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A Comprehensive Study of Isoskeletal Analogs of Dibenzo[a,c]anthracene**

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Abstract. While reviewing the chemistry of cyclopentadienone derivatives and aza isoskeletal analogs of dibenzo[a,c]anthracene, additional molecular orbital (MO) and spectroscopic results and insights are presented. The MO tendency for coplanarity of phenyl substituents on benzenoids is demonstrated. Perpendicularly oriented phenyl substituents resulting from steric interactions strongly shield appropriately situated protons in NMR spectra. The principles of alternating polarity and parallel correspondence in conjunction with MO methods are used to relatively order aza arene isoskeletal analogs according to their chemical properties. Since less than 1.87% of the isoskeletal analogs of benzo[a,c]-anthracene have been reported, this summary work will help one to forecast the major chemical properties of those not yet synthesized.

Keywords. Dibenzo[a,c]anthracene; Dibenzo[a,c]phenazine; Aza arenes; Dibenzo[a,c]acridine; Ionization energies; Cyclopentadienone; MO Calculations; NMR; Mass spectrometry.

Eine umfassende Untersuchung von Analogen des Dibenzo[a,c]anthracen mit identem Grundskelett

Zusammenfassung. Im Zuge eines Überblicks über die Chemie von Cyclopentadienon-Derivaten und Aza-Analogen von Dibenzo[a,c]anthracen werden zusätzliche Erkenntnisse aus Molekülorbitalrechnungen (MO) und spektroskopischen Untersuchungen präsentiert. Es wird die Tendenz der MO's zur Koplanarität von Phenylsubstituenten an Benzenoiden gezeigt. Aus sterischen Gründen rechtwinkelig orientierte Phenylsubstituenten ergeben in den NMR-Spektren starke Abschirmeffekte für die entsprechend liegenden Protonen. Aus den rechnerischen und experimentellen Ergebnissen wird eine relative Ordnung der Aza-Arenanalogen bezüglich ihrer chemischen Eigenschaften abgeleitet. Da bis jetzt nur ca. 1.87% der möglichen isoskelettalen Analogen von Dibenzo[a,c]anthracen in der Literatur beschrieben sind, sollten die präsentierten Richtlinien dazu geeignet sein, die wesentlichsten chemischen Eigenschaften der noch nicht synthetisierten Analogen vorauszusagen.

Introduction

Benzyne reactions of cyclopentadienone derivatives offer a potential synthetic route toward larger benzenoids. While pursuing preliminary studies of this route, an investigation of tetracyclone (tretraphenylcyclopentadienone) and its fused analog,

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phencyclone, was made necessary. Concurrent with a review of the chemistry and spectra of these compounds, our additional significant mass spectral and molecular orbital results will be reported.

While investigating synthetic methods directed toward synthesis of large total resonant sextet benzenoids [1, 2], we had the opportunity to study 9,14-diphenyldibenzo[a,c]anthracene which is an analog of two incidental carcinogens, dibenzo[a,c]anthracene and dibenzo[a,c]phenazine. Dibenzo[a,c]anthracene is cited as an experimental carcinogen, and dibenzo[a,c]phenazine is said to induce neoplasms in animal studies [3]. Thus, this paper also reports the synthesis, spectra, and molecular orbital characteristics of 9,14-diphenyldibenzo[a,c]anthracene and, at the same time, reviews all the known isoskeletal analogs (**3–16**) of dibenzo[a,c]anthracene shown in Fig. 1.

There are 12 benzenoid skeletons (isomers) with the formula of $C_{22}H_{14}$ of which dibenzo[a,c]anthracene (db[a,c]a) represents one [4]. There are 7 monoaza, 49 diaza, 182 triaza, and 511 tetraaza heterocyclic isoskeletal analogs of dibenzo[a,c]anthracene [5]. Although, no literature search is ever really complete,

