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BENZANNELATED [9] AND [13] ANNULENES: FORMATION, STRUCTURAL PROPERTIES AND THE EFFECT OF BENZANNELATION ON THE AROMATICITY OF THE $(4n+2)$ π ANIONIC SYSTEMS[1]

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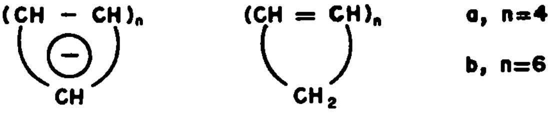
Abstract—The synthesis of benzannelated[9] and [13] annulenenes is described, 1,2:3,4-dibenzocyclononatetraene **3** and its diphenyl derivative **10** show upon deprotonation the initial formation of a non-planar partially delocalized anions **4** and **11** respectively, which undergo into the planar aromatic-diatropic dibenzocyclononatetraenyl anions **4a** and **12**. The immediate formation of the aromatic 1,2:5,6 - dibenzocyclononatetraenyl anion **14** upon deprotonation of 1,2:5,6 - dibenzocyclononatetraene **13** precludes peri H–H repulsions in the aromaticity development of the dibenzocyclononatetraenyl anions. The deprotonation of tetrabenzo[13]annulene **15** afforded anion **17**, which shows reduced diatropic character as compared with non-benzannelated[13] annulenyl anion. The spatial arrangement of **17** is discussed.

The concept of aromaticity based on HMO calculations, which was theoretically established by Huckel,[2] has stimulated continuous efforts to prepare "Huckeloid" $(4n+2)$ systems to test the theory experimentally. Cyclononatetraenyl anion **1a** and [13]annulenyl anion **1b** are predicted to possess aromatic character due to 10π- and 14π electron delocalization, respectively. Cyclononatetraenyl anion **1a** exhibited diatropic aromatic character[3] as predicted, but its anionic homolog **1b** has not yet been prepared; only its dehydro derivative was claimed to show diatropicity.[4] On the other hand, the lack of stability of the parent hydrocarbon [9]annulene **2a** due to valence isomerization into dihydroindene, proved to be an inherent characteristic of this molecule.[5] Benzene annelation may serve as an efficient way to inhibit such isomerization which would involve disruption of the aromatic stabilization of the benzene rings.

Recently, benzene annelation of annulenes has evoked considerable interest since the polycyclic systems formed may be considered as polycyclic nonbenzenoid aromatic molecules, isoelectronic or homoelectronic to classical fused polycyclic benzenoid systems e.g. anthracene, phenanthrene, and pyrene. However, the development of aromaticity in the fused polycyclic systems is not free of limitations. In the benzene annelated annulene, the annulene moiety is "forced" to share common π bonds with the benzene rings of "ultimate aromaticity". The delocalization of π electrons over the annulene skeleton can therefore be inhibited by the benzene rings.[6] Furthermore, steric interactions between the fused rings, e.g. biphenyl *ortho* interactions,[7] and H-H *peri* repulsions,[8] can play an important role by precluding aromaticity due to lack of planarity of the polycyclic system. We present a comprehensive study of benzene annelated [9]- and [13]-annulene systems and discuss the steric effects which influence the development of the aromaticity of the derived Huckeloid anions.

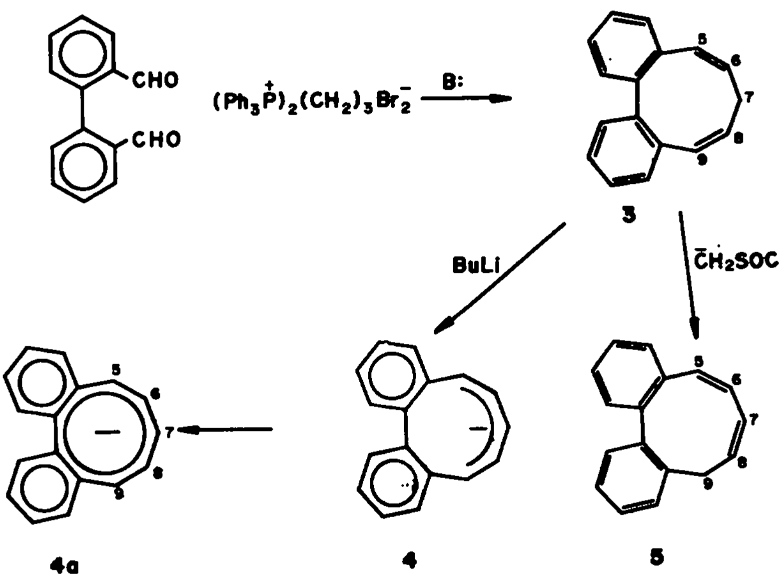
RESULTS AND DISCUSSION

The first attempt to prepare a benzene-annelated cyclononatetraene led to the preparation of 7H - 1,2:3,4 - dibenzocyclononatetraene **3**.[1a,7] The synthesis of **3** was



