

Deamination of 1-Alkyl-9-aminomethyltriptycenes. Participation of a Neighboring 1-Alkyl Substituent

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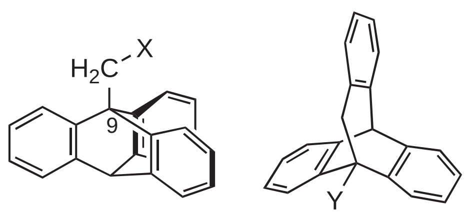
Deamination reactions of 1-alkyl-9-aminomethyltriptycenes (alkyl = Me, Et, *i*-Pr, and *t*-Bu) and 9-(1-aminoethyl)-1-methyltriptycene were performed in $CHCl_3$ and in AcOH, and product distributions were studied. The results suggest that the loss of N_2 from a primary alkanediazonium ion predominantly takes place concomitantly with participation of a C–H bond of the neighboring 1-alkyl group to form a nonclassical cationic species with a three-center two-electron bonding, while the loss of N_2 from a secondary alkanediazonium ion occurs spontaneously to form a secondary carbocation. Solvent effects ($CHCl_3$ vs AcOH) are explained in terms of lower nucleophilicity/basicity of the AcO^- in AcOH than in $CHCl_3$ due to solvation.

Deamination reactions of aliphatic primary amines via diazotization of the amino group have attracted much attention because they are said to generate poorly solvated (so-called "hot") carbocations.[1] Reaction paths for the formation of cationic species from diazonium ions depend on the structure of the substrate and the solvent used. It is highly intriguing to know whether N_2 is eliminated from the diazonium ion in an S_N1 fashion or in an S_N2 fashion, and how the neighboring groups participate in the loss of N_2.

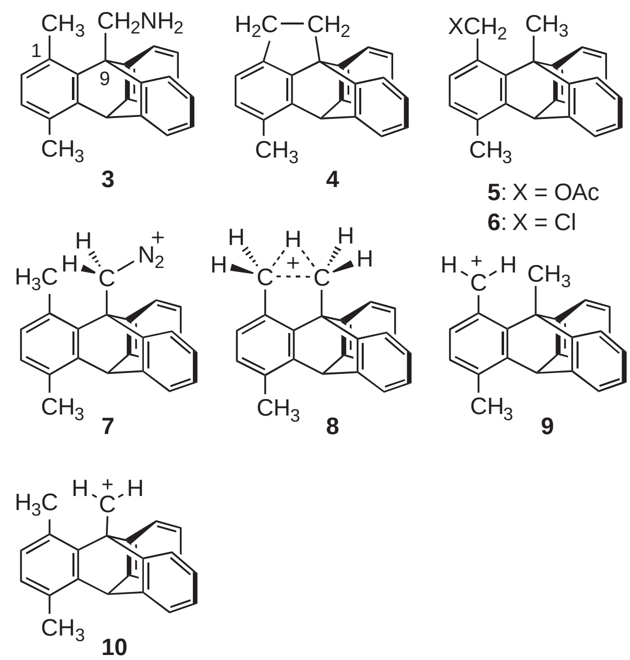
In 1970, Cristol and Pennelle reported that the reaction of 9-aminomethyltriptycene (**1**: X = NH_2) with nitrous acid ($NaNO_2$/HCl) in AcOH gave skeletally rearranged homotriptycene derivatives **2** (Y = OH) and **2** (Y = OAc) in yields of 42 and 56%, respectively, while the reaction of **1** (X = NH_2) with nitrosyl chloride in CH_2Cl_2 gave the rearranged chloride **2** (Y = Cl) and the unrearranged chloride **1** (X = Cl), in 66 and 12%, respectively (Chart 1).[2] Although the authors made no conclusive discussion, it is certain that the high ability of N_2 as a leaving group is responsible for these reactions. These results are in contrast with the fact that the halides and the acetate with the structure **1** resist solvolysis. 9-Chloromethyltriptycene (**1**: X = Cl) was recovered unchanged after treatment with AgOAc in AcOH at 210 °C for 24 h, and 9-acetoxymethyltriptycene (**1**: X = OAc) was recovered unchanged after boiling for 2 h in 1 M $HClO_4$ (1 M = 1 mol dm^{-1}) in AcOH.[2] Heating 9-bromomethyltriptycene (**1**: X = Br) in *m*-cresol around 360 °C gave 1-methyltriptycene (**1**: X = H) as the sole identifiable product in 31% yield.[3]

In 1987, we reported the diazotization of 9-aminomethyl-1,4-dimethyltriptycene (**3**) with nitrous acid in AcOH, which gave the cyclic hydrocarbon **4** (46%), the acetate **5** (34%), and the chloride **6** (8%) together with small amounts of skeletally rearranged homotriptycene derivatives (Chart 2).[4] We postulated that the C–H bond of the 1-methyl group participates in the decomposition of the predominant *ap*-rotamer **7** of the diazonium ion from the rear of the leaving N_2 in an S_N2-like fashion to afford a pentacoordinate carbocationic species, **8**, with a three-center two-electron bond, which either gives **4** upon loss of a proton or migrates to the benzylic cation **9**, the latter affording **5** and **6** upon addition of nucleophiles. Alternatively and less likely, the diazonium ion **7** could afford



1 **2**

Chart 1.