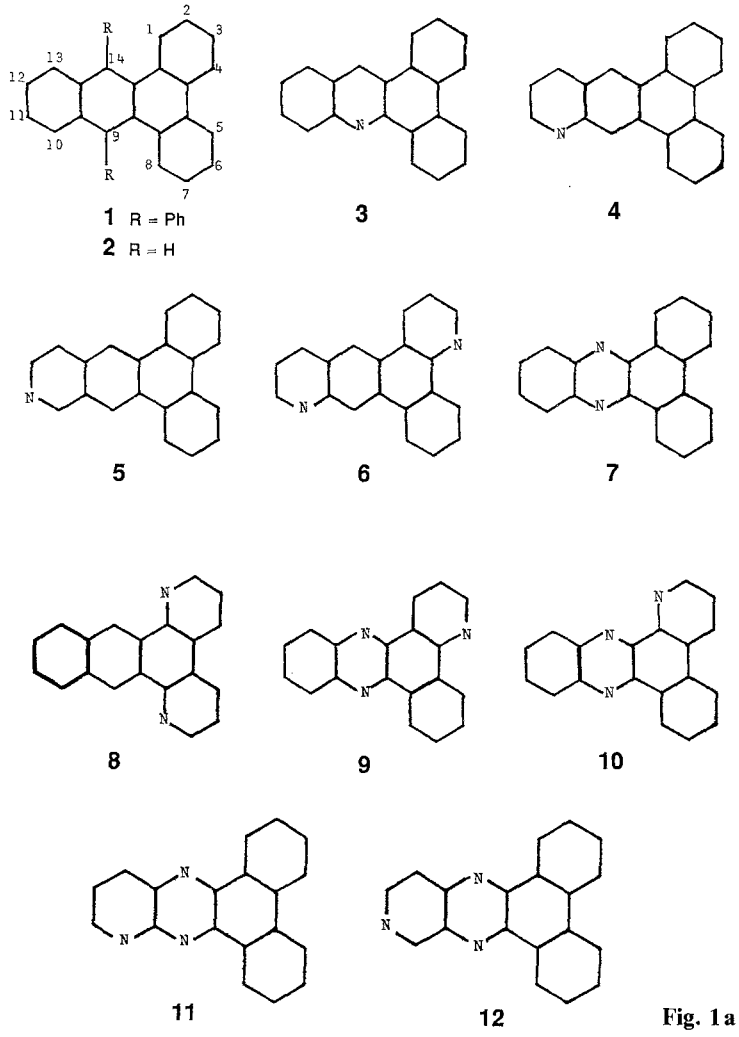


Fig. 1a

Fig. 1. Isoskeletal analogs of dibenzo[a,c]anthracene

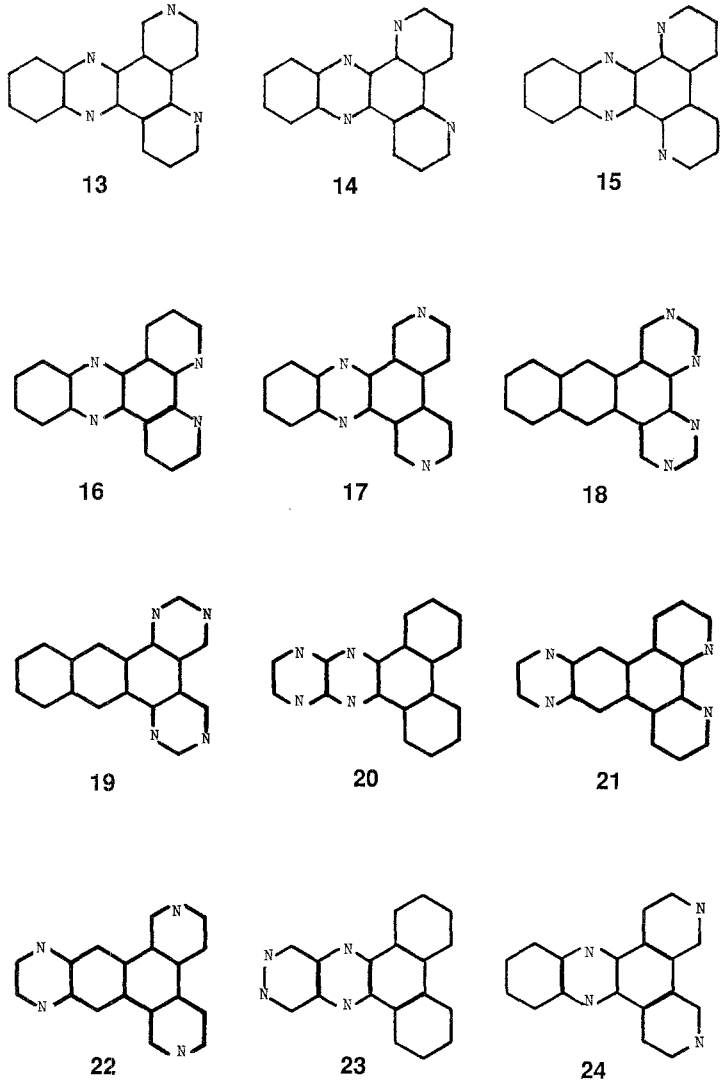


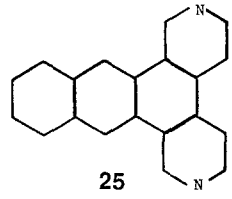
Fig. 1b

our thorough literature search has only uncovered syntheses for 3 of the 7 monoaza, 3 of the 49 diaza, 4 of the 182 triaza, and 4 of the 511 tetraaza isoskeletal analogs of db[a,c]a; (Fig. 1) no aza isoskeletal analogs of db[a,c]a having more than four nitrogens could be found in the chemical literature. Evidently, only 1.87% of the isoskeletal analogs of db[a,c]a having up to four nitrogens have been synthesized and identified. Thus, this paper addresses the problem of forecasting the properties of isoskeletal isomers and analogs from a representative number of known compounds without having to synthesize all of them.

Results and Discussion

Chemistry

The synthesis of **1** was accomplished in approximately 70% yields by reacting benzyne with phencyclone (Scheme 1); the benzyne can be generated either from



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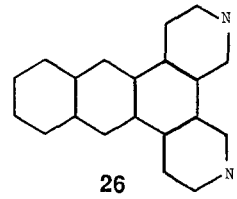

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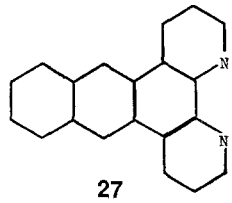

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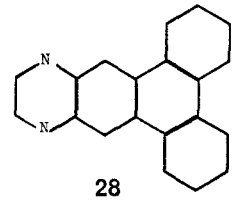

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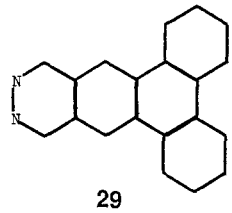

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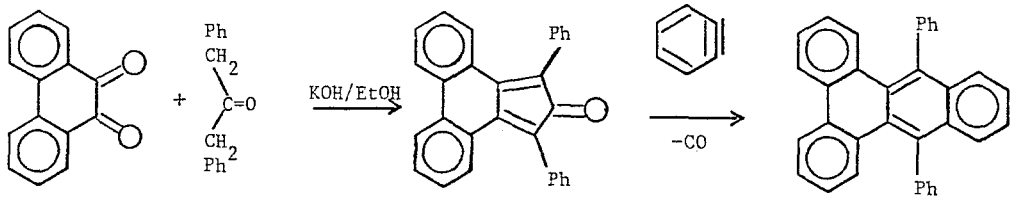
Fig. 1c

thermolysis of diphenyliodonium-2-carboxylate monohydrate or amyl nitrite diazotization of anthranilic acid [6]. Several synthesis of **2** have been reported [4]. The *bis*-Wittig reaction on 9,10-phenanthrenequinone and [4,7]phenanthroline-5,6-quinone led to **2** and **8**, respectively, in better than 20% yields [7, 8]. A series reactions incorporating three separate succinoylations steps has also been shown to lead to **2** [15]. Dibenzo[a,c]acridine (**3**) was synthesized in 50% yield by allowing phenanthraquinone to react with *o*-nitrobenzyl chloride in the presence of stannous chloride, concentrated hydrochloric acid, and methanol [10]. Alternatively, pyrolysis at 200° in diphenyl either of the Mannich base of phenanthraquinone with aniline gave **3** in a 62% yield [11]. Skraup synthesis of **4** and **6** was accomplished by reacting glycerol, sulfuric acid, and arsenic acid with 2-aminotriphenylene and 3-acetamido-9-aminophenanthrene, respectively [12].

The phenazines **7**, **9**, **10**, and **13–16** were synthesized by condensing *o*-phenylenediamine with the appropriate quinone precursor [13–15]. Condensing phenanthrenequinone with the appropriate *o*-diaminopyridine led to **11** and **12** [16, 17].



