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Benzo- and Naphtho-derivatives of Triptycene: Synthesis and Properties

Makoto Sugihashi,* Ryosuke Kawagita, Tetsuo Otsubo,
Yoshiteru Sakata, and Soichi Misumi**
The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka

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Several benzo- and/or naphtho-derivatives of triptycene were prepared in a manner of addition reaction of dehydronaphthalene (XIII) or a new type of aryne, dehydroanthraquinone (XVI) generated from 3-amino-anthraquinone-2-carboxylic acid (XV), with a few acenes. The absorption bands in longer wavelength region of their UV spectra and the chemical shift of bridgehead protons in their NMR spectra led to a conclusion that the spectra of those annelated triptycenes are elucidated in terms of a superposition and a sum of magnetic effects of separated component chromophores, respectively, and thereby indicate a negligible existence of the across-space π-electron interactions, if any, among three aromatic nuclei.

Triptycene (II) is an interesting, rigid cage molecule having a higher order of symmetry (D_{3h}). Since the first synthesis by Bartlett and his co-workers,1) this unique geometry of the molecule has attracted numerous investigators for studies of spectral properties. Thus an electronic interaction of three separated benzene nuclei in this molecule has early been considered to contribute significantly on the electronic spectrum, because σ-type overlap of $2p\pi$ orbitals was anticipated as in the case of parent compound, barrelene (I).2) Many efforts have so far been done for examination of such σ-type interactions.3) However, most of observed spectra of triptycene and its derivatives were

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* Present address: Nippon Paint Co., Ōyodo-ku, Osaka.

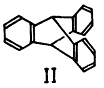
** To whom inquiries should be addressed.

1) P. D. Bartlett, M. J. Ryan, and S. G. Cohen, *J. Amer. Chem. Soc.*, **64**, 2649 (1942).

2) C. F. Wilcox, Jr., S. Winstein, and W. McMillan, *ibid.*, **82**, 5450 (1960); J. Paldus and J. Koutecky, *Collect. Czech. Chem. Commun.*, **27**, 2139 (1962); *Tetrahedron*, **19**, Suppl. **2**, 201 (1963); R. Hoffmann, E. Heilbronner, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 706 (1970). F. A. Van-Catledge, *ibid.*, **93**, 4365 (1971).

3) P. D. Bartlett and E. S. Lewis, *ibid.*, **72**, 1005 (1950); C. F. Wilcox, Jr., *J. Chem. Phys.*, **33**, 1874 (1960); C. F. Wilcox, Jr. and A. C. Craig, *J. Org. Chem.*, **26**, 2491 (1961).


I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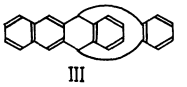
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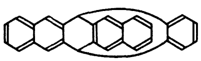
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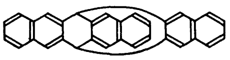
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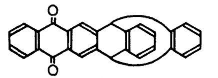
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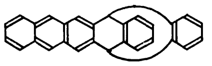
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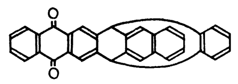
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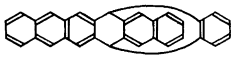

IX

found to be explained in terms of a sum of three benzenoid chromophores and not of the interaction among those chromophores. Present authors also reported that the electronic spectra of several chloro-substituted triptycenes could be interpreted by a superposition of three benzenoid chromophores.[4]

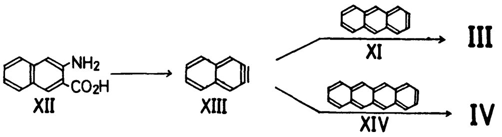
On the other hand, there have been interesting investigations that CD spectra of a number of optically active triptycene derivatives were consistent with an explanation of interactions among electric transition moments of benzenoid chromophores[5] and that a triplet state arising from photoexcitation of tribenzotriptycene (V) was located in any one of naphthalene nuclei at 20°K, but delocalized among three naphthalene nuclei at 77°K.[6]

A stepwise annelation or condensation with additional aromatic nuclei to the triptycene molecule is of great interest in connection with the interaction in question. Since the spectral properties of condensed aromatic nuclei as naphthalene and anthracene have been well investigated, it is expected, from the examination of electronic absorption and emission spectra, that such annelated derivatives of triptycene may afford valuable informations about the intramolecular across-space interactions. In addition, it appears that they are appropriate systems for a study of magnetic anisotropies of containing aromatic nuclei because of their rigid structures.