3 **4** **5**: X = OAc **6**: X = Cl **7** **8** **9** **10**

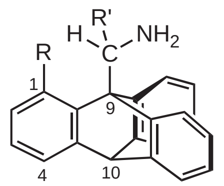
Chart 2.

Published on the web October 10, 2006; doi:10.1246/bcsj.79.1585

the primary carbocation **10** in an S_N1-like fashion, and then the 1-methyl group could interact with the cation center of **10** to give **8**.

The protonated ethane species $C_2H_7^+$ has been extensively studied both experimentally and theoretically.[5] The bridged structure similar to **8** has been shown to exist in an energy minimum as one of the possible isomers of $C_2H_7^+$.

In order to have a deeper insight into this intriguing reaction, we systematically studied the diazotization reactions of 9-aminomethyltriptycene derivatives with a variety of 1-substituents under various reaction conditions. In this article, the results of the deamination reactions of four 1-alkyl-9-aminomethyltriptycenes **11–14** as well as the 1-trideuteriomethyl compound **11a** (Chart 3) with isopentyl nitrite in $CHCl_3$ and AcOH, and the mechanisms are discussed mainly based on the product distributions.[6] Also included are the results for 9-(1-aminoethyl)-1-methyltriptycene (**15**), an amine with a secondary alkyl group.



	R	R'
11	CH_3	H
11a	CD_3	H
12	CH_2CH_3	H
13	$CH(CH_3)_2$	H
14	$C(CH_3)_3$	H
15	CH_3	CH_3

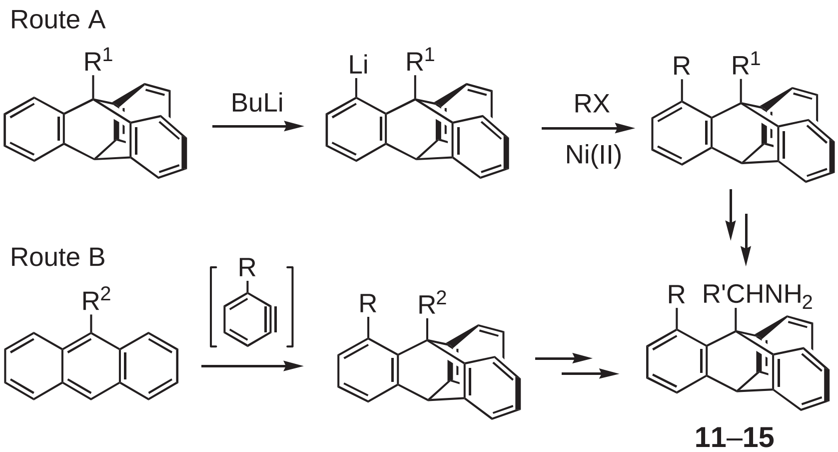
Chart 3.

Results and Discussion

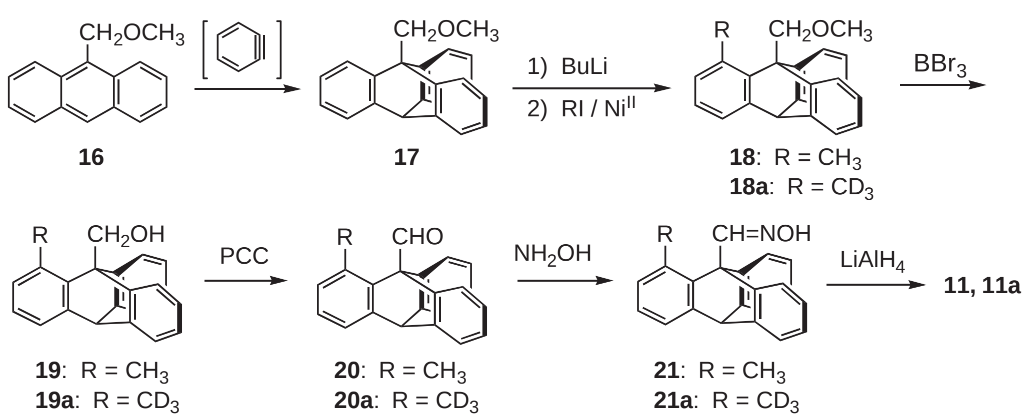
Synthesis of the Substrates. At the outset, two synthetic routes to the amino compounds **11–15** were considered (Scheme 1). One route makes use of the directed lithiation of a suitable 9-substituted triptycene followed by alkylation to give 1-alkyl-substituted triptycenes, which are then converted to 9-aminomethyl compounds by functional transformations of the 9-substituent (Route A). The other route uses the reaction of a 3-alkyl-substituted benzyne with a 9-substituted anthracene to afford a 1-alkyl-substituted triptycene together with the undesired regioisomer. The 1-alkyl compound is then separated and converted to a 9-aminomethyl compound by suitable functional transformations of the 9-substituent (Route B).