1 **2**

achieved by a method similar to the preparation of the dibenzoheteronines,[9] *via* a bis-Wittig condensation[10] of biphenyl - 2,2' - di - carboxaldehyde and bis[triphenylphosphonium propane]dibromide (Scheme 1). The reaction was carried out in the presence of sodium methoxide in DMF. The structure elucidation of the reaction product is attained from its spectral properties. The nine-membered ring protons appear in the ^{1}H NMR spectrum as an ABX_2 pattern. The AB part ($\delta_A = 6.30$, $\delta_B = 5.50$ ppm; J = 12.0 Hz) is attributed to the vinylic protons, the X_2 part which consists of a triplet of triplets ($\delta_{X_2} = 2.67$ ppm) is attributed to the two allylic protons. This assignment was confirmed by double resonance experiments. The vinylic coupling constant (12.0 Hz) as well as the appearance of a single AB pattern point to a similar *cis* configuration of both double bonds.[11] A coupling constant of a similar magnitude has been reported in various conjugated medium-sized ring systems with a *cis* double bond configuration.[1c,10,12] Molecular models of **3** indicate that the nine-membered ring is in a boat dissymmetric conformation. The observed equivalence of the respective methylene protons 7 and 7' can be rationalized in terms of a fast ring inversion. However, low temperature experiments (−90°C) in an attempt to freeze this process did not show any significant change of the spectrum thus, a low barrier to inversion is proposed. Deprotonation experiments of **3** with dimsyl sodium[13] failed, despite the appearance of colour, and the resulting product was identified as an allyl isomer of **3**, viz. 9H-1,2:3,4 - dibenzocyclononatetraene **5**. This result is explained by allylic double bond isomerization via the intermediate anion **4** (*vide infra*).[14] Protonation of this anion by proton abstraction from the solvent represents an acid-base equil-



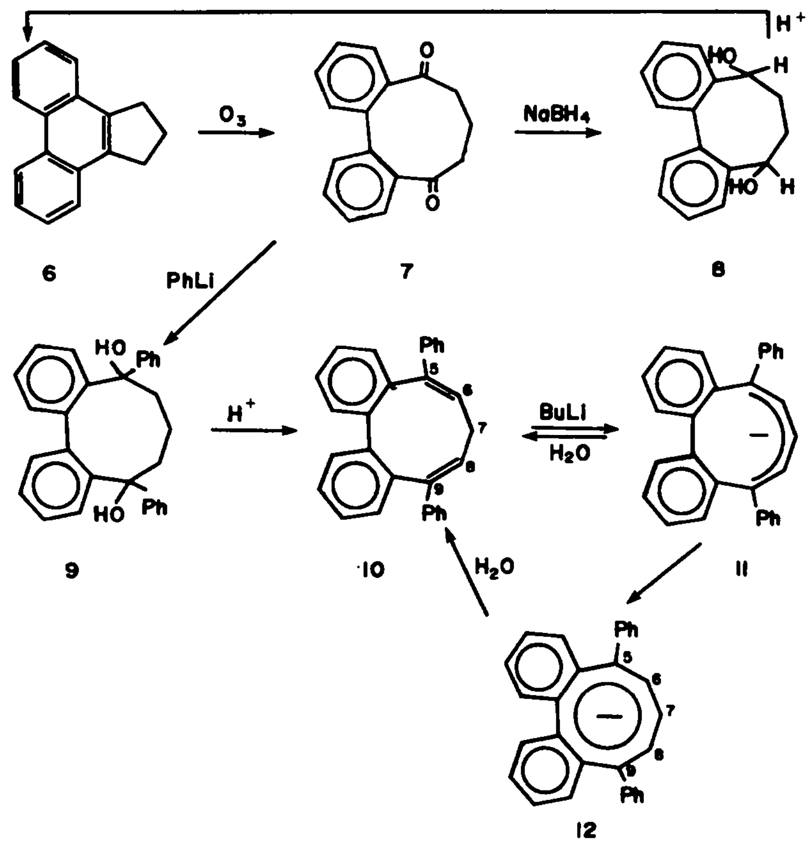
Scheme 1.

ibrium between the acidic hydrocarbon and the base. This isomerization is rationalized in terms of the formation of the thermodynamically more stable isomer (due to conjugation).

The small quantities achieved in the formation of 3 by the bis-Wittig reaction limited the research on this system and urged us to look for an alternative general route for the formation of 1,2:3,4 - dibenzannelated cyclononatetraene derivatives (Scheme 2). The key step was the bicyclic ring cleavage of 2,3 - dihydro - 1H - cyclopenta[l]phenanthrene 6[15] with ozone to form the respective nine-membered ring diketone 7. Hydride reduction of 7 afforded diol 8. Dehydration of 8 which was aimed at the formation of 3 failed and the starting hydrocarbon, i.e. 6 was formed. The dehydration pathway in which 6 is formed is explained by a transannular reaction that favours the more stable fused benzenoid system, i.e. phenanthrene over the conjugated 9-membered ring system.[16] The sensitivity of the nine-membered ring towards transannular reactions was further demonstrated in an attempt to perform the Wolf–Kishner reduction of 7. Upon treatment of 7 under standard Wolff–Kishner conditions, the starting hydrocarbon 6 was obtained. We assume that in this process an intermediate intramolecular azine is formed and it eliminates nitrogen transannularly, combined with oxidation to form 6. A similar mechanism was suggested[17] for the formation of phenanthrene from diphenyl - 2,2 - dicarboxaldehyde under similar conditions. However, reaction of 7 with PhLi followed by dehydration of diol 9 produced 5,9 - diphenyl - 7H - 1,2:3,4 - dibenzocyclononatetraene 10. The spectral parameters of 10 resemble those of the parent dydrocarbon 3. The vinylic protons appear in the ^{1}H NMR spectrum as a triplet at 5.95 ppm (J = 6.0 Hz) while the protons at position 7 appear at 3.00 ppm as a triplet (J = 6.0 Hz). This spectrum did not change even at − 90° thus indicating a conformationally flexible system.