Scheme 1

Table 1. Dibenzo[a,c]anthracene analogs

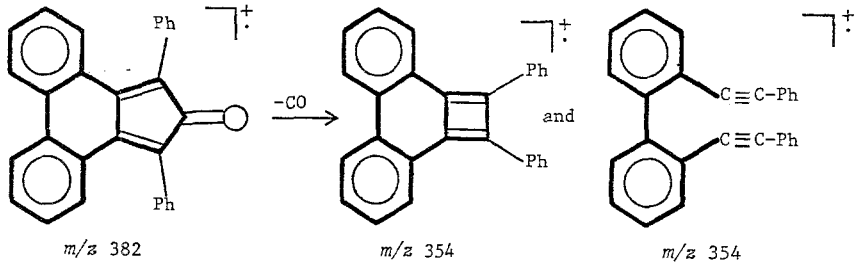
No.	Formula	Name	M.p. [°C]	Reference
1	$C_{34}H_{22}$	9,14-Diphenylbenzo[a,c]anthracene	286–288	
2	$C_{22}H_{14}$	Dibenzo[a,c]anthracene	207–209	
3	$C_{21}H_{13}N$	Dibenzo[a,c]acridine	204	[10, 11]
4	$C_{21}H_{13}N$	Phenanthro[9,10-g]quinoline	204	[12]
5	$C_{21}H_{13}N$	Phenanthro[9,10-g]isoquinoline	139–150	[18]
6	$C_{20}H_{12}N_2$	Benzo[h]quino[6,7-f]quinoline	208	[12]
7	$C_{20}H_{12}N_2$	Dibenzo[a,c]phenazine	227–228	[31]
8	$C_{20}H_{12}N_2$	Naptho[2,3-f][4,7]phenanthroline	233–234	[8]
9	$C_{19}H_{11}N_3$	Benzo[c]pyrido[3,2-a]phenazine	221–222	[15]
10	$C_{19}H_{11}N_3$	Benzo[c]pyrido[2,3-a]phenazine	216–218	[15]
11	$C_{19}H_{11}N_3$	Phenanthro[9,10-b]pyrido[2′,3′-e]pyrazine	217–218	[16]
12	$C_{19}H_{11}N_3$	Phenanthro[9,10-b]pyrido[3′,4′-e]pyrazine	234	[17]
13	$C_{18}H_{10}N_4$	Dipyrido[3,4-a: 2′3′-c]phenazine	244–245	[15]
14	$C_{18}H_{10}N_4$	Dipyrido[2,3-a: 2′,3′-c]phenazine	220	[13]
15	$C_{18}H_{10}N_4$	Dipyrido[2,3-a: 3′,2′-c]phenazine	291–292	[13, 15]
16	$C_{18}H_{10}N_4$	Dipyrido[3,2-a: 2′,3′-c]phenazine	250	[14]

The $NaBH_3CN$ reduced product of the imine formed by reacting aminoacetaldehyde dimethyl acetal with the 2-carboxaldehyde of triphenylene was condensed to **5** with polyphosphoric acid [18].

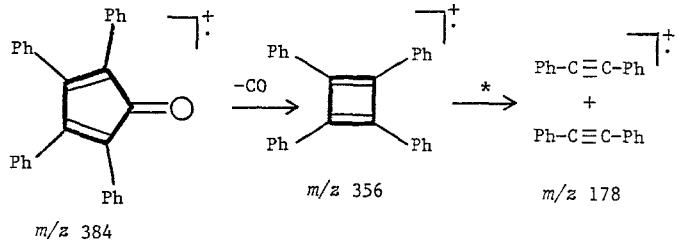
Although, only **16** has been reported as forming a 1 : 1 copper chelate complex salt, compounds **10, 14,** and **15** should also be capable of forming copper and other metal chelate complexes. Many substituted dibenzo[a,c]phenazines can be found in Beilstein's Handbook of Organic Compounds (near System No. 3493). A review on cyclopentadienone derivatives has been published [19]. The syntheses of **3–16** (Table 1) have been reported.

Spectra

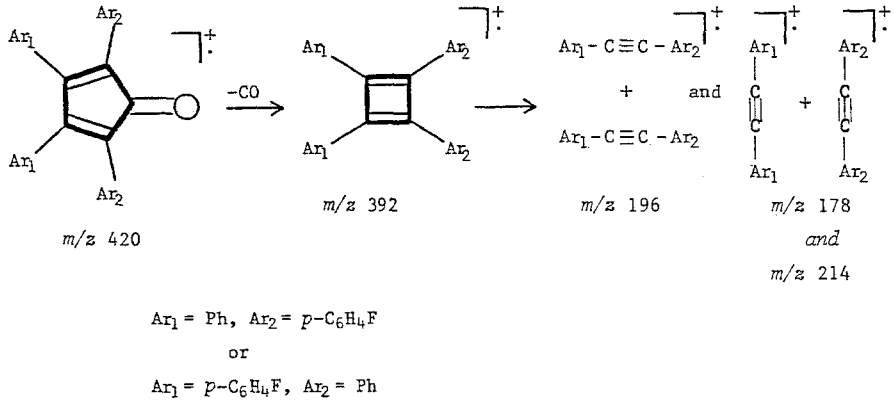
The mass spectra of phencyclone and tetracyclone both showed loss of CO from their molecular ions (Schemes 2 and 3). In addition, the latter exhibited fission to one neutral and one ionized diphenylacetylene fragment after CO loss (*m/z* 356 → *m/z* 178). The formation of the antiaromatic containing species, tetraphenylcyclo-



Scheme 2



Scheme 3



Scheme 4

butadiene (*m/z* 356), is corroborated by the mass spectra of 2,5- and 3,4-bis (*p*-fluorophenyl)diphenylcyclopentadienone (Scheme 4) [20]. Fission the cyclobutadiene ring can occur in two perpendicular ways. For ionized tetraphenylcyclobutadiene generated by electron impact fragmentation of tetracyclone, both cleavages lead to the same fragment (Scheme 3). But for the analogous daughter ions of 2,5- and 3,4-bis (*p*-fluorophenyl)diphenylcyclopentadienone (Scheme 4), both cleaveage modes lead to the three different fragment ions of diphenylacetylene (*m/z* 178), *p*-fluorophenylphenylacetylene (*m/z* 196), and bis-(*p*-fluorophenyl)acetylene (*m/z* 214). For the analogous cyclobutadiene daughter ion (*m/z* 354) formed by electron impact fragmentation of phencyclone, one direction of cleavage of the cyclobutadiene ring would lead to a single ion having two alkyne bonds (*m/z* 354 in Scheme 2) and the other cleavage direction would produce diphenylacetylene and the highly unstable dibenzo[c,e]benzyne species and obviously does not occur.

The mass spectra of 1,2,3,4-tetraphenylnapththalene and 9,14-diphenyldibenzo[a,c]anthracene exhibited molecular ion peaks of $[M]^{+\cdot} = 432$ and $[M]^{+\cdot} = 430$ daltons, respectively, with no significant fragment ion peaks. These mass spectral results are typical of the mass spectra of benzenoids and their aza analogs [5, 20].