Literature search revealed that there have been only two annelated derivatives (III[7] and V[6]) of triptycene containing naphthalene ring as condensed aromatic nucleus. In the present paper we wish to report the synthesis and spectral properties, electronic and NMR, of several triptycene derivatives (III—IX) including naphthalene, anthracene, and anthraquinone nuclei.

Results and Discussion

Synthesis. Since triptycene was prepared by the Diels-Alder reaction of anthracene with benzyne, various triptycene derivatives have generally been synthesized through the addition reaction of arynes. In the present investigation triptycene derivatives were also prepared in a manner of aryne reaction except tribenzotriptycene (V) which was obtained by the addition reaction of 1,4-dihydronaphthalene-1,4-oxide with pentacene, followed by dehydration with acetic anhydride.[6] The synthesis of mono- and di-benzotriptycenes (III and IV) was carried out by the reaction of anthracene (XI) and tetracene (XIV) with an aryne, 2,3-dehydronaphthalene (XIII), generated from 3-amino-2-naphthoic acid (XII) according to Friedman,[7] in 11 and 25% yields, respectively. In order to obtain two triptycene derivatives (VII and IX) containing anthracene nucleus, a reaction path *via* reduction of phthaloyl derivatives, VI and VIII, was chosen in the present study because 2,3-dehydroanthracene corresponding to XIII might be difficult to generate for a reason of its self-condensation. The phthaloyl derivatives VI and VIII were obtained by the reaction of anthracene and tetracene with a new aryne, 2,3-dehydroanthraquinone (XVI), generated from 3-aminoanthraquinone-2-carboxylic acid (XV), in 24 and 29% yields, respectively. The aryne precursor XV was prepared *via* five steps from toluene in good yield according to the procedure of Hosoda.[8] The quinone derivatives VI and VIII were reduced by the Meerwein-Pondorf-Verley reaction using aluminum tri(cyclohexyl oxide)[9] to give two anthracene derivatives in 35% of VII and 29% yield of IX, respectively. All the triptycene derivatives (III—IX) are thermally stable and kept without any change for a long time. The addition reaction of tetracene was carried out in a nitrogen atmosphere and with degassed solvent, otherwise it would result in yielding mainly an oxidative product, tetracene quinone, instead of regular addition compounds IV and VIII.



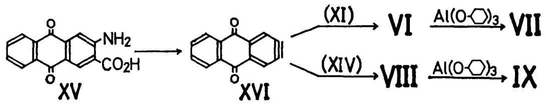


Table 1. Chemical shifts of bridgehead protons (τ value)

Compound	Solvent $AsCl_3$	 $CDCl_3$
II	4.55	4.61
III	4.43	4.50
IV	4.29	4.37
V	4.17	4.25
VI	4.29	—
VII	4.40	4.47
VIII	4.18	—
IX	4.27	—

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[4] I. Mori, T. Kadosaka, Y. Sakata, and S. Misumi. This Bulletin, **44**, 1649 (1971).

[5] F. Ogura and M. Nakagawa, *ibid.*, **38**, 155 (1965).

[6] G. Wittig, H. Harle, E. Knauss, and K. Niethammer, *Chem. Ber.*, **93**, 951 (1960).

[7] L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, **85**, 1549 (1963); *J. Org. Chem.*, **34**, 3089 (1969).

[8] Y. Hosoda, "Senryo Kagaku," Gihodo, Tokyo (1957), p. 556.

[9] S. Coffey and V. Boyd, *J. Chem. Soc.*, **1954**, 2468.