As the starting material for Route A, 9-methoxymethyltriptycene was chosen,[7] and the 1-methyl compounds **11** and **11a** were synthesized by this route (Scheme 2).

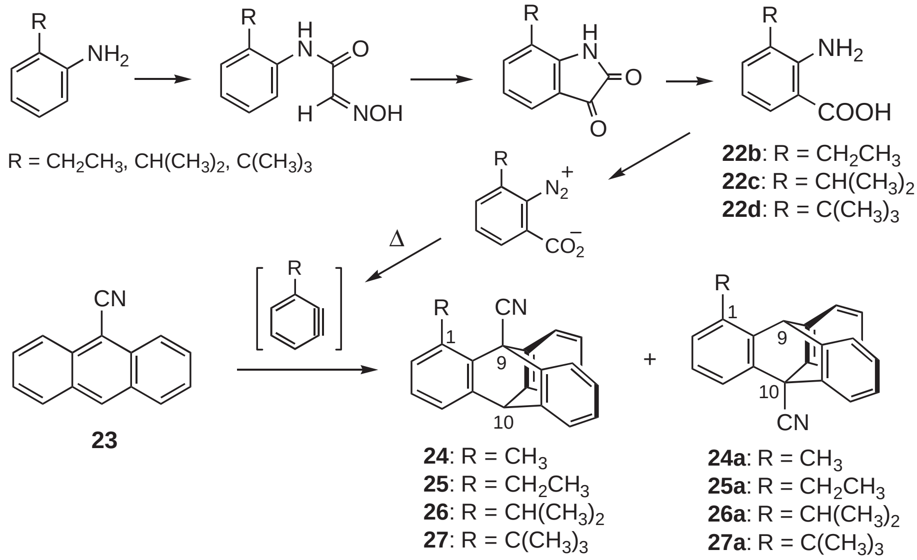
9-Methoxymethyltriptycene (**17**), prepared from 9-methoxymethylanthracene (**16**), was reacted with butyllithium to afford selectively the peri-lithiated intermediate,[7] which was treated with methyl iodide in the presence of a nickel(II) catalyst to afford the 1-methyl compound **18** in 49% yield. Treatment of **18** with boron tribromide afforded the expected alcohol **19** with the cleavage of the CH_3–O bond. The alcohol **19** was oxi-



Scheme 1.



Scheme 2.



Scheme 3.

dized with pyridinium chlorochromate (PCC) to afford the corresponding aldehyde **20**. Reaction of **20** with hydroxylamine gave the corresponding oxime **21**, which upon reduction with $LiAlH_4$ afforded the amine **11**. The 1-trideuteriomethyl compound **11a** was synthesized in the same way.

In preliminary experiments, we found that an ethyl group could be introduced in the peri-position in a similar manner, but several attempts to introduce an isopropyl or an isopropenyl group failed presumably because of steric hindrance.

In the meantime, we explored the synthesis by way of Route B in Scheme 1, and found that 9-cyanoanthracene (**23**) reacted with benzyne to afford 9-cyanotriptycene, though **23** had been reported not to react with benzyne.[8] Since 9-cyanotriptycene was expected to afford 9-aminomethyltriptycene in one step, compound **23** was chosen as the starting anthracene. The 3-alkylanthranilic acids **22b–22d**, the precursors for the 3-alkylbenzynes, were synthesized from the corresponding 2-alkylanilines, by way of the respective *N*-phenyl-2-hydroxyiminoacetamides and isatins, as shown in Scheme 3, while 3-methylanthranilic acid (**22a**) was commercially available. Thermal decomposition of 6-alkylbenzenediazonium-2-carboxylates, prepared from the corresponding anthranilic acids and isopentyl nitrite, in the presence of **23** afforded 1-alkyl-9-cyanotriptycene **24–27** together with the regioisomeric 1-alkyl-10-cyanotriptycenes **24a–27a**.

Isomer assignments were made from the ^{1}H NMR chemical shifts of the bridgehead protons: the 10-H signal of the 9-cyano compounds **24–27** appeared in a narrow range (δ 5.38–5.41), while the 9-H signal of the 10-cyano compounds **24a–27a** appeared at a lower field (δ 5.67–6.25), which significantly depended on the bulkiness of the alkyl group presumably reflecting the steric compression of the alkyl group.