A comparison of the NMR spectra of dibenzo[a,c]anthracene, dibenzo[a,c]-phenazine, and 9,14-diphenyldibenzo[a,c]anthracene (Table 2) reveal several distinctive features. The spectrum of hydrocarbon **2** (db[a,c]a) has a characteristic singlet at 9.0 ppm for the 9,14 protons which is absent in the spectra of analogs **7** (db[a,c]p) and **1** (dpdb[a,c]a). A broad singlet at 7.5 ppm is present in the spectrum of dpdb[a,c]a for the phenyl protons. The 2, 3, 6, 7, 11, 12 proton multiplet and

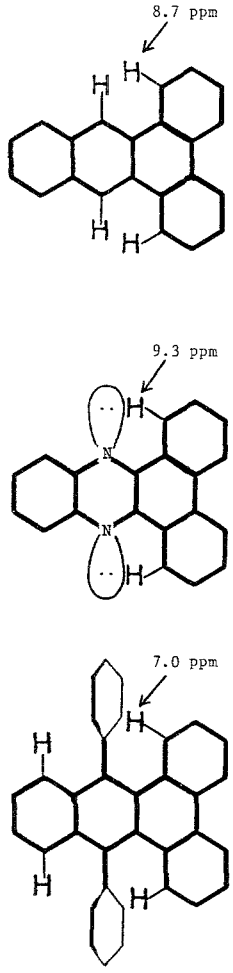


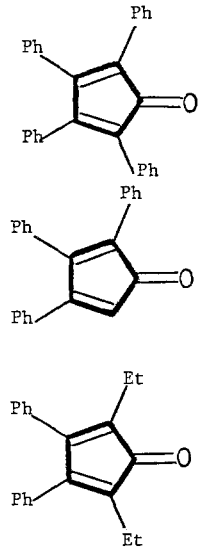
Fig. 2. NMR chemical shifts of the 1,8-hydrogens

Table 2. NMR spectra (in ppm from *TMS*) of heterocyclic isoskeletal analogs of dibenzo-[a,c]anthracene[a]

No.	1,8-H's	2,3,6,7-H's	4,5-H's	9,14-H's	10,13-H's	11,12-H's	Solvent
1	7.0	7.3	8.2	7.5[b]	7.9	7.3	$CDCl_3$
2	8.7	7.6	8.5	9.0	8.0	7.5	$CDCl_3$
3	9.5, 8.6	7.6, 7.7	8.5	−, 9.2	8.3	7.8	$CDCl_3$
5	8.7	7.6	8.5	8.9, 9.1	9.5 (s), 7.8 (d)	−, 8.5 (d)	$CDCl_3$
7	9.3	7.8	8.5	−	8.3	7.8	$CDCl_3$
8	−	8.5, 8.1	8.9	9.6	7.5	7.5	$CDCl_3$
9	9.4, 9.1	7.8, 9.1, 7.9	−, 9.1	−	8.3	7.9	*d_6-DMSO*
10	8.2	8.5, 7.4, 7.3	8.5	−	7.8	7.8	CD_3OD
13	10.3 (s), 9.4	8.8 (d), 9.1, 7.9	9.0 (d)	−	8.3	8.0	*d_6-DMSO*
15	−	8.2, 7.0	7.9	−	7.8	7.8	CD_3OD
16	9.5 (d)	8.8, 10.3 (d)	−	−	8.7	8.6	CF_3DO_2D

[a] Multiplets or doublets of doublets unless otherwise indicated, except the 9,14-protons which are singlets

[b] 9,14-Diphenyl protons



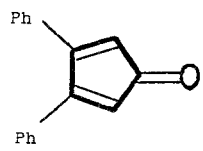
HOMO-LUMO, β	λ(π→π*), nm
0.5295	333
0.6100	306
0.7300	292

Fig. 3. HOMO-LUMO electronic transitions

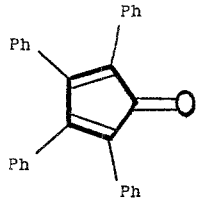
the 4,5 multiplet are least affected by the nitrogen or phenyl moieties. In going from the spectrum of db[a,c]a to the spectrum of db[a,c]p, a moderate deshielding of the 1,8 protons is observed and is the result of these protons sterically interacting with the lone pair of electrons on the proximate nitrogens. In going from the spectrum of db[a,c]a to the spectrum of dpdb[a,c]a, a strong shielding of the 1,8 protons is observed which results from the diamagnetic field of the perpendicularly oriented phenyl groups in the latter molecule (Fig. 2). Overall, there is a general deshielding of the protons in db[a,c]p by the nitrogens and shielding of the protons in dpdb[a,c]a by the perpendicularly oriented phenyl group compared to db[a,c]a.

As the number of nitrogens in the dibenzo[a,c]anthracene skeleton increases, the molecule's solubility in less polar solvents, like chloroform, decreases and use of more polar solvents, like methanol and *DMSO*, becomes necessary for obtaining NMR spectra. In hydrogen-bonding solvents, like methanol, deshielding effect of the nitrogen lone-pair of electrons sterically interacting with proximate hydrogens located in the same bay region becomes nullfied as is apparent from the NMR spectrum of **10** in CD_3OD (Table 2). The chemical shifts of aza db[a,c]a analogs in $CDCl_3$ and d_6-*DMSO* appear to be very similar. Using CF_3CO_2D as an NMR solvent in **16** lead to an overall deshielding of all protons because of protonation (deuteration) of the 4,5-nitrogens, because of their proximity the 3,6-protons are most strongly deshielded and give a doublet at 10.3 ppm. Since **16** reacts with 1,2-dibromoethane to give the 4,5-diquaternary salt where the 3,6-protons give an NMR doublet at 10.4 ppm, it is suggested that the parent compound **16** may be doubly protonated (deuterated) at its 4,5-nitrogens in CF_3CO_2D solvent.

The $\pi \rightarrow \pi^*$ transitions in the UV spectra of tetracyclone (tetraphenylcyclopentadienone) and phencyclone are correlated by their frontier orbitals. In the computation of the HOMO-LUMO data in Fig. 3, it was assumed that the 3,4-phenyl groups are essentially coplanar with the cyclopentadienone system. If the phenyls are skewed by an angle of 15° from the cyclopentadienone plane, the HOMO-LUMO values (Fig. 4) calculated for tetracyclone and 3,4-diphenylcyclo-



θ	k	HOMO-LUMO, β
0°	1.0	0.7300
15°	0.966	0.7366
45°	$\sqrt{2}/2$	0.7862
90°	0	0.8721



θ	k	HOMO-LUMO, β
0°	1.0	0.5295
15°	0.966	0.5422
45°	$\sqrt{2}/2$	0.6453
90°	0	0.8721

Fig. 4. Change in HOMO-LUMO versus dihedral angle between the phenyl groups and the cyclopentadienone system

pentadienone became 0.5422 and 0.7366β, respectively. This latter computation was accomplished by weighting the bridging bond to these phenyls by $k = \cos\theta$ where $\theta = 0°$ is the coplanar orientation and $\theta = 90°$ is the perpendicular orientation; for $\theta = 90°$ the pπ system of the phenyl groups and cyclopentadienone unit would be noninteracting and independent. The carbonyl group was not weighted (i.e., $\alpha_c = \alpha_o$ and $\beta_{co} = \beta_{cc}$ were assigned) in these calculations.