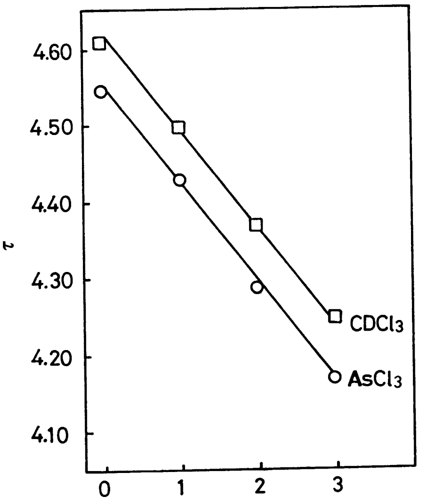


Fig. 1. Relation between the chemical Shifts of bridgehead protons of benzo-derivatives (III—V) and the number of naphthalene nuclei in deuterochloroform and arsenic trichloride.

Nuclear Magnetic Resonance Spectra. Table 1 shows the chemical shift of bridgehead protons of triptycene and some annelated triptycenes (III—IX) in arsenic trichloride and/or in deuterochloroform, because VI, VIII, and IX are sparingly soluble in the latter solvent. The chemical shifts of bridgehead protons in triptycene (II) and mono-, di-, and tri-benzotriptycenes (III, IV, and V) afford straight lines when plotted against number of naphthalene nuclei as is shown in Fig. 1. The figure reveals that the slope of the lines remains nearly constant even if the solvent is changed from deuterochloroform to arsenic trichloride and that the resonance positions of the bridgehead protons regularly shift to lower field by average 0.13 ppm along with the increase of the number of naphthalene nuclei. This finding seems to be accounted for in terms of additional ring current effect of naphthalene nuclei introduced stepwise into the triptycene molecule and therefore to substantiate the Schaefer's conclusion[10] about non-existence of "round-the-barrel" current in the triptycene molecules. In other words, the difference in the chemical shifts of bridgehead protons may be represented by a difference in the magnetic anisotropies of contained aromatic nuclei.

Thus, the chemical shifts $\Delta\sigma_1$ and $\Delta\sigma_2$ of the bridgehead protons in triptycene (II) and benzotriptycene (III) are expressed as follows:

$$\Delta\sigma_1 = 3\Delta\sigma_b + \Delta\sigma_0 \tag{1}$$

$$\Delta\sigma_2 = 2\Delta\sigma_b + \Delta\sigma_n + \Delta\sigma_0' \tag{2}$$

where $\Delta\sigma_b$ and $\Delta\sigma_n$ are chemical shifts due to ring current of a benzene nucleus and a naphthalene one, and $\Delta\sigma_0$ and $\Delta\sigma'_0$ are chemical shifts caused by various effects, *i.e.* the electric field, the van der Waals, the solvent, the electron density effects and so on, other than the ring current in II and III, respectively.

In a series of similarly constructed compounds the anisotropic effects of particular C–C and C–H bonds and the other effects are generally approximated to be equal, *i.e.* $\Delta\sigma_0 = \Delta\sigma'_0$. From Eqs. (1) and (2):

$$\Delta\Delta\sigma = \Delta\sigma_1 - \Delta\sigma_2 = \Delta\sigma_b - \Delta\sigma_n \tag{3}$$

Eq. (3) implies that the difference ($\Delta\Delta\sigma$) in the chemical shifts of the bridgehead protons in triptycene and benzotriptycene can be represented as a difference in ring current effects of a benzene nucleus and a naphthalene one. Since $\Delta\sigma_b$ and $\Delta\sigma_n$ are the chemical shifts only due to magnetic anisotropy of ring current in each aromatic nucleus, they should be correlated with the McConnell equation[11] assuming that a center of the anisotropy is situated at the center of each benzene ring (Eqs. (4) and (5)). Thus, in the case of naphthalene nucleus two centers of the anisotropy are placed at the center of each benzene ring:

$$\Delta\sigma_b = -\frac{\Delta\chi(1-3\cos^2\theta_1)}{3R_1^3} \tag{4}$$

$$\Delta\sigma_n = -\left\{\frac{\Delta\chi'(1-3\cos^2\theta_2)}{3R_2^3} + \frac{\Delta\chi'(1-3\cos^2\theta_3)}{3R_3^3}\right\} \tag{5}$$

where R_n is a distance between a bridgehead proton and a center of each benzene ring, $\Delta\chi$ and $\Delta\chi'$ are the vectors which represent the anisotropies due to the ring currents of benzene ring and each benzene component in naphthalene nucleus, respectively, and θ is an angle between a line represented as R and $\Delta\chi$ or a main axis of each benzene, *i.e.* $\theta = 90°$ in this case. Jonathan[12] calculated some ratios of ring current intensities of condensed aromatic nuclei to benzene ring as is shown in Table 2; *e.g.* for naphthalene nucleus, Eq. (6) are assumed.