The assignments were further confirmed by the X-ray structural analysis of compound **26** (Fig. 1). Noteworthy in the molecular structure of **26** is the conformation of the 1-isopropyl group: the α-hydrogen points toward the cyano group. It has been shown that an isopropyl group bonded to an aromatic ring prefers a conformation in which the α-hydrogen is located in

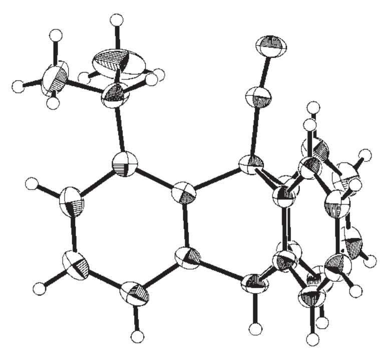


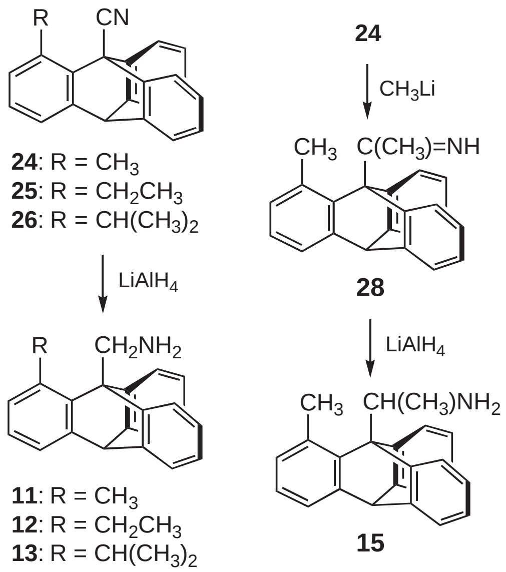
Fig. 1. ORTEP drawing of compound **26** with 50% probability thermal ellipsoids.

the plane of the aromatic ring, and further that, when two ortho positions are substituted, the α-hydrogen tends to point to the bulkier substituent.[9] The conformation of the isopropyl group in **26** conforms to the general findings.

The formation ratio of the regioisomers, as detected by the NMR integration of the crude reaction mixture, was 37:63 for **24**:**24a**, 45:55 for **25**:**25a**, 50:50 for **26**:**26a**, and 60:40 for **27**:**27a**. The bulkier the alkyl group, the larger the formation ratio of the apparently more crowded 1-alkyl-9-cyanotriptycene. This type of regioselectivity, that the more crowded regioisomer is easily formed, has often been reported in other Diels–Alder reactions,[10] and has been explained in terms of the transition state where two less hindered sites in the diene and the dienophile become closer together.

The nitriles **24–26** were sufficiently reduced to the corresponding amines **11–13** with $LiAlH_4$ (Scheme 4), but the nitrile **27** with a *t*-butyl group was not reduced probably due to steric hindrance. Treatment of the methyl nitrile **24** with methyllithium gave the imine **28**, which was reduced with $LiAlH_4$ to the 9-(1-aminoethyl) compound **15**.

The *t*-butyl amine **14**, which could not be obtained by reduction of the nitrile **27**, was therefore synthesized by way of the phthalimide **30**, which was synthesized by the addition



Scheme 4.

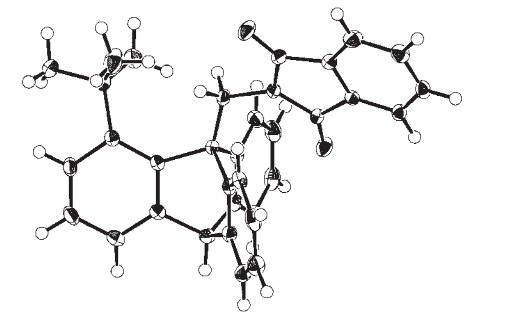
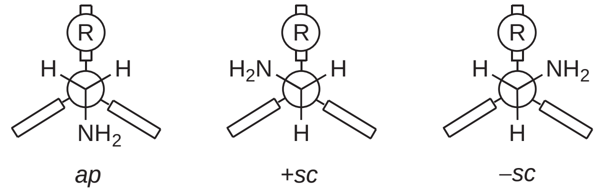
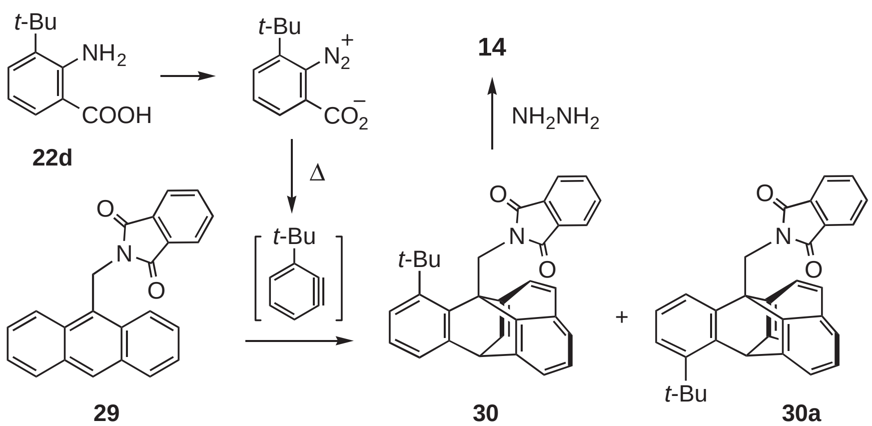