Figure 4 summarizes the effect of skewing the phenyl groups out of the cyclopentadienone plane on the HOMO-LUMO values. From this data, it is evident that for angle deviations of less than 15° an estimated error of $\Delta\lambda \leqslant 4$ nm would result in assuming coplanarity of the phenyl groups with the cyclopentadiene system. This error is less than the errors associated with varying experimental conditions for data collected from different literature sources [19]. The correlation coefficient for the plot λ^{-1} versus HOMO-LUMO is $\rho = 0.966$ for the data in Fig. 3; a regression analysis using this data predicts a $\lambda(\pi - \pi^*)$ of 223 nm (HOMO-LUMO = 1.236β) for 2-cyclohexen-1-one which agrees well with its experimental value of $\lambda = 225$ nm.

The data in Fig. 5 is consistent with the phenyl and naphthyl groups being sterically skewed out of the plane of the cyclopentadienone system [19]. If the phenyl groups in phencyclone were coplanar with the cyclopentadienone system, the calculated HOMO-LUMO value of 0.4548 would predict a $\lambda(\pi \rightarrow \pi^*)$ transition at 346 nm. If they are perpendicular to the cyclopentadienone system, the calculated HOMO-LUMO value of 0.6203 predicts a $\lambda(\pi \rightarrow \pi^*)$ at 310 nm which agrees more closely with the experimental value of 301 nm. Thus, the phenyl groups on phencyclone must be perpendicular to the cylcopentadienone system. Similarly, the napthyl groups in 2,5-dinaphthyl-3,4-diphenylcyclopentadienone must be perpendicular to the cyclopentadienone system, where the experimentally observed $\lambda(\pi \rightarrow \pi^*)$ value of 287 nm corresponds to the electron transition associated with the noninteracting pi electron system of the 3,4-diphenylcyclopentadienone.

Table 3 summarizes the known ultraviolet spectra of dibenzo[a,c]anthracene (**2**) and its aza analogs in ethanol solution which is a hydrogen bonding solvent that suppresses the n $\rightarrow$ π^* electronic transitions associated with the latter [21]. The α and ρ bands in **7** were not determined. All these absorptions are very similar, except the β and β' absorptions in **16** which is the only tetraaza analog. Since **16**

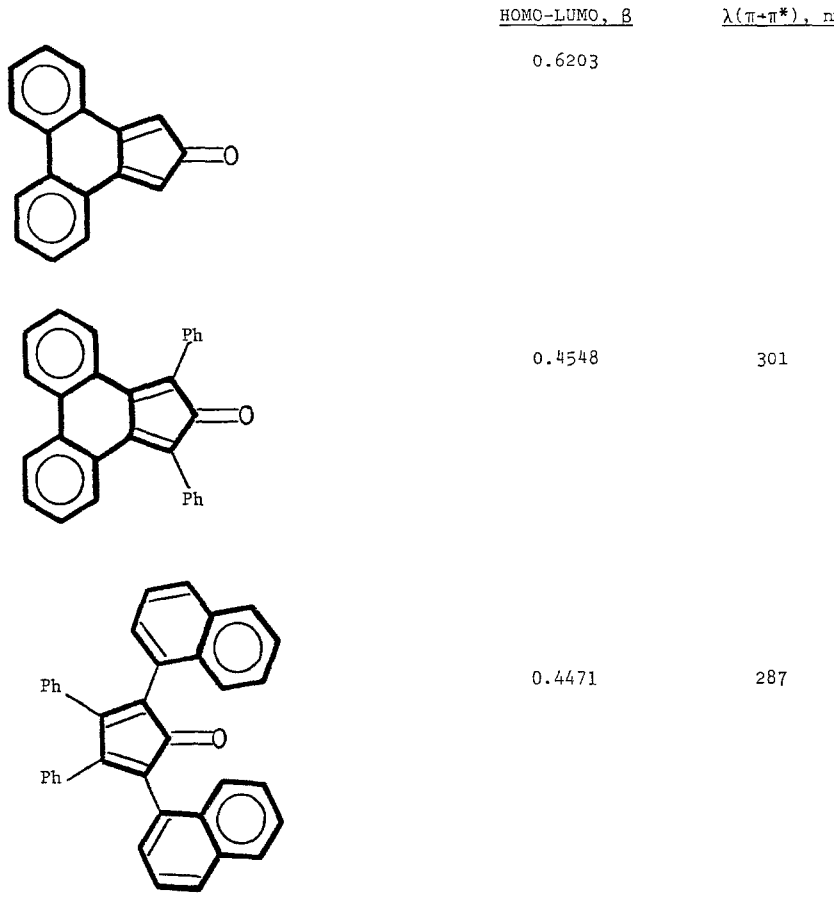


Fig. 5. HOMO-LUMO electronic transitions

Table 3. UV spectra of aza arene analogs of dibenzo[a,c]anthracene

No.	λ(α), nm	λ(p), nm	λ(β), nm	λ(β′), nm	IP, eV
2, db[a,c]a	375 (2.83)	350 (3.52)	287 (5.15)	258 (4.57)	7.39, 7.89, 8.28, 9.14, 9.39, 9.92
3, db[a,c]ac	373 (4.12)	355 (4.08)	280 (4.92)	256 (4.76)	
5, p[9,10-g]iq	379 (3.25)	357 (3.49)	287 (4.85)	255 (4.55)	
7, db[a,c]p			280 (4.63)	252 (4.87)	
8	374 (3.25)	355 (3.59)	279 (3.59)		
16	378 (3.88)	357 (3.88)	269 (4.71)	241 (4.35)	

forms a hemihydrate, it is possible that an exceptional interaction between the lone pair electrons on the 4,5-nitrogens, which are capable of chelating, may occur. The spectroscopic similarity of the Table 3 compounds are consistent with the similar MO ΔX_1 and ΔX_2 values presented in Table 4 which are known to correlate the ρ and β' absorption bands, respectively [22].