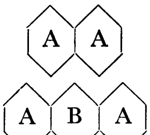
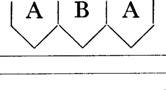
$$\Delta\chi' = 1.1\Delta\chi \tag{6}$$

From Eqs. (3), (4), (5), and (6):

$$\Delta\Delta\sigma = -\frac{\Delta\chi(1-3\cos^2\theta_1)}{3R_1^3} + \frac{1.1\Delta\chi(1-3\cos^2\theta_2)}{3R_2^3} + \frac{1.1\Delta\chi(1-3\cos^2\theta_3)}{3R_3^3} \tag{7}$$

The observed value of $\Delta\Delta\sigma$ (-0.13×10^{-16}) and the values of the distances, $R_1 = 3.5$, $R_2 = 3.4$, and $R_3 = 5.5$ Å which are measured on the geometry drawn by reference to X-ray analysis,[13] are substituted in Eq.

TABLE 2.

Molecule	Ring	Current intensity
	A	1.000
	A	1.093
	A	1.085
	B	1.280

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[10] K. G. Kidd, G. Kotowycz, and T. Schaefer, *Can. J. Chem.*, **45**, 2155 (1967).

[11] H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

[12] N. Jonathan, S. Gordon, and B. P. Dailey, *ibid.*, **36**, 2443 (1962).

[13] K. J. Palmer and D. H. Templeton, *Acta Crystallogr.*, **B24**, 1048 (1968).

(7). A calculated value of the magnetic anisotropy of benzene, $\Delta\chi = -33\times10^{-30}$ cm^3/mol, is good agreement with the Craig's value[14] ($\Delta\chi = -31\times10^{-30}$ cm^3/mol) obtained by substracting a sum of Pascal's constants[15] from the observed value of magnetic susceptibility of benzene.

Using the value of $\Delta\chi$ calculated above and the ring current intensity of each benzene ring in Table 2, the chemical shifts of bridgehead protons in the triptycene derivatives containing anthracene nucleus, VII and IX, are calculated to be τ 4.39 and 4.30, respectively. Those values were found to be well compatible with the observed values of VII and IX, τ 4.40 and 4.27 in arsenic trichloride.

Consequently, it was found that the application of Jonathan's values and the assumption which the various effects other than ring current, $\Delta\sigma_0$ and $\Delta\sigma_0'$, are approximated to be equal were valid for study on magnetic anisotropies and relative intensities of ring currents in this system.

Electronic Spectra. The electronic absorption spectra of the annelated triptycenes above-stated are shown in Figs. 2, 3, and 4 and in Table 3.

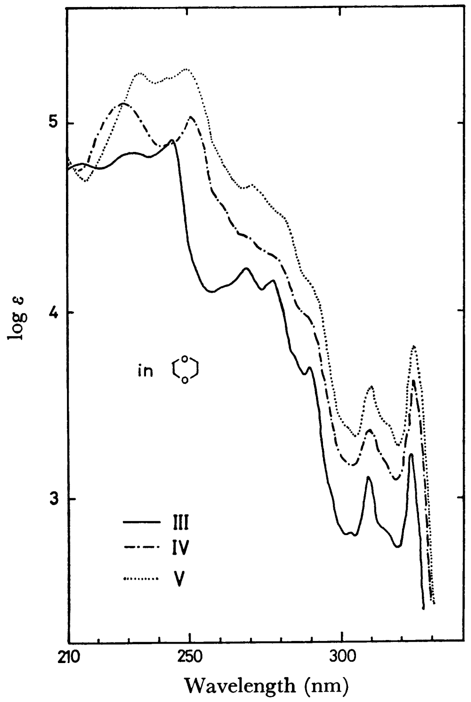

Fig. 2. The electronic spectra of benzo-(III), dibenzo-(IV), and tribenzo- (V) triptycenes in dioxane.