Fig. 2. ORTEP drawing of compound **30** with 50% probability thermal ellipsoids.



Scheme 6.



Scheme 5.

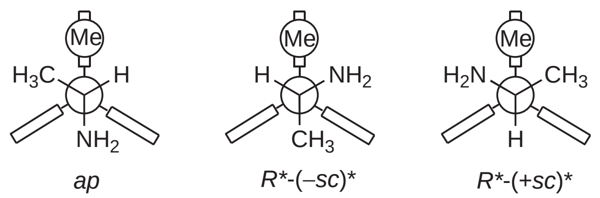
of 3-*t*-butylbenzyne to 9-phthalimidomethylanthracene (**29**) as shown in Scheme 5. In this case, the formation ratio of **30** and its regioisomer **30a** was ca. 2:3. The structure of **30** was determined by ^{1}H NMR spectra: The bridgehead proton appeared at δ 5.36 and 6.25 for **30** and **30a**, respectively. X-ray crystallography confirmed the assignment (Fig. 2). Hydrazinolysis of **30** gave the desired amine **14**.

In ^{1}H NMR spectra of the amines **11–13** at room temperature, the signals were broad due to rotation of the aminomethyl group on the NMR timescale. At $-44\,^\circ$C, the rotation was sufficiently slow and two sets of signals corresponding to two distinguishable rotational isomers, *ap* and $\pm$*sc* (+*sc* and $-$*sc* are NMR-equivalent),[11] were observed for the 1-methyl (**11**) and 1-ethyl (**12**) compounds (Scheme 6). The isomer ratio was 95:5 for **11** and 96:4 for **12**. The major isomer was assigned to *ap* because the methylene protons gave a singlet, while the minor to $\pm$*sc* because the methylene protons gave an AB-type quartet. In compound **13** with a 1-isopropyl group, the methylene protons gave a sharp singlet at $-44\,^\circ$C, indicating that the fraction of the minor $\pm$*sc* isomer was too small to be detected at this temperature. In the amine **14** which has a *t*-butyl group, the methylene signal remained a sharp singlet throughout the temperature range of 24 to $-80\,^\circ$C, suggesting that the rotamer equilibrium is almost one-sided to the *ap* isomer.

Therefore, it is reasonable to assume that the conformational equilibrium is far shifted toward the *ap* isomer for compounds **11–14** at room temperature, at which the deamination reactions were performed.

As for 1-(1-aminoethyl)-9-methyltriptycene (**15**), rotation about the bridgehead-to-substituent bond was slow on the NMR timescale at room temperature and two rotamers were observed in an equilibrium ratio of 36:64 in $CDCl_3$. Three rotamers are assumed for **15** as shown in Scheme 7, but the R^*-(+*sc*)* rotamer is probably energetically unfavorable due to steric reasons and thus absent. The R^*-($-$*sc*)* rotamer was assigned to the major isomer because the amino group is less bulkier than the methyl group. NOE experiments supported this deduction; two methyl groups were close to each other in the minor isomer, but remote in the major.

Deamination Reactions. Reactions were run in $CHCl_3$ and in AcOH according to the procedures given in the Experimental section, and the product ratio was determined by integration



Scheme 7.

of the [1]H NMR signals of the crude reaction mixture. Each reaction product was separated by GPC, isolated, and characterized mainly by [1]H NMR spectroscopy.

Deamination of 9-aminomethyl-1-methyltriptycene (**11**) in $CHCl_3$ afforded a cyclization product, 1,2,6,10b-tetrahydro-6,10b-*o*-benzenoaceanthrylene (**31**), together with small amounts of a rearranged acetate, 1-acetoxymethyl-9-methyltriptycene (**32**) and a homotriptycene, 10-acetoxy-10,11-dihydro-1-methyl-5,10-*o*-benzeno-5*H*-dibenzo[*a*,*d*]cycloheptene (**33**) in a ratio of 95:3:2 (Scheme 8). In AcOH, the proportion of **32** significantly increased at the expense of **31** together with a small increase in **33**.