Phenyl substitution at positions 5 and 9 precluded the assignment of the configuration of the double bonds by NMR. The appearance of IR bands at 700 and 760 cm^{-1} and the absence of bands in the 960 cm^{-1} region as well as the resemblance of the other spectral data to those of 3 provides additional support for the assignment of a *cis* configuration to the double bonds.

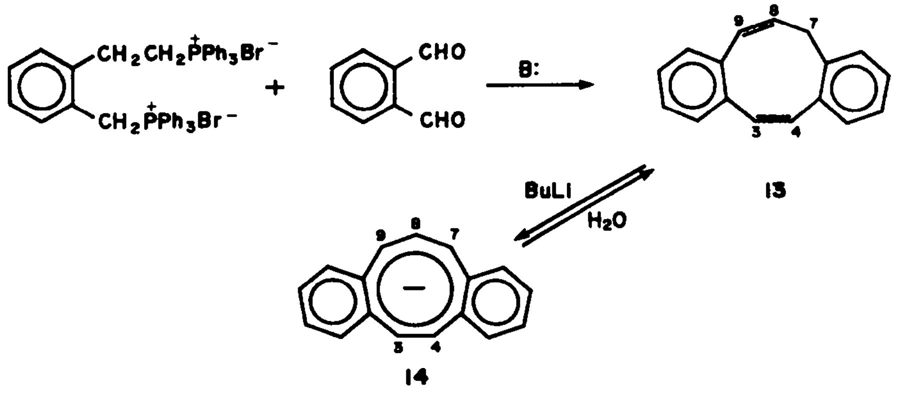
Treatment of 10 with n-BuLi in diethyl ether-d$_{10}$ produced a dark-violet solution. The NMR spectrum of this solution consists of a multiplet in the region 7.50–6.33 ppm including a well identified doublet at 6.60 ppm (J = 8.0 Hz), and a triplet at 3.76 ppm (J = 8.0 Hz). This spectrum is attributed to a nonplanar species which consists of a partially delocalized pentadienyl anion 11 (Scheme 2). The high field triplet is assigned to the proton at position 7 and the doublet at 6.60 is attributed to protons at positions 6 and 8, as was shown by double resonance experiments. The chemical shifts as well as the coupling constants are in accord with a pentadienyl delocalized anion.[18] A gradual change of the initial ^{1}H NMR spectrum was observed and a new spectrum appeared ($t_{1/2}$ 70 h). The high-field triplet disappeared and only a multiplet in the region 6.00–8.00 ppm was observed. It should be noted that low field signals were observed in this final anionic species, despite the shielding effect of the negative charge. We assign this phenomenon to the formation of a fully delocalized planar aromatic diatropic anion 12 (Scheme 2). In the low field region 7.8–8.0 ppm of this multiplet a two proton multiplet was clearly observed. This band is attributed to protons at positions 13 and 14 which suffer a mutual ring current effect in the planar anionic system. This band resembles the deshielded phenanthrene protons at positions 4 and 5. Quenching of 11 or 12 with water produced hydrocarbon 10, hence the deprotonation occurred without any further skeleton changes. The observed hindrance in the formation of the planar aromatic anion is attributed to steric repulsions of the biphenyl *ortho* protons. Independently, Garratt[7] reported the preparation of 3 by a route similar to that outlined in Scheme 1. Garratt reported a gradual development of the planar anion 4a via an initial nonplanar anion[7] as a result of reaction with base and ascribed it to the biphenyl steric interaction of 4. Benzo-*cis*^{4}-cyclononatetraenyl anion was reported by Anastassiou[8] to undergo a configurational isomerization into *cis*^{3}-*trans*-benzocyclononatetraenyl anion. This process was however attributed to a relief of strain in the 9-membered ring system



Scheme 2.

by removal of a pair of H-H *peri* repulsions. Such H-H repulsions were predicted theoretically by Simmons[19] to be significant in medium-sized ring anions e.g. cyclononatetraenyl anion 1a. Thus, the gradual development of aromaticity in anions 4a and 12 may arise due to: either biphenyl *ortho* H-H interactions or *peri* H-H interactions or a combination of both.

In order to verify the conclusion that the biphenyl *ortho* H-H interactions are the operating factor, we synthesized 1,2:5,6 - dibenzocyclononatetraene 13. The respective anion, viz. 1,2:5,6 - dibenzocyclononatetraenyl anion 14 lacks the biphenyl backbone but contains four pairs of *peri* H-H interactions. This system can thus indicate which factors are operative. The synthesis of 13[1c] is described in Scheme 3.[20] Ozonolysis of indene in CH_2Cl_2 followed by reduction of the ozonide afforded homophthaloyl alcohol.[20a] The dibromide prepared from the alcohol[20b] was reacted with triphenylphosphine in DMF to yield the respective phosphonium salt. The bifunctional bis-Wittig condensation between homophthaloyl - bis[triphenylphosphonium bromide] and phthalaldehyde in the presence of LiOEt afforded 13. The structure of 13 was confirmed by its spectral properties. The allyl bridge protons H_7–H_9 appear in the ^{1}H NMR spectrum as an ABX_2 pattern. The AB part (H_8, H_9) appears at: $\delta_A = 6.40$, $\delta_B = 5.78$ ppm while protons H_7 and $H_{7'}$ appear as the X_2 part. The coupling constant of the vinylic AB spectrum (J = 12.0 Hz) confirms the assigned *cis* configuration.[11] Although the configuration of the vinylic bridge (H_3, H_4) could not be established by the proton spectrum (being included in the aromatic multiplet), the



Scheme 3.

other spectral data confirm its *cis* configuration. The presence of IR bands in the 700 cm^{-1} region, and the absence of bands at the 960 cm^{-1} region, as well as the appearance of a *cis*-stilbene chromophore in the UV spectrum, further point at a *cis* configuration of the two double bonds.