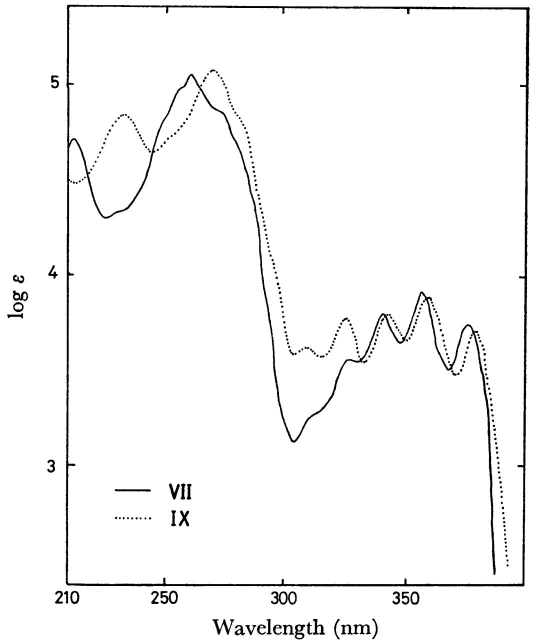

Fig. 3. The electronic spectra of phthaloyl- (VI) and benzophthaloyl- (VIII) triptycenes in dioxane.

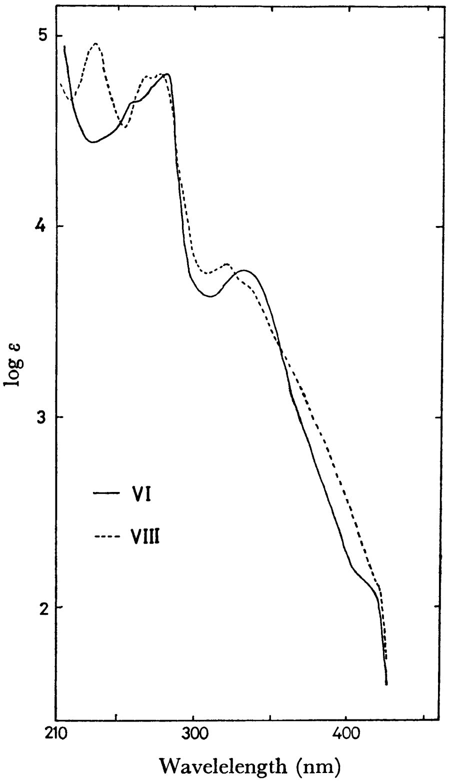

Fig. 4. The electronic spectra of naphtho- (VII) and benzonaphtho- (IX) triptycenes in dioxane.

It has been pointed out from the spectrum of triptycene that the electronic interaction among three separated benzene nuclei in the molecule would not be so large in spite of the presumption of significant overlaps among those π-electron systems.[3] If the strong interaction between naphthalene nuclei in benzo-derivatives of triptycene, III, IV, and V, is expected to occur, the spectra of dibenzo- and tribenzotriptycenes should reveal longer wavelength shifts of absorption maxima than that of monobenzotriptycene. However, Fig. 2 and Table 3 exhibit that the longest wavelength bands of these triptycene derivatives appear at nearly the same position. Similar phenomena are observed at longer wavelength region of VII and IX in Fig. 3 and of VI and VIII in Fig. 4. In addition, absorption bands of benzonaphtho-triptycene IX in

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[14] D. P. Craig, Aromaticity in "Non-benzenoid Aromatic Compounds," ed. by D. Ginsburg, Interscience, N. Y. (1959), p. 27.

[15] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N.Y. (1969), p. 224.