Structure determinations and NMR spectral assignments of these products were made as follows. Compound **31** showed, together with the signals due to the triptycene skeleton, AA′BB′ multiplets at δ 3.25 and 3.35, to which 1-H and 2-H, respectively, were assigned based on NOE (10-H $\rightarrow$ 1-H, 3-H $\rightarrow$ 2-H). 1-C and 2-C were shown to appear at δ 22.8 and 33.2, respectively, based on CH-COSY. For compound **32**, NOE unambiguously showed that this compound was 1-acetoxymethyl-9-methyltriptycene and not 9-acetoxymethyl-1-methyltriptycene; irradiation of the methyl signal at δ 2.65 enhanced the intensity of the two-proton multiplet signal at the lowest-field of the aromatic region (δ 7.39), which were assigned to 8/13-H. For compound **33**, the one-proton singlet at δ 4.90 was characteristic of the bridgehead proton of the homotriptycene skeleton, and NOE enhancement of the aromatic methyl signal at δ 2.04 upon irradiation of the methylene signal at δ 3.12 clearly showed that the methyl group was attached to 1-C and not to 9-C.

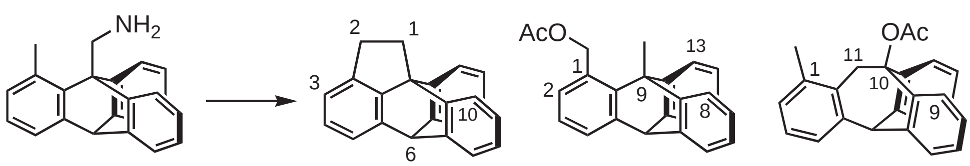
We propose the following mechanistic scheme to explain the product distributions and the solvent dependence (Scheme 9). As described above, the rotamer equilibrium in the amine **11** is shifted to the *ap* isomer, and thus the diazonium ion **11′** formed from **11** will also exists mainly as the *ap* rotamer. S_N1-type elimination of N_2 from **11′** should give a primary carbocation. However, this process should be energetically very unfavorable. N_2 elimination requires nucleophilic assistance by an outer nucleophile (AcO^-, AcOH, or H_2O) or a neighboring group from the backside of the leaving N_2 in an S_N2 fashion. Since no direct substitution products of the amino group in **11** were observed, an S_N2 reaction of an outer nucleophile was eliminated. As a neighboring group, a benzene ring of the triptycene skeleton would be considered, as in the case of **1** (X = NH_2), which would give a homotriptycene skeleton. Formation of the homotriptycene **33** was actually observed but only in a small amount: Rearrangement of the backside benzene ring in *ap*-**11′** to give a tertiary carbocation followed by reaction with AcO^- would afford **33**. Another homotriptycene **34** would be formed from $\pm$*sc*-**11′**; however, it was not detected.

The most abundant product in both $CHCl_3$ and AcOH was 1,2,6,10b-tetrahydro-6,10b-*o*-benzenoaceanthrylene (**31**), and its formation is explained as follows. Nucleophilic participation of the σ-electrons of a C–H bond of the 1-methyl group from the backside of the leaving N_2 in *ap*-**11′** would afford a "protonated ethane" type intermediate species **35**, as was postulated previously[4] (see **8**). Cleavage of the three-membered ring in **35** would result in the elimination of the bridging proton and formation of **31**, while another way of the ring cleavage gave a benzylic carbocation **36**, which afforded the rearranged acetate **32** upon reaction with AcO^-. The third way of cleavage to give the primary carbocation **37** would be far less favorable, and no products from **37** were found.

In $CHCl_3$, the cationic species **35** forms a tight ion-pair, and the counter anion AcO^- easily abstracts the bridging proton from **35**. Thus, only a small amount of **35** can survive long enough to give **36**. In AcOH, on the other hand, outer nucleophiles such as AcO^- are well solvated and less reactive than in $CHCl_3$, which renders the abstraction of the bridging proton less efficient and instead allows rearrangement to the benzylic cation **36**, resulting in the increase in the formation ratio of **32** in AcOH.