Deprotonation of 13 with n-BuLi afforded a dark-red solution attributed to 1,2:5,6 - dibenzocyclononatetraenyl anion 14. The ^{1}H NMR spectrum of the anion consists of an unresolved multiplet at 6.10–6.60 ppm which corresponds to eleven protons and a sharp singlet at 7.62 ppm attributed to H_3 and H_4. This spectrum did not change with time, and quenching with water recovered the starting material 13. The chemical shifts of the anion appear at a relatively low field despite the shielding effect of the negative charge. The chemical shifts of the protons of 14 and the protons of 13 are presented in Table 1. It may be seen that protons H_3 and H_4 are shifted to low field by 0.62 ppm.

We attribute this phenomenon to the formation of a diamagnetic ring current in the aromatic 1,2:5,6 - dibenzocyclononatetraenyl anion 14 due to π-electron delocalization.[21] The appearance of protons H_3 and H_4 as a singlet further emphasize the equivalence of these protons in a planar diatropic system. The benzene protons (Table 1) show an upfield shift (δ arom. = −0.6 ppm), and we therefore assume that the negative charge is delocalized over the whole framework. This system may thus be regarded as a peripheral [17]annulenyl anion perturbed by cross-links which bridge the polycyclic system. The *immediate* formation of the diatropic anion 14 as compared with the gradual formation of the aromatic anions **4a** and 12 respectively, clearly demonstrates that *peri* H-H repulsions are not operative in the processes leading to the formation of these aromatic species, and the biphenyl H-H interactions seem to govern this process.

The aromatic polycyclic ions **4a**, 12 and 14 represent homoelectronic systems of benzene-fused polycyclic compounds. Fluorenyl anion and 1,2:3,4 - dibenzotropylium cation[22] are isoelectronic with the neutral phenanthrene thus representing 14π delocalized systems. Anions **4a** and 12 represent homoelectronic systems (18π delocalized electrons) to the neutral phenanthrene. On the other hand 1,2:5,6 - dibenzotropylium cation[23] and 1,2:5,6 - dibenzocyclooctatetraene dication[24] represent linearly charged benzene annelated aromatic systems isoelectronic to the neutral anthracene, while anion 14 and 1,2:5,6 - dibenzocyclooctatetraene dianion[25] represent the linear homoelectronic systems (18π electrons) to the neutral anthracene. According to this presentation there is a parallelism between monocyclic non-benzenoid Huckeloid ions and the fused polycyclic series, thus emphasizing the extension of non-benzenoid aromaticity into various series of polycyclic systems.

The respective benzannelated [13]annulenes contributed the higher homologs of the dibenzannelated [9]annulenes. The parent [13]annulenyl anion has not yet been prepared, probably due to its facile bond isomerizations. We studied the stabilizing effect of benzene annelation on the [13]annulene system and its influence on the formation of the respective aromatic anion.

A bifunctional Wittig condensation[10] between biphenyl - 2,2′ - dicarboxaldehyde and diphenylmethane - 2,2′ - bis[triphenylphosphonium bromide] in the presence of LiOEt afforded *trans trans* - 1,2:3,4:7,8:10,11 - tetrabenzo [13] annulene 15 (Scheme 4).[1d] The assignment of the configuration of the double bonds was based on the ^{1}H NMR spectrum. The vinylic protons appear as an AB pattern ($\delta_A = 6.81$, $\delta_B = 6.25$ ppm, $J_{AB} = 16$ Hz). The magnitude of the coupling constant is in agreement with a *trans, trans* double bond configuration.[11] Molecular models of 15 reveal a flexible non-planar structure. The appearance of a single vinylic AB pattern together with the equivalence of the methylene protons H_9, $H_{9'}$ point at a fast exchanging species. ^{1}H NMR spectrum taken at −90° did not show any significant change in the spectrum, thus indicating a low barrier to inversion.