Table 3. The electronic spectrum data of triptycene derivatives (III—IX) in dioxane

Triptycene derivative		Absotption maximum (λ_{max}, nm) and intensity (ε)									
Benzo-(III)	λ	214	228	243	268	277	289	302	309	316$^{a)}$	323
	ε	59300	69800	83000	23800	15200	5400	800	1400	760	1800
Dibenzo-(IV)	λ		229.5	251	269$^{a)}$	278$^{a)}$	289$^{a)}$		310.5	314$^{a)}$	325
	ε		130000	111000	25300	20300	9800		2570	1600	4600
Tribenzo-(V)	λ		234	250	271	280$^{a)}$	290$^{a)}$		310.5	316$^{a)}$	325
	ε		186000	197000	47300	37000	2900		4140	2700	6950
Phthaloyl-(VI)	λ		257	282		334	412$^{a)}$				
	ε		37800	66200		66150	120				
Benzo-phthaloyl-(VIII)	λ	236	266	279	320	337$^{a)}$	412$^{a)}$				
	ε	142000	63700	66400	6620	5200	130				
Naphtho-(VII)	λ	213		255$^{a)}$	260	273$^{a)}$	310$^{a)}$	324	339	356	375
	ε	49400		99600	116000	80000	1900	3700	6400	8430	5900
Benzo-naphtho-(IX)	λ		233		269	283$^{a)}$	309	323.5	340.5	357.5	376
	ε		81200		130000	75000	4010	5100	6310	8040	5300

a) shoulder.

longer wavelength region more than 300 nm are compared with a sum of those of benzotriptycene III and naphthotriptycene VII in Table 3 as follows:

IX: λ_{max} nm (ε) 309(4010), 323.5(5100), 340.5(6310), 357.5(8040), and 376(5300)

III+VII: λ_{max} (ε) 310(3300), 324(5500), 339(6400), 356(8430), and 375(5900)

An excellent agreement between observed and calculated values of wavelength and intensity of absorption bands demonstrates additivity or superposition of component chromophores on the spectra of the annelated triptycenes.

On the other hand, absorption bands other than the longest wavelength bands of three benzo-derivatives, III, IV, and V, show a few features as follows: a) broadening of all the absorption bands with increasing number of naphthalene nuclei, especially of the bands at 270—290 nm (Fig. 2), b) differences in position of B_b bands (220—260 nm) in contrast to nearly the same position of L_a bands (260—300 nm) and L_b bands (300—330 nm) (Fig. 2), c) the intensity of L_b bands per naphthalene chromophore is in order of III<IV<V, but the intensity of L_a bands in order of III>V>IV (Table 3).

A plausible elucidation may be put on these spectral changes. When two of the same chromophores, which are fixed closely with each other, interact slightly, the exciton theory[16] is applicable to this system just as molecular aggregate in crystal system which shows unambiguous shift and splitting of absorption bands due to interaction among the component chromophores. Thus, the phenomenon a) above-stated is explainable with the splitting of degenerated levels —Davydov splitting— due to exciton interaction as well as in the other phenomena b) and c).

The spectra of VII and IX, containing anthracene nucleus, in concentrated sulfuric acid were changed with time as shown in Fig. 5. The formation of cation radical of anthracene itself in that medium was demonstrated by ESR measurement[17] and by the fact that the position of the longest wavelength maximum of

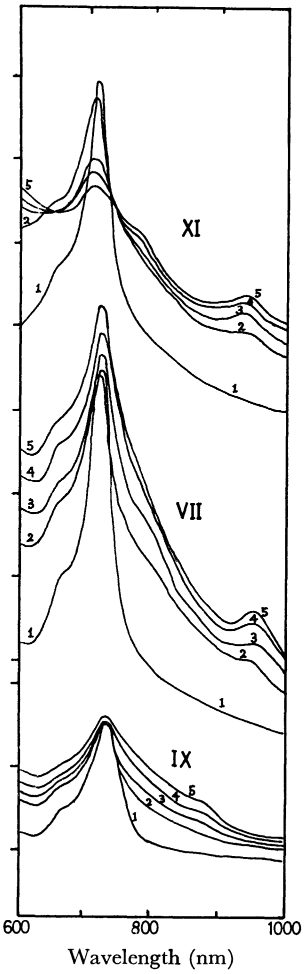

Fig. 5. The electronic spectra of cation radicals of anthracene (XI), naphthotriptycene (VII), and benzo-naphthotriptycene (IX) in conc. sulfuric acid at 15°C: curve 1, 45 min after dissolution; curve 2, 165 min; curve 3, 285 min; curve 4, 405 min; curve 5, 525 min.

