, relative area, and assignment. The nmr spectra used for the line-shape analysis were recorded on a Varian HA-100 spectrometer equipped with a V-4343 temperature controller. The temperature of the sample was checked by use of the chemical shift of the water resonance in the sample. Temperatures were measured to an accuracy of ±1° and were determined to better than ±0.5°. The sample used for the line-shape analysis was prepared on a vacuum line and sealed following several freeze-pump-thaw cycles. The solvent consisted of ~30% DMSO-d_6, ~70% acetone-d_6, and less than 1% TMS. The concentration of the solute was 5×10^{-2} *M*.

4a-Azoniatriptycene Perchlorates (see Table I).—The following synthesis of azoniatriptycene **4a** is representative of the procedure used for preparing the benzyne adducts of Table I.

9,10-Dihydro-4a-azonia-9,10-*o*-benzenoanthracene Perchlorate, *i.e.*, **4a-Azoniatriptycene Perchlorate (4a).**—To a refluxing solution of 4a-azoniaanthracene perchlorate (**3a**) (28.0 g, 0.10 mol) in 150 ml of acetonitrile were concurrently added, *via* two dropping funnels, over a 15-min period, solutions of isoamyl nitrite (23.0 g, 0.2 mol) and anthranilic acid (24.7 g, 0.18 mol), each in 250 ml of acetonitrile. The resulting solution was concentrated to one-quarter volume and the product precipitated by the addition of ether–ligroin (bp 30–60°) (2:1 v/v), as an oil which subsequently crystallized. The uv spectrum of this product showed no absorptions at wavelengths longer than 270 nm, establishing the absence of **3a**. One recrystallization from methanol (Darco)–ether gave 27.7 g (78%) of **4a** as stubby white needles: nmr

(DMSO-d_6) δ 6.61 (s, 1), 7.23–8.00 (m, 10), 8.45 (m, 2), 9.47 (d of m, 1).

Azoniatriptycene Perchlorate 8.—A sample of **4c** was deacetylated with methanolic potassium hydroxide solution; the solution was acidified with 6 *N* hydrochloric acid and treated with dilute sodium perchlorate solution to yield **8** as a white crystalline precipitate. This product was recrystallized as white needles from CH_3CN, mp 230–250° dec. Its nmr spectrum was consistent with the assigned structure.

Anal. Calcd for $C_{23}H_{22}ClNO_6$: C, 64.5; H, 5.1; N, 3.3. Found: C, 64.2; H, 5.3; N, 3.5.

Pyridylanthracenes and -pentaphenes (Table II). 9-(2-Pyridyl)anthracene (5).—A mixture of **4a** (2.00 g, 0.056 mol), anhydrous sodium acetate (1.0 g), and 25 ml of acetic anhydride was refluxed for 5 min, cooled, and diluted with 100 ml of water. The resulting crystals were collected, dried, and recrystallized as thick yellow needles (1.24 g, 86%) from methylcyclohexane: uv max (CH_3CN) 223 nm (log ε 4.08), 253 (5.13), 316 (3.08), 328 (3.49), 345 (3.81), 363 (4.00), 382 (3.97).

TABLE II

PYRIDYLANTHRACENES AND -PENTAPHENES

Compd	Mp, °C	Calcd, %			Found, %		
		C	H	N	C	H	N
5	155–156	89.5	5.1	5.5	89.2	5.1	5.6
6	187–191	78.0	4.7	3.1	78.4	5.2	3.1
15	217–219	89.0	4.6	6.5	89.0	4.4	6.1
18	293–294	89.0	4.6	6.5	89.1	4.6	6.4

Anthracene **6** was similarly prepared, but required a 4-hr reflux period to maximize the yield (62%): uv max (CH_3CN) 225 nm (log ε 4.34), 259 (4.97), 338 sh (3.52), 356 (3.78), 371 (3.92), 391 (3.90).