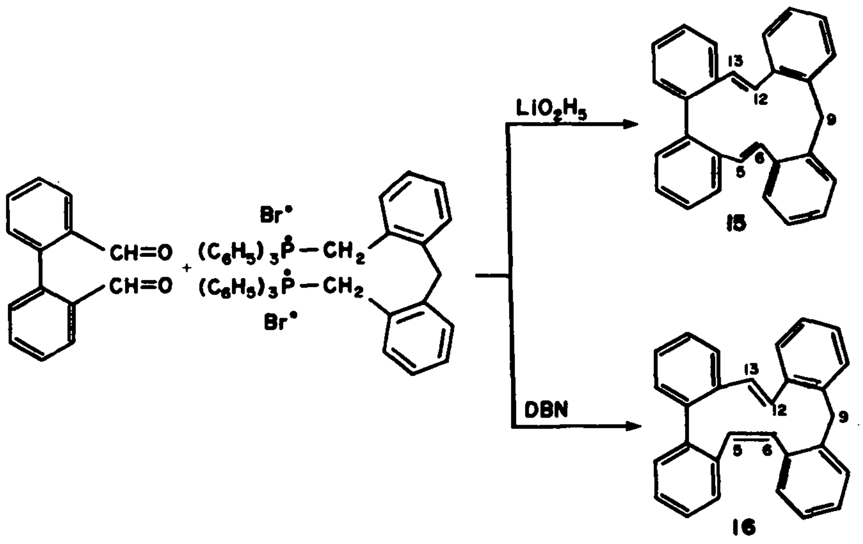
A Wittig condensation similar to the preparation of 15, but in the presence of 1,5 - diazabicyclo [4.3.0] non - 5 - ene (DBN)[26] afforded the *cis, trans* isomer 16.[1d] The assignment of the double bond configuration is based on the ^{1}H NMR spectrum; in the vinylic region two AB patterns ($\delta_{A'} = 6.76$, $\delta_{B'} = 6.52$ ppm, $J_{AB'} = 16.0$ Hz; $\delta_{A''} = 6.42$, $\delta_{B''} = 6.16$ ppm, $J_{AB''} = 12.0$Hz) are observed. Protons H_9 and $H_{9'}$ also appear as an AB quartet ($\delta_A = 4.17$, $\delta_B = 3.45$ ppm, $J_{AB} = 15$ Hz). The appearance of two coupling constants of the vinylic protons point at a *cis, trans* configuration of 16, and the AB pattern of the methylene protons appears to be due to a lack of symmetry which is also supported by molecular models. The formation of two structural isomers with two different bases is a result of the sensitivity of the bis-Wittig condensation in directing the configuration of the formed double bonds.[27]

Treatment of 15 with t-BuLi furnished a dark-red solution characterized as the 1,2:3,4:7,8:10,11 - tetrabenzo [13] annulenyl anion 17. However, deprotonation of 16 did not succeed with diverse bases. The ^{1}H NMR spectrum of 17 consists of a multiplet (18H) in the region 6.30–7.40 ppm, two doublets at 4.25 ppm and 3.42 ppm respectively (J = 13.0 Hz) (each corresponding to one proton), and a singlet at 3.49 ppm corresponding to one proton. Quenching of 17 with water afforded recovered

Table 1. ^{1}H NMR chemical shifts of 13 and 14[a]

Compound	H_3,H_4	H_7	H_8	H_9	H_{arom}
<u>13</u>	7.0	6.40	5.78	3.42	7.0
<u>14</u>	7.62	6.40	6.40	6.40	6.40
$\Delta\delta_i$[b]	2x0.62[c]	0.0	0.62[c]	3.02[c]	8x(-0.6)[d]

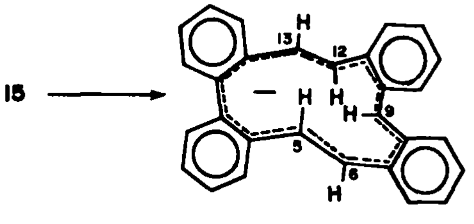
(a) Chemical shifts of multiplets were taken at the center of the absorption; (b) Chemical shift difference between hydrocarbon and anion of the respective protons; (c) To high field; (d) To low field.



Scheme 4.

15, and therefore no structural modification was assumed to occur in the deprotonation process. The two distinct high field doublets are attributed to two "inner" protons H_5 and H_{12} respectively, in a *trans* configuration. The high-field singlet can be assigned only to proton H_9 in an "inner" position. The decrease of the *trans* coupling constant reflects the charge delocalization over the system and together with the downfield shift of H_6 and H_{13} manifests the formation of a planar delocalized 14π-electron diatropic aromatic system. The appearance of *two* distinct high-field doublets reveals that the two original vinylic double bonds are fixed in a *trans* configuration of a different sense. The rationale of this phenomenon, also supported by molecular models, is that "through-space" steric overcrowding between protons H_5 and H_{13} or H_6 and H_{12} is relieved when the molecule is forced into a planar structure. The enforcement of H_9 into the core of the ring system is explained by a release at the ring juncture of two couples of *peri* H-H interactions with the benzene ring protons. Similar factors were reported by Anastassiou[8] to operate in the isomerization of *cis*-benzocyclononatetraenyl anion into the *cis*[3], *trans*-isomer. However, Ogawa[28] reported the opposite process in the [15]annulenyl cation series, where the cationic center has isomerized into an "outer" position. We assume that the [13]annulenyl anion 17 is subjugated to such a "molecular spatial arrangement" so as to relieve steric strain in the planar aromatic anion. On the other hand, the failure in the deprotonation of 16 can be explained by the rigidity of the molecular framework and the difficulty in maintaining a planar configuration.

To our knowledge anion 17 is the first ionic aromatic system to show both steric effects, i.e. "through space" or trans annular interactions and ring juncture *peri* H-H interactions operating in the development of the aromatic system. The observed difference in chemical shifts of the inner protons H_5 and H_{11} between 15 and 17 (*ca.* 3 ppm) as compared with that of the nonbenzannelated dehydro [13]annulenyl anion (*ca.* 11.0 ppm) should be noted.



17

It seems that the observed chemical shift of the inner protons in 17 is not an average due to a rapidly inverting system, since low temperature NMR (−80°) did not reveal any change in the spectrum. Furthermore, the diamagnetic ring current of the fused benzene rings, which should counterbalance the paratropic shift of the inner protons in the [13]annulenyl anion, cannot be a dominant factor as H_9 with two neighboring benzo rings appears at similar field to that of H_5 and H_{12}.