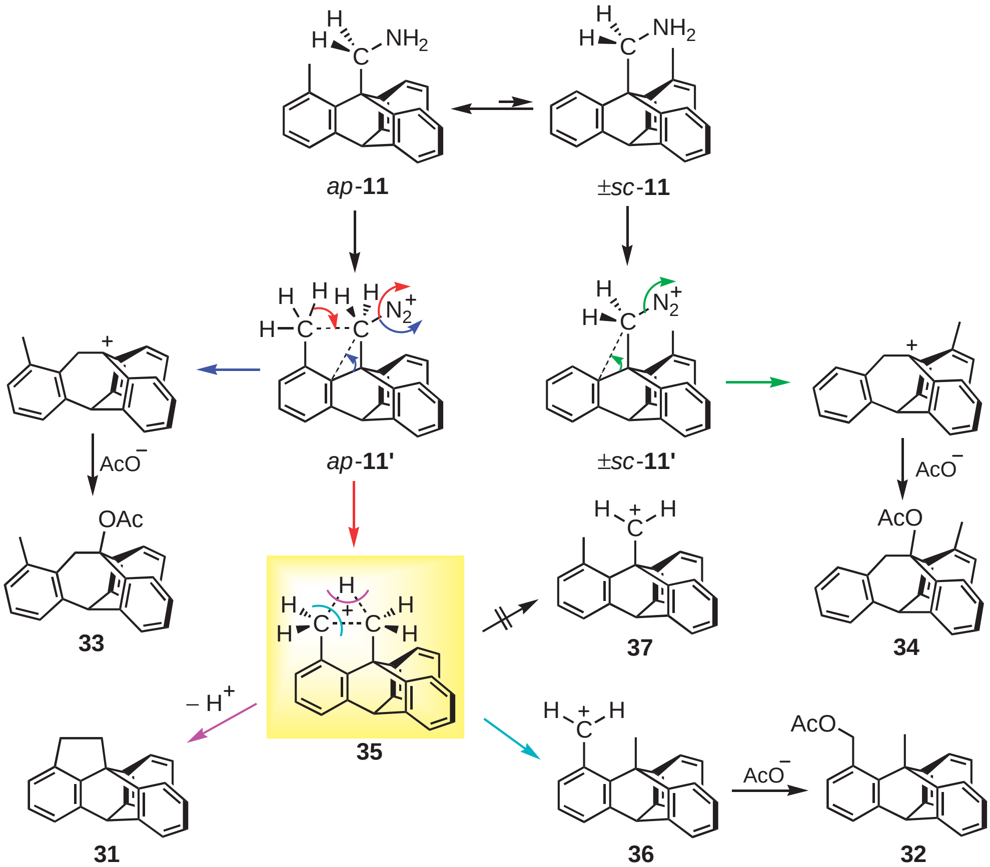
There is no experimental evidence for the nonclassical cationic species **35**; however, it is proposed as a logical intermediate which reasonably explain the observed results.

Deamination of 9-aminomethyl-1-[D_3]methyltriptycene (**11a**) gave the results shown in Scheme 10; products with the homotriptycene skeleton were not detected. Structures of the products and the deuterium distribution were determined by MS and NMR. For **31a**, it was unambiguously shown by both [1]H and [13]C NMR that no deuterium was incorporated at C^1, while two deuterium atoms were at C^2. The 9-methyl group of **32a** contained one deuterium atom, while the methylene group contained two deuterium atoms. These results are consistent with the intermediacy of **35**, in which no deuterium scrambling occurs. The increase in the ratio of **32a**/**31a** (35/65) relative to

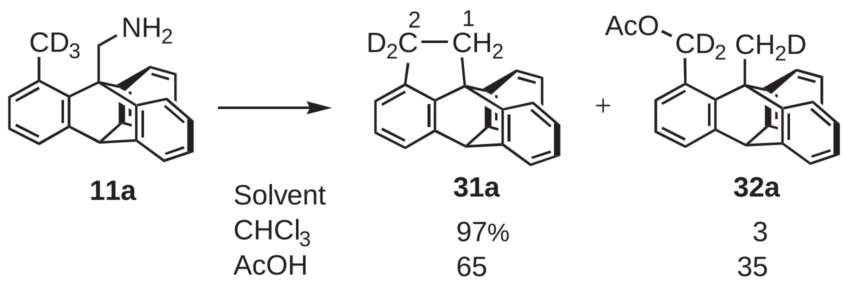


11 Solvent	**31**	**32**	**33**
$CHCl_3$	95%	3	2
AcOH	70	26	4

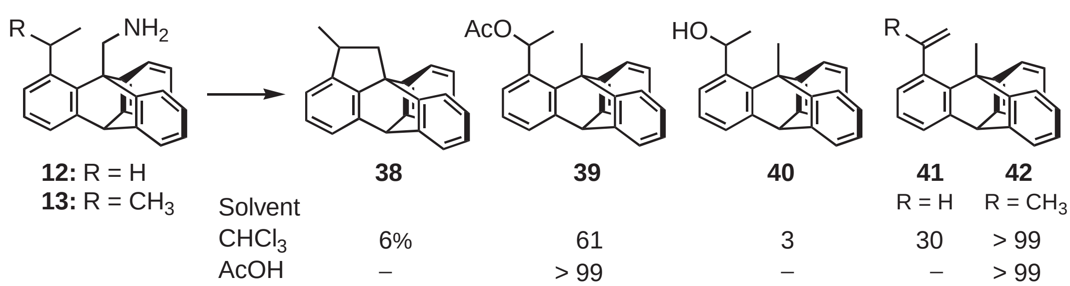
Scheme 8.