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[16] M. Kasha, H. R. Rawls, and M. Ashraf El-Bayoumi, "Molecular Spectroscopy VIII," Butterworth, London, 1965 and references cited there on.

[17] H. Kon and M. S. Blois, Jr., *J. Chem. Phys.*, **28**, 743 (1958); S. I. Weissman, E. de Boer, and J. J. Conradi, *ibid.*, **26**, 963 (1957).

the cation radical coincided with that of the anion radical of anthracene, an alternant hydrocarbon, in absorption spectra.

The cation radicals of the triptycene derivatives VII and IX show the longest wavelength absorption bands at longer wavelength region only by 10 and 20 nm, respectively, than that of anthracene itself. It indicates that there is weak interaction among the aromatic nuclei in triptycene radicals in contrast to an increase of interaction in the anion radical of [2.2]paracyclophane.[18] However, the maxima at 720—730 nm of the cation radicals of VII and IX remain unchanged with time, while the intensity of the maximum of anthracene radical decreases rapidly with time and falls to half after 10 hr. This phenomenon is possibly interpreted partly by stabilization due to delocalization of the cation radical in VII and IX, and mainly by stabilization due to protecting effect of bulky π-electron cloud in benzene and naphthalene nuclei.

Experimental

All melting points are uncorrected. The IR and UV spectra were obtained on a JASCO autorecording spectrometer DS-402G and on a Hitachi ESP-3T, respectively. The molecular weights were determined with a Hitachi mass spectrometer RMU-7 and/or with Knauer vapour pressure osmometer. The NMR spectra were measured on a Hitachi Perkin-Elmer R-20 spectrometer (60 M) using TMS as an internal standard. A frequency counter was used to measure the frequency separation between signals.

Materials. Tetracene was synthesized from tetralin and phthalic anhydride *via* 3 steps in 3.3% of over-all yield according to Fieser.[19] Pentacene was prepared by reduction of pentacene-6,13-dione, which was obtained from phthaldehyde and cyclohexane-1,4-dione in a 65% yield, with aluminum tri(cyclohexyl oxide).[20]

Triptycene (II). The synthesis of triptycene was carried out according to the procedure of Fieser[21] in a 42% yield, mp 262.0—262.5°C (lit, 255°C).

Benzotriptycene(III). III was prepared by the reaction of anthracene with 2,3-dehydronaphthalene (XIII), generated from 3-amino-2-naphthoic acid (XII) and isoamyl nitrite, in tetrahydrofuran according to the procedure of Friedman,[7] 11% yield, mp 263.5—265.0°C (lit, 257—258°C).

Dibenzotriptycene (IV). To a mixture of tetracene (1.0 g, 4.3 mmol) and 3-amino-2-naphthoic acid (2.1 g, 11 mmol) in dioxane (500 m*l*) was dropwise added a solution of isoamyl nitrite (10 m*l*, 75 mmol) in dioxane (50 m*l*) for 2 hr at 70°C with stirring in nitrogen atmosphere. After the addition, the reaction mixture was stirred for 30 min at 80°C. Colorless solid obtained by evaporating the solvent under reduced pressure was chromatographed on alumina (150 g). Early benzene fractions (200 m*l*) were collected and the solvent was removed *in vacuo*. The residue was re-chromatographed on silica gel (30 g) in each 100 m*l* fraction using the following solvents: petroleum ether (100 m*l*) and then petroleum ether–carbon tetrachloride (1: 1, 750 m*l*). From the third fraction was obtained 19 mg of white solid, which was recrystallized from acetone to give colorless needles, mp 213.5—214.5°C, of 5,12-dihydrotetracene (lit,[22] mp 212°C). NMR (in $CDCl_3$): τ 5.93 (s, 4H, methylene), 2.1—2.9 (m, 10H, aromatic).