Bis(2-pyridyl)pentaphenes 15 and 18.—As a representative example, crude bisbenzyne adduct **17** was prepared by the general procedure described above for the synthesis of **4a**. Thus, solutions of anthranilic acid (41.1 g, 0.30 mol) and isoamyl nitrite (41.0 g, 0.35 mol), each in 250 ml of acetonitrile, were concurrently added over a 15-min period to a refluxing solution of **16**[8] (24.0 g, 0.05 mol) in 500 ml of acetonitrile. The resulting dark solution was concentrated to a syrup, which in turn was triturated in 300 ml of acetone and filtered, leaving 2.35 g of orange, crystalline acridone as a residue.

The acetone filtrate was concentrated to a syrup which was partially dissolved in 200 ml of methanol and reprecipitated as a tan amorphous solid (**17**, 45.0 g) by the addition of 500 ml of ether. Its uv spectrum showed no absorptions at wavelengths longer than 265 nm.

A mixture of 45.0 g of this product, 20.0 g of sodium acetate, and 400 ml of acetic anhydride was heated at reflux for 2 hr, and then concentrated to a dark syrup. The syrup was freed of residual acetic acid and anhydride by trituration in 400 ml of water containing an excess of sodium carbonate, and was extracted into 400 ml of methylene chloride and clarified by passing through a Florisil magnesium silicate bed disposed in a 600-ml, coarse, sintered-glass Büchner funnel. The eluate was concentrated to *ca.* 100 ml and introduced onto the top of a Florisil column (4.5 × 56 cm) and chromatographed, 4 l. of methylene chloride–ethyl acetate (4:1 v/v) being used as a developer. Fifteen 250-ml fractions of eluate were collected. Analysis by tlc[9] showed the desired product to be in fractions 9–13. These were combined and concentrated giving 5.0 g (23% from **13**) of essentially pure crystalline pentaphene **18**. The analytical sample was recrystallized as thick yellow needles from benzene.

Bis(pyridinium) Salts 19 and 21.—The procedure used in preparing both of these compounds consisted in heating on a hot plate a mixture of 0.5 g of **15** or **18** in 10 ml of methyl *p*-toluenesulfonate to the boiling point. The solution was cooled and the product precipitated as a yellow solid by the addition of ether. This product was converted to its bisperchlorate salt by ion exchange and was recrystallized from acetonitrile–ether. Melting points of **19** and **21** were >300°.

Anal. Calcd for $C_{34}H_{26}Cl_2N_2O_8$: N, 4.2; Cl, 10.7. Found for **19**: N, 4.3; Cl, 10.6. Found for **21**: N, 4.5; Cl, 10.4.

Mono(pyridinium) Salts 20.—A solution of **18** (0.40 g, 0.9 mmol) in 30 ml of methyl iodide and 15 ml of methylene chloride was allowed to stand at room temperature for 18 hr. Tlc analysis of the mixture during this period indicated the absence of starting **18** by the end of the first 6 hr. The solution was concentrated to a crystalline solid, which was dissolved in warm water–methanol (4:1 v/v) and treated with sodium perchlorate. The resulting yellow crystalline perchlorate **20** was recrystallized from pyridine–ether as fine yellow needles, mp 185–187°.

Anal. Calcd for $C_{33}H_{23}ClN_2O_4$: C, 72.4; H, 4.0. Found: C, 72.0; H, 4.1.

Registry No.—**5**, 20308-96-7; **6**, 30318-88-8; **8**, 30318-86-6; **15**, 30318-87-7; **18a**, 30319-26-7; **18b**, 30319-27-8; **18c**, 30319-28-9; **19a**, 30319-29-0; **19b**, 30319-30-3; **20a**, 30344-36-6; **20b**, 30275-72-0; **20c**, 30319-31-4; **20d**, 30344-37-7; **21a**, 30319-32-5; **21b**, 30319-33-6; **21c**, 30319-34-7.

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(8) C. K. Bradsher and J. C. Parham, *J. Org. Chem.*, **29**, 856 (1964).

(9) Thin layer chromatographies (tlc) were performed employing precoated silica gel F-254 tlc plates, containing a fluorescent indicator, distributed by Brinkmann Instruments Inc., Westbury, N. Y. Development was achieved with methylene chloride.