It seems therefore, that the induction of ring current in the annulene skeleton is considerably weakened by benzene annelation, analogous to benzo[14] and benzo[18] annulenes.[6]

CONCLUSION

The results described above show that benzene annelation serves as an adequate tool for the stabilization of hydrocarbons and anions. It appears that steric factors are of major importance in the development of the aromaticity in these systems and the following are of significant importance and should be emphasized: (a) The biphenyl barrier, (b) steric *peri* H–H repulsions due to interactions over the ring juncture between the benzene ring protons and the adjacent annulene protons; and (c) steric interactions in the annulene ring itself (trans-annular or through-space). All these factors operate mutually in the development of a planar system in the respective anions to form an aromatic system. It seems that there is a delicate balance between these factors which results in the most satisfactory configuration to permit an efficient $p\pi$ overlap.

EXPERIMENTAL

M.ps were measured on a Fisher–Johns apparatus and are uncorrected. Electronic spectra (UV and visible) were recorded with the aid of a Unicam SP 800 spectrometer. Infra-red spectra were recorded with a Perkin–Elmer 337 spectrometer. Mass spectra were obtained with an Atlas–MAT CH4 instrument at

70 eV. ^{1}H NMR spectra were recorded on Varian T-60 and HA100D spectrometers at 60 and 100 MHz, respectively. The chemical shifts (δ) are reported downfield relative to TMS. Decoupling experiments were performed with a Hewlett–Packard 4204 A Oscillator. The usual workup procedure consisted of washing the organic solution with water, dilute acid, and aqueous bicarbonate followed by separation of the organic layer and drying with $MgSO_4$. The excess solvent was filtered and evaporated. SiO_2 or Florisil were used for column chromatography. TLC plates were obtained from Merck. Commercial 2,3 - dihydro - 1H - cyclopenta[1]phenanthrene (Aldrich) was used.

7H-1,2:3,4-*dibenzocyclononatetraene* 3

A suspension of 1,3 - bis(triphenylphosphonium)propane dibromide[29] (18.6 g, 26 mmoles) in 600 ml of dry DMF was heated under N_2, to 70° with vigorous stirring. Freshly prepared dry sodium methoxide (5.3 g, 60 mmoles) was added in one portion and the reaction mixture was stirred for an additional 10 minutes. A solution of biphenyl - 2,2' - dicarboxaldehyde (5.33 g, 26 mmoles) in 100 ml of dry DMF was added during 15 min. The reaction mixture was further stirred for 3 h, poured over dilute HCl and extracted with CH_2Cl_2. The combined extracts were worked up as described above. The residue was chromatographed on SiO_2 and eluted with hexane. In the first fraction an oily product (0.35 g, 6.5%) was obtained and identified as 3, which crystallized slowly, with a m.p. 40°. Compound 3 shows a single spot in TLC (silica-hexane-$R_f = 0.4$).

Calc. for $C_{17}H_{14}$: C, 93.57; H, 6.42. Found: C, 93.9; H, 6.2% IR ν_{max}^{neat}: 3050, 3000, 2900, 1630, 1460, 1430, 1160, 1005, 760, 715, 695, 680 cm^{-1}. UV λ_{max}^{EtOH}: 217(ϵ = 20,000), 243^{s}(7,000), 272^{s}(1500), 280^{s}(700), 293^{s}nm(280). ^{1}H NMR δ_{ppm}^{CDCl}3: 7.30–7.00 (8H, m), 6.50 (1H, broad-s), 6.30 (1H, broad s), 5.50 (2H, td, J_1 12Hz, J_2 6.0Hz), 2.67 (2H, tt, J_1 6.0Hz, J_2 1.6 Hz). Irradiation at 2.67 ppm converts the olefinic region into an AB pattern: δ_A 6.0 ppm, δ_B 5.75 ppm, J_{AB} 12 Hz. MS *m/e* 218 (M^+, 100%), 217, 216, 204, 203, 191, 189, 178, 165, 152.

9H-1,2:3,4-*Dibenzocyclononatetraene* 5

A three necked flask equipped with a magnetic stirrer under inert atmosphere was used to prepare dimsyl sodium,[13] from 0.08 g sodium hydride and 50 ml dry DMSO. A solution of 0.2 g of 3 in 20 ml of dry DMSO was added dropwise and the solution was then stirred for 3 h. The reaction mixture was decomposed as described for 3, worked up as described above and chromatographed (SiO_2-hexane). The oily product (0.15 g, 75%) showed only one spot (hexane $R_f = 0.4$) in TLC. Calc. for $C_{17}H_{14}$: C, 93.57; H, 6.42. Found: C, 93.4; H, 6.2%. IR ν_{max}^{neat}: 3050, 3000, 2920, 1650, 1480, 1440, 1010, 760, 745, 680 cm^{-1}. UV λ_{max}^{EtOH}: 216(ϵ = 19,600), 250^{s}(4,000), 265^{s}(2,200), 273^{s}(1560), 293^{s}(440), 328^{s}nm(100). ^{1}H NMR δ_{ppm}^{CDCl} 3: 7.40–6.90 (8H, m), 6.10–5.4 (4H, m), 3.1 (2H, m). Irradiation at 5.80 ppm rendered the multiplet at 3.1 ppm into a broad singlet. Irradiation at 3.10 ppm changed the vinylic multiplet only slightly. MS *m/e* 218 (M, 100%), 203, 189, 178, 165, 154.