The residue obtained from 4—9th fractions was recrystallized from ethanol to give 582 mg (37.5% based on tetracene) of pure IV, mp 277—280°C. Found: C, 94.98, H, 4.98%; mol wt, 354 (mass spectrometry). Calcd for $C_{28}H_{18}$: C, 94.88, H, 5.12%; mol wt 354. IR (KBr-disk): 890 (s), 882 (s), 739 (s), 562 (s), 477 (s) cm^{-1}.

Tribenzotriptycene (V). According to the procedure of Wittig,[6] the reaction of pentacene with 1,4-dihydronaphthalene-1,4-oxide, followed by treatment of the adduct with hydrochloric acid in acetic anhydride, afforded 28% yield of tribenzotriptycene (V), mp 386.5°C (lit,[6] 387—389°C). The IR spectrum of the compound is completely superimposable on the reported one.

Phthaloyltriptycene (VI). To a stirred mixture of 3-aminoanthraquinone-2-carboxylic acid (1.5 g, 6 mmol) and anthracene (3.2 g, 18 mmol) in dioxane (400 m*l*) was added dropwise a solution of isoamyl nitrite (34 m*l*) in dioxane (58 m*l*) over a period of two hours at 70°C and the mixture was stirred at 85°C for 30 min. After removal of the solvent the residue was chromatographed on alumina (250 g). From benzene fractions 555 mg (24.1%) of V was obtained. Recrystallized from ethyl acetate, mp 341—344°C. Found: C, 87.32; H, 4.23%; mol wt, 384 (mass spectrometry), 413 (vapour pressure osmometry). Calcd for $C_{28}H_{16}O_2$: C, 87.48; H, 4.20%; mol wt, 384. IR (KBr-disk): 1665 (s), 1352 (m), 1324 (s), 1300 (s), 951 (m), 734 (m), 709 (m) cm^{-1}.

Phthaloyl-benzotriptycene (VIII). Through the procedure described for VI, the synthesis of VIII was carried out with 3-aminoanthraquinone-2-carboxylic acid (XV) and tetracene (XIV), except the use of degassed dioxane as a solvent. Chromatography on alumina using benzene gave a 29% yield of VIII. Recrystallized from ethyl acetate, mp 352.0—352.5°C. Found: C, 88.20; H, 4.00; mol wt, 434 (mass spectrometry). Calcd for $C_{32}H_{18}O_2$: C, 88.46; H, 4.18%; mol wt, 434. IR (KBr-disk): 1670 (s), 1659 (s), 1592 (s), 1325 (s), 1300 (s), 954 (m), 742 (m), 714 (m) cm^{-1}.

Naphthotriptycene (VII). A mixture of VI (260 mg, 0.7 mmol) and aluminum tri(cyclohexyl oxide)[9] (3 m*l*) in cyclohexanol (1.5 m*l*) was refluxed for 48 hr. The mixture was poured into water and was stirred for one hour. It was extracted with benzene and the extract was washed with aqueous calcium chloride solution and then water and dried over calcium chloride. Removal of the solvent *in vacuo* gave 83 mg (35%) of VII, which was recrystallized from cyclohexane to give colorless leaflets, mp 287—288°C. Found: C, 94.78; H, 5.02%; mol wt, 354 (mass spectrometry), 349 (vapour pressure osmometry). Calcd for $C_{28}H_{18}$: C, 94.88; H, 5.02%; mol wt, 354. IR (KBr-disk): 907 (m), 733 (s), 625 (s) cm^{-1}.

Benzo-naphtho-triptycene (IX). The reduction of VIII was carried out in a manner similar to that described for VII. Recrystallization of the crude material (yield 33%) from ethyl acetate afforded pure IX as pale yellow columns, mp 295.5—296.0°C. Found: C, 94.98; H, 4.87%; mol wt, 405 (mass spectrometry), 403 (vapour pressure osmometry). Calcd for $C_{32}H_{20}$: C, 95.02; H, 4.98%; mol wt, 404.5. IR (KBr-disk): 902 (m), 887 (m), 882 (m), 736 (s), 629 (m), 572 (m), 511 (m), 473 (m), 459 (m) cm^{-1}.

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