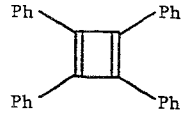
Table 4. HMO parameters of aza analogs of dibenzo[a,c]anthracene

No.	E_π, β	HRE[a], β	ΔX_1^b, β	ΔX_2, β	HOMO, β	2nd HOMO, β
2	30.9418	8.94	0.9982	1.4280	0.4991	0.7140
7	32.0256	8.90	0.9505	1.4303	0.6463	0.7286
8	32.0469	8.92	0.9958	1.4073	0.5021	0.8021
15	33.1165	8.87	0.9372	1.3996	0.6467	0.8110
16	33.1235	8.88	0.9572	1.4248	0.6598	0.7815
17	33.1222	8.88	0.9689	1.4298	0.6815	0.7290
18	33.1404	8.89	0.9397	1.4264	0.5185	0.7702
19	33.1533	8.91	0.9905	1.4259	0.5199	0.8695
20	33.1063	8.86	0.9126	1.4318	0.7082	0.7322
21	33.1187	8.87	0.9364	1.4257	0.5905	0.7719
22	33.1157	8.87	0.9510	1.4281	0.6135	0.7175
23	33.0884	8.84	0.9544	1.4118	0.6897	0.7592
24	33.1150	8.87	0.9433	1.4036	0.6609	0.8030
25	32.0392	8.92	0.9767	1.4277	0.5170	0.7145
26	32.0419	8.92	0.9939	1.4074	0.5173	0.7912
27	32.0428	8.92	0.9879	1.4174	0.5043	0.7693
28	32.0184	8.90	0.9311	1.4284	0.5803	0.7170
29	32.0183	8.90	1.0100	1.3912	0.5556	0.7364

[a] $E_\pi = 2.5616\beta$ for the imine of formaldehyde where $h = 0.5$ and $k = 1.0$
[b] ΔX_1 = HOMO-LUMO

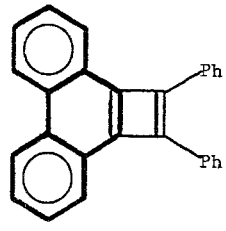
Molecular Orbital Calculations

All calculations performed were done on molecules having a mirror plane of symmetry. Mirror plane decomposition per McClelland method led to fragment subgraphs having weighted edges and vertices [5, 23]. Nitrogen atoms were weighted



±0.0
±0.75515
±1.0,±1.0,±1.0,±1.0
±1.108111
±1.25928,±1.25928
±1.79032
±2.046587
±2.1010,±2.1010
±2.60923

E_π=38.0599

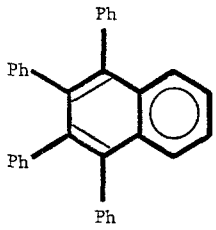


±0.06435
±0.77611
±0.78944
±1.0,±1.0
±1.10102
±1.23306
±1.2562
±1.3240
±1.84483
±1.95476
±2.0802
±2.2465
±2.66612

E_π=38.6731

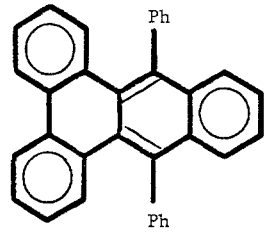
Fig. 6a

Fig. 6. Eigenvalues of phenyl substituted aromatic compounds



±0.40995
±0.62182
±1.0,±1.0,±1.0
±1.13539
±1.28651
±1.53258
±1.68329
±2.0
±2.05365
±2.14454
±2.19228
±2.58770

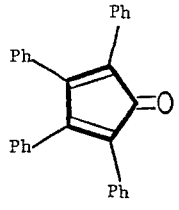
E_{π}=47.2954



±0.37538
±0.69235
±0.77809
±1.0,±1.0,±1.0,±1.0
±1.12385
±1.26118
±1.32566
±1.53171
±1.72376
±1.95599
±2.0
±2.17994
±2.30369
±2.63832

E_{π}=47.7799

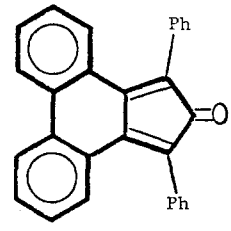
Fig. 6b



-2.4039	0.33635
-2.3370	0.60849
-2.0746	1.1225
-2.0562	1.3823
-1.7847	1.3895
-1.7020	1.8381
-1.1849	2.0520
-1.1478	2.1074
-0.68673	2.1514
-0.19317	2.5826

±1.0,±1.0,±1.0,±1.0,±1.0

E_{π}=41.1421



-2.5327	0.29028
-2.3307	0.67962
-2.1398	0.77967
-1.9572	1.1126
-1.7782	1.2973
-1.7594	1.3839
-1.3156	1.3894
-1.1733	1.8786
-1.1353	1.9556
-0.77263	2.1368
-0.74354	2.2585
-0.16451	2.6406

±1.0,±1.0,±1.0

E_{π}=41.6057

Fig. 6c

according to $\alpha_N = \alpha_c + 0.5\beta$ and $\beta_{cN} = \beta_{cc}$. The characteristic polynomials for the resulting edge/vertex weighted graphs were generated by Balasubramanian's method [24] and factored for their eigenvalues by using Bairstow's method [25]; in the latter degenerate eigenvalues of ± 1.0 had to be divided out of the polynomial (by synthetic division) in order to permit the iterations of converge.

The HMO pπ-energies (E_π) of this work demonstrate that a strong preference for coplanarity of the phenyl substitutents exists. If all the phenyl substitutents on tetraphenylcyclobutadiene and 1,2-diphenylphenanthro-[9,10-c]cyclobutadiene (Fig. 6) were coplanar with the cyclobutadiene systems, their E_π values would be 38.0599β and 38.6731β, respectively. Instead, if all the phenyl substituents were perpendicular to the cyclbutadiene systems in these compounds, then their E_π values

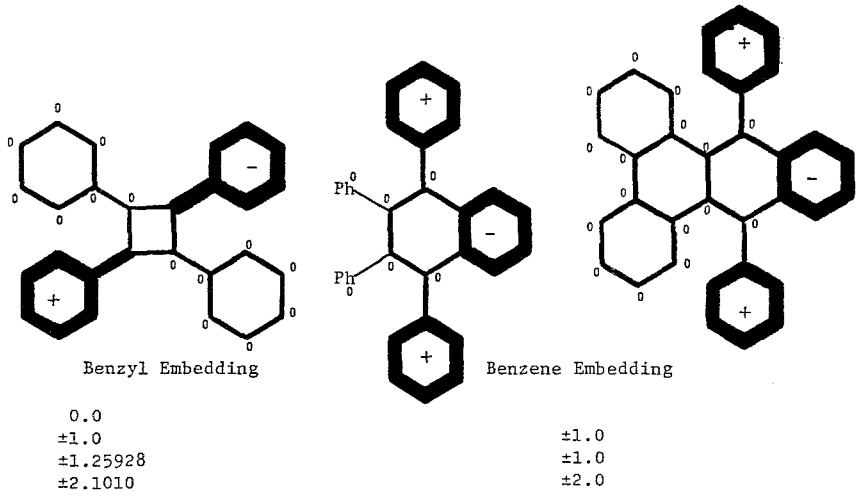
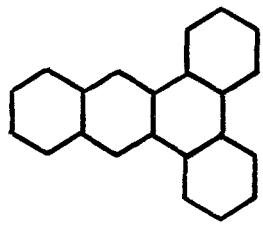


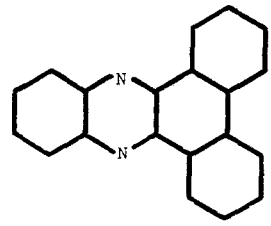
Fig. 7. Embedding of smaller structures onto larger ones

would be 36.0000β and 37.6928β, respectively. Similar results are deduced for the phenyl substituted molecules in Figs. 7 and 8. For example, if the phenyl groups in 9,14-diphenyldibenzo[a,c]anthracene were coplanar with the dibenzo[a,c]-anthracene system, then the value for E_π would be 47.7799β compared to 46.9418β for perpendicular phenyl groups. Our NMR spectroscopic results unequivocally demonstrate that the phenyl groups are oriented perpendicular to the db[a,c]a system in **1** (Fig. 2); steric factors associated with 1,8-hydrogens override the MO tendency for more complete conjugation of the pπ-system in hydrocarbon **1**. The UV absorption spectrum of phencyclone is clearly consistent with the phenyl groups being oriented perpendicular to the cyclopentadienone system.