7H-1,2:3,4-*Dibenzocyclononadiene-5,9-dione* 7

2,3 - Dihydro - 1H - cyclopenta[1]phenanthrene (30 g) in 500 ml of 4:1 methanol dichloromethane was ozonized for a period of 4 h per g of starting material at −60° (Welsbach 90 kV). The reaction mixture was decomposed with KI in acetic acid, treated with $Na_2S_2O_3$ and worked up. The hexane fractions contained the starting material, while elution with CH_2Cl_2 afforded 7 (ethanol, m.p. 190°) in 90% yield. Calc. for $C_{17}H_{14}O_2$: C, 81.60; H, 5.60. Found: C, 81.4; H, 5.6%. IR ν_{max}^{KBr}: 3050, 2950, 1680, 1600, 1430, 1400, 1320, 1280, 1030, 930, 790, 760, 750 cm^{-1}. UV λ_{max}^{EtOH}: 230(ϵ = 16,250), 285^{s}nm(2,200). ^{1}H NMR $\delta_{ppm}^{CDCl_3}$: 7.83–7.20 (8H, m), 3.03–2.50 (4H, m), 2.50–1.80 (2H, m). MS *m/e* 250(m), 222, 194, 180 (100%), 165, 152.

Hydride reduction of 7 *to the diol* 8

To 2.0 g of 7 in 100 ml of ethanol and 50 ml of THF was added 0.5 g of $NaBH_4$. After decomposition with water and the usual workup procedure, 0.7 g (35%) of white crystals (trituration with CH_2Cl_2) of 8 m.p. 175°. Calc. for $C_{17}H_{18}O_2$: C, 80.31; H, 7.08. Found: C, 80.6; H, 7.4%. IR ν_{max}^{Nujol}: 3350, 3050, 2910, 1600, 1450, 1300, 1020, 770, 560 cm^{-1}. UV λ_{max}^{EtOH}: 218(ϵ = 19,000), 257(500), 263(520), 272 nm (370). ^{1}H NMR $\delta_{ppm}^{CDCl_3}$: 7.92–7.33 (8H, m), 4.4 (2H, m), 2.16–1.50 (6H, m), 1.7 (2H, OH).

5,9 - *Diphenyl* - 7H - 1,2:3,4 - *dibenzocyclononadiene* - 5,9 - *diol* 9

PhLi (0.04M) was prepared in 150 ml of dry ether in a 1 l three necked flask equipped with a reflux condenser and magnetic stirrer. A suspension of 7 (5 g, 0.02 M) was then added in 200 ml of dry benzene. The reaction was kept at room temperature followed by 2 h of reflux. The reaction mixture was decomposed on dil HCl and worked up. Evaporation of the solvents afforded an oil which was recrystallized from benzene-hexane 1:1, (6.4 g, 80%) m.p. 180°. Calc. for $C_{29}H_{26}O_2$: C, 85.71; H, 6.4. Found: C, 85.4; H, 6.3%. IR ν_{max}^{Nujol}: 3600, 3400, 3050, 2900, 1600, 1490, 1440, 1400, 1040, 760, 700 cm^{-1}. UV λ_{max}^{EtOH}: 254 (ϵ = 1250), 260 nm (1240). ^{1}H NMR δ_{ppm}^{CDCl}3: 8.08 (2H, dd, $J_1 = 8.0$, $J_2 = 2.0$ Hz), 7.20 (4H, m), 7.16 (10 H, s), 6.40 (2H, dd, $J_1 = 8.0$, $J_2 = 2.0$ Hz), 2.15 (8 H, m). Irradiation at 7.30 ppm rendered the absorptions at 8.08 ppm and 6.40 ppm into doublets (J – 2.0 Hz and 8.0 Hz respectively). MS *m/e* 406(M), 388, 370, 355, 328, 255(100%), 215, 195, 180, 165.

5,9-*Diphenyl* - 7H - 1,2:3,4 - *dibenzocyclononatetraene* 10

A solution of 5.4 g of 9 in 300 ml of benzene was refluxed with 1 g of TsOH for 3 h with a Dean–Stark separator. After the usual workup procedure and chromatography on silica followed by elution with hexane, white oil was obtained. Recrystallization from ethanol afforded 3.8 g (75%) of a white crystalline product, m.p. 113°. Calc. for $C_{29}H_{22}$: C, 94.05; H, 5.95. Found: C, 93.9; H, 5.9%. IR ν_{max}^{KBr}: 3050, 2930, 1610, 1490, 1440, 765, 700, 630 cm^{-1}. UV, λ_{max}^{EtOH}: 245 (ϵ = 22,000), 265^{s}(15,400), 317 nm (90). ^{1}H NMR δ_{ppm}^{CDCl} 3: 7.13 (18H, s), 595 (2H, t, J = 6.0 Hz), (2H, t, J = 6.0 Hz). Irradiation at 3.0 ppm renders the triplet at 5.95 ppm into a singlet and vice versa. MS *m/e* 370 (M, 100%), 356, 289, 278, 265, 215, 191, 180.