Rather than rotate all the phenyl substitutents out of coplanarity at the same time, let us consider the rotation of some of them. If all the phenyl groups of 1,2,3,4-tetraphenylnaphthalene are coplanar with the naphthalene system, then $E_\pi = 47.2954\beta$. If only the 1,4-phenyl substituents are coplanar with the 2,3-phenyl substituents perpendicular, $E_\pi = 46.4917\beta$, or alternatively, if the 2,3-phenyl substituents are coplanar with the 1,4-phenyls perpendicular, $E_\pi = 46.4653\beta$. Thus, the former is preferred both sterically and electronically. Coincidentally, the former is also embeddable by benzene per Figure 7. When a larger molecule is embeddable by a smaller one, then the larger one possesses the eigenvalues of the smaller molecule [4, 5]. Previously, it was shown that a molecule possessing greater than a two fold axis of symmetry will have doubly degenerate eigenvalues subset [5, 26]. Deletion of any carbon vertex, replacement of any carbon vertex by a heteroatom, or placement of a substituent at any position of such a molecule generates a successor molecule still possessing half the eigenvalues in the originally doubly degenerate subset. Thus, tetraphenylcyclobutadiene is doubly degenerate in the eigenvalues of benzyl as shown in Fig. 6. The consequence of this is that perpendicular rotation of one phenyl substituent or two diagonally located ones in tetraphenylcyclobutadine leads to a hydrocarbon system still possessing the eigenvalues of benzyl once. Such a rotational process should involve minimal electronic reorganization and, other things being equal, would more facile than in less symmetrical conjugated hydrocarbons.



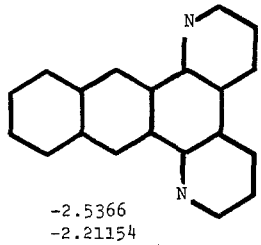
±2.55882
±2.22195
±1.97101
±1.72227
±1.37967
±1.31648
±1.20195
±1.09486
±0.790825
±0.71398
±0.49909



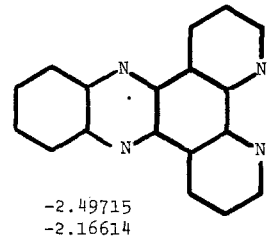
-2.5232
-2.18311
-1.96496
-1.69381
-1.31425
-1.28073
-1.17889
-1.08428
-0.783663
-0.70169
-0.304196
0.646294
0.728624
0.80703
1.103814
1.226694
1.320054
1.552565
1.754222
1.98525
2.26613
2.62211

a

h=0.5,k=1.0

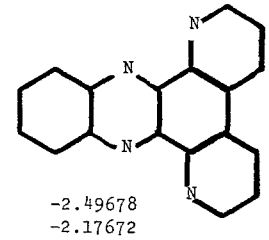


-2.5366
-2.21154
-1.88686
-1.72189
-1.37945
-1.26942
-1.15702
-1.06289
-0.69891
-0.60524
-0.49363
0.50214
0.80210
0.86925
1.15142
1.22342
1.38002
1.44078
1.72315
2.0989
2.2369
2.59542



-2.49715
-2.16614
-1.92148
-1.64177
-1.30883
-1.25504
-1.14753
-1.05129
-0.64329
-0.63184
-0.297 40
0.65977
0.78149
0.90155
1.20302
1.28298
1.3 2334
1.58418
1.80673
2.05620
2.31632
2.64619

b



-2.49678
-2.17672
-1.87957
-1.69359
-1.27634
-1.25770
-1.14484
-1.057845
-0.695764
-0.588585
-0.290521
0.646725
0.811001
0.880337
1.166721
1.252856
1.44082
1.55626
1.75546
2.10817
2.29053
2.64937

c

Fig. 8. Eigenvalues of dibenzo[a,c]anthracene isoskeletal aza arene analogs

From the experimental results summarized in Schemes 2 and 3, it is of interest to try to surmise which m/z 354 ion in Scheme 2 is most probable. Both antiaromatic character and ring strain disfavor the intact cyclobutadiene containing m/z 354 ion while greater rotational entropy favors the alkynyl m/z 354 ion. However, ionization has diminished the degree of antiaromatic character associated with the neutral precursor, and $E_\pi = 38.6087\beta$ for the m/z 354 cyclobutadiene ion compared to $E_\pi = 37.7643\beta$ for the alkynyl m/z 354 ion. Overall, there would be greater reduction of pπ-energy ($\Delta E_\pi = -0.8444\beta$) in scission from the cyclobutadiene m/z 354 ion to the alkynyl one, than in the scission of the ion-radical of tetraphenylcyclobutadiene (m/z 356) to diphenylacetylene ($\Delta E_\pi = -0.8086\beta$).

In the determination of Hückel's resonance energies (HRE's), for the aza analogs of db[a,c]a having N_N nitrogens, the following relationship was used

$$\text{HRE} = E_\pi - N_c - 1.5616N_N,$$

where the 1.5616 coefficients comes from $E = 2.5616\beta$ for the imine of formaldehyde (h = 0.5 and k = 1.0). In Table 4, HRE measures the relative stabilization of pπ electron system relative to the reference noninteracting equivalent system having alternating localized double and single bonds. To evaluate the effect of the nitrogen atoms on the σ-bond skeleton system, one must superimpose the effect of alternating electrostatic polarity on the additive bond dissociation energies. The net bond dissociation energy of the σ-bond system of all the tetraaza analogs **13–24** should be identical, except **23** will be electrostatically destabilized by the 11, 12 adjacent nitrogens and **19** will be stabilized the alternating electrostatic effect of next nearest neighbouring nitrogens [28].

Using the conjugated circuit method for computing resonance energies (RE's), it was determined that **3** had RE = 3.325 eV and **4** had RE = 3.3229 eV [27]. Within the conjugated circuit model, isomers with the same heteroatoms in different positions of the same ring will have the same RE value. On this basis, one would except the smallest difference in E_π for the isomer groups of **4–5**, **9–10**, **11–12**, and **13–16** in Fig. 1. If more than one heteroatom are permitted within a single ring, then the above smallest difference effect would probably become subordinated by alternating polarity effect where adjacent ring nitrogens (*ortho*-nitrogens) would be less stable than *para*-nitrogens which in turn would be less stable than *meta*-nitrogens [28].

The Hückel molecular orbital resonance energy (HRE) values in Table 4 decrease slightly in going from db[a,c]a (**2**) to its aza analogs. This is contrary to first order perturbation molecular orbital (PMO) theory where the RE of alternant hydrocarbons and their aza analogs predicted to be the same [29]. By the conjugated circuit method the RE values increase from 3.121 eV for **2** to 3.325 eV for **3** and 3.229 eV for **4**. No explanation is offerred for the lack of agreement between these three methods.

The ionization bands for db[a,c]a appear in Table 3. In general, as the number nitrogens increase (in the range of 1–4 N's), the first ionization energies (IP_1) should increase for the aza analogs of db[a,b]a. It has been shown than the HOMO energy level can be used to predict pπ ionization energies (IPs) of benzenoids [22], and it is expected that the same will be true for their aza analogs [30]. Thus, the relative order of increasing IP_1 for the compounds in Table 4 is expected to be **2** < **8** < **27** < **25** < **26** < **18** < **19** < **29** < **28** < **21** < **22** < **7** < **15** < **16** < **24** < **17**

$< \mathbf{23} < \mathbf{20}$. All the phenazine related aza analogs in Table 4 appear as a segregated group with predicted higher first ionization energies (i.e., $\mathbf{7} < \mathbf{15} < \mathbf{16} < \mathbf{24} < \mathbf{17} < \mathbf{23} < \mathbf{20}$). The second segregated group having next to the highest predicted first ionization energies comprises of $\mathbf{28} < \mathbf{21} < \mathbf{22} < \ldots < \mathbf{20}$, all having 10,13-nitrogens. Note that **20** belongs to both the above characteristic subsystems and has the largest predicted IP_1. The relative anticipated order of increasing IP_2 for the compounds in Table 4 is $\mathbf{2} < \mathbf{25} < \mathbf{28} < \mathbf{22} < \mathbf{7} < \mathbf{17} < \mathbf{20} < \mathbf{29} < \mathbf{23} < \mathbf{27} < \mathbf{18} < \mathbf{21} < \mathbf{16} < \mathbf{26} < \mathbf{8} < \mathbf{24} < \mathbf{15} < \mathbf{19}$. The aza arene group with the highest predicted IP_2 values possess nitrogens at either the 1,8- or 3,6-positions ($\mathbf{26} < \ldots < \mathbf{19}$), and the group with the next highest IP_2 values posses nitrogens at the 4,5-positions ($\mathbf{27} < \ldots < \mathbf{16}$). These topological observations are consistent with the HOMO and 2nd HOMO values observed for the diaza analogs of **7**, **8**, and **25** to **29** (Table 4). The HOMO value of phenazine (**7**) is distinctly larger and separate from the rest of the values in this group. The 2nd HOMO values of the diaza analogs of **8** and **26** are also distinctly larger from the remaining values in this group. Thus, these corresponding substructural components make a more dominant contribution to the HOMO and 2nd HOMO values when found in the tetraaza analogs of db[a,c]a. Using the principle of parallel correspondence [29], one would anticipate that the order of increasing IP_1 for the monoaza arenes to be $\mathbf{5} < \mathbf{4} < \mathbf{3}$ and for the triaza arenes to be $\mathbf{10} < \mathbf{9} < \mathbf{12} < \mathbf{11}$.

Conclusion

The synthesis of azaphencyclones should provide a general route to 9,14-diphenylazadibenzo[a,c]anthracenes via Scheme 1. Although, dibenzo[a,c]anthracene and dibenzo[a,c]phenazine are cited as experimental carcinogens, no other similar biological activity has been reported for the other isoskeletal aza analogs.

All the isoskeletal analogs thus far synthesized (**3**–**16**) can be distinguished by a combination of IR, MS, and NMR. The UV $\pi \rightarrow \pi^*$ transitions provide little information, and the $n \rightarrow \pi^*$ transitions need to be studied. Phenyl substitution is a useful probe for the NMR study of benzenoids because it increases solubility and is capable of invoking strong chemical shifts of appropriately situated hydrogens. Photoelectron spectoscopy can provide considerable information concerning isoskeletal aza arenes and needs to be more extensively utilized on these molecules. Phenazines are expected to have distinctively higher IP_1 values. The ^1H and ^{13}C NMR of dianions formed by reacting Li and Na with aza arenes lead to spectra with high field chemical shifts in d_8-*THF*. This type spectroscopy offers another dimension in the structure elucidation of aza arenes and benzenoids [31]. For semi-empirical correlations and relative comparisons of benzenoid related molecular species, Schmidt has shown that HMO calculations lead to slightly better results than EHMO and SCF-MO calculations [22]. Thus, we believe that the observations and review presented herein will facilitate our understanding of this important group of compounds.

Experimental

Melting points were determined on Fisher-John's apparatus. ^1H NMR spectra were recorded in $CDCl_3$ (1% *TMS*) by a Perkin-Elmer R 32 instrument, and mass spectra were recorded by an upgraded

Nuclide 12-90-G single focusing instrument at 70 and 12 eV. Analytical TLCs were performed on Merck HF_{254} silica plates using 4: 1-hexane/ethyl acetate as the mobile phase and were visualized by a UV lamp and in an I_2 vapor chamber. Aldrich reagents were used and phenanthrenequinone was purified per a procedure in Organic Syntheses, Collective Volume IV, page 757 (1963).

9,14-Diphenyldibenzo[a,c]anthracene (**1**)

A mixture of diphenyliodonium-2-carboxylate monohydrate (2.0 g) and phencyclone (2.0 g) in diglyme (10 ml) was heated at 215–220° for 5–10 min until a pale yellow solution was obtained. When the reaciton mixture cooled to 90°, it was diluted with hot 95% ethanol (10 ml). The ice cold product was collected by suction filtration which was washed repetitively with ethanol: yield, 1.6 g of cream colored crystals; m.p. 286–288°; pmr 8.2 (d, 2 H, 4,5-H's), 7.9 (m, 2 H, 10,13-H's), 7.5 (broad s, 10 H, 9,14-phenyls), 7.3 (m, 6 H, 2,3,6,7,11,12-H's), and 7.0 (m, 2 H, 1,8-H's) δ; ms (70 eV) 430 $[M]^{+\cdot}$. Vacuum sublimation gave cream to yellow colored crystals with the above characteristics unaltered.

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