1,2:5,6-*Dibenzocyclononatetraene* 13

The dibromide (9.0 g), prepared according to the literature,[20b] was reacted with triphenylphosphine (17 g) in boiling DMF for 3 h. A crystalline hygroscopic phosphonium salt (21.5 g, 93%), m.p. 148°, was obtained after solvent evaporation. This phosphonium salt (16.5 g, 0.02 moles) and ortho-phthalaldehyde (2.88 g, 0.02 moles) were both dissolved in 600 ml of dry DMF. The solution was heated to 85° and stirred under argon. A solution of lithium ethoxide (3.12 g, 0.06 moles) in 95 ml of absolute ethanol was added dropwise during 3 h, with vigorous stirring. The reaction mixture was stirred for an additional 6 h, decomposed with water, extracted with CH_2Cl_2 and worked up as usual. The oily product was chromatographed (Florisil, hexane elution), and crystallized on standing (0.44 g, 10%) m.p. 20°. Calc. for $C_{17}H_{14}$: C, 93.57; H, 6.42. Found: C, 93.29; H, 6.51%. IR $\nu_{max}^{CHCl_3}$: 3050, 2920, 1490, 1430, 1100, 750, 735, 710 cm^{-1}. UV λ_{max}^{EtOH}: 250^{s} (ϵ = 9,600), 320^{s}(1,180), 343 nm (825). ^{1}H NMR $\delta_{ppm}^{CDCl_3}$: 7.30–6.70 (10H, m), 6.45 (1H, dt, $J_1 = 12.0$ Hz), 5.81 (1H, dt), 3.42 (2H, dd, $J_1 = 5.7$, $J_2 = 2.0$ Hz). Irradiation at 3.42 ppm transformed the vinylic absorption into an AB pattern, δ_A 6.40, δ_B 5.78, J_{AB} 12 Hz. MS *m/e* 218 (m, 100%), 217, 215, 191, 165, 152.

trans - *trans* - 1,2:3,4:7,8:10,11 - *tetrabenzo*[13]*annulene* 15

A solution of diphenylmethane 2,2' - bis[triphenylphosphonium bromide] (12 g, 14 mmol) and diphenyl - 2,2' - dicarboxaldehyde (2.94 g, 14 mmol) in dry dimethylformamide (800 ml) was heated to 80° under dry N_2. A solution of lithium ethoxide (prepared from 0.28 g lithium) in absolute ethanol (100 ml) was added dropwise during 2.5 h with stirring. The solution was stirred for an additional 12 h at room temp., and then diluted with water (500 ml). The mixture was extracted with dichloromethane, and the organic extract washed with 10% hydrochloric acid, 5% sodium hydrogen carbonate and water, dried and evaporated. The residue was chromatographed on Florisil (500 g) and eluted with hexane. Evaporation of the first four fractions (160 ml each) gave 15 accompanied by triphenylphosphine and traces of 16.

Preparative layer chromatography of the residue (silica gel, hexane), separated three fractions. The faster moving band was extracted and evaporated to give 15 yield: 828.8 mg (16%); m.p. 117°. Calc. for $C_{29}H_{22}$: C, 94.01; H, 5.99. Found: C, 94.00; C, 6.20%. IR ν_{max}^{KBr}: 975, 760 cm^{-1}. UV $\lambda_{max}^{ethanol}$: 260 nm (ϵ _ 28,000). ^{1}H NMR $\delta_{ppm}^{CDCl_3}$: 7.4 ppm (m, 8H), 6.81 (d, 2H, J–16 Hz), 6.25 (d, 2H, J–16 Hz), 4.09 (s, 2H). MS *m/e* (relative intensity) = 370(M), 279, 192 (100%).

cis, trans - 1,2; 3,4; 7,8; 10,11 - *Tetrabenzo*[13]*annulene* 16

A solution of diphenylmethane 2,2′ - bis[triphenylphosphonium bromide][29] (12 g, 14 mmol) and biphenyl - 2,2′ - dicarboxaldehyde (2.94 g, 14 mmol) in dry dimethylformamide (700 ml) was heated under nitrogen to 80°. A solution of 1,5 - diazabicyclo[4.3.0]non - 5 - ene (3.5 g, 28 mmol) in dry dimethylformamide (80 ml) was added dropwise within 2.5 h with stirring. Stirring was continued for 4 h at 80° and overnight at room temperature. The solvent was evaporated in vacuo and the resulting residue extracted with dichloromethane. The extract was washed with dilute hydrochloric acid and water. The organic layer was dried and the residue after evaporation, was chromatographed on Florisil (500 g). Elution with hexane (400 ml) gave a white residue. Further preparative layer chromatography of this residue (silica gel), after three consecutive elutions with hexane, extraction, and evaporation of the second band, yielded pure 16; yield 622 mg (12%); m.p. 97°. Calc. for $C_{29}H_{22}$: C, 94.01; H, 5.99. Found: C, 93.94; H, 6.18%. IR ν_{max}^{KBr}: 975, 760 cm^{-1}. ^{1}H NMR $\delta_{ppm}^{CDCl_3}$: 7.40 ppm (m, 8H), 6.76(d, 1H, J = 16 Hz), 6.52(d, 1H, J = 16 Hz), 6.42 (d, 1H, J = 12 Hz), 6.16(d, 1H, J = 12 Hz), 4.17(d, 1H, J = 15 Hz), 3.45(d, 1H, J = 15 Hz). MS *m/e* (relative intensity) 370(M), 279, 265, 192 (100%).

General procedure for deprotonation

The hydrocarbon (~ 15 mg) was dissolved in THF-d_8 (0.5 ml), in a NMR tube or in a flask, and cooled to −70°. The deprotonating agents (BuLi in cyclohexane or t-BuLi in pentane) were added slowly under argon atmosphere. The reaction was followed by the NMR spectrum. The reaction mixtures were quenched with water or D_2O.

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