Scheme 9.



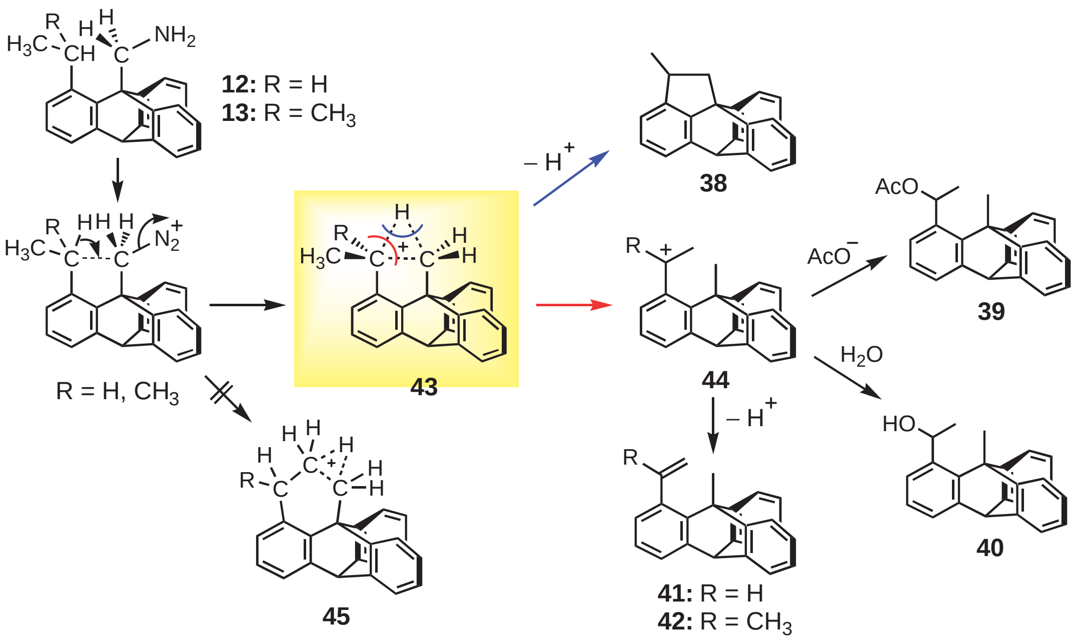
Scheme 10.



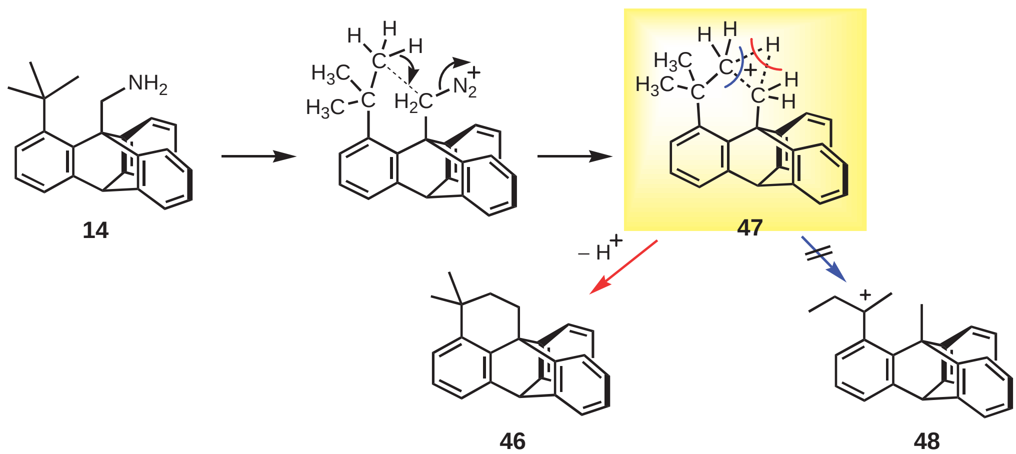
Scheme 11.

that of **32**/**31** (26/70) found in AcOH may be due to isotope effects; i.e., the bridging deuteron is less easily removed from **35a** than the bridging proton is from **35**.

Deamination of 9-aminomethyl-1-ethyltriptycene (**12**) in $CHCl_3$ mainly gave rearranged products **39**–**41** together with a small amount of the cyclization product **38**, while in AcOH the rearranged acetate **39** was detected as the sole product (Scheme 11). Deamination of 9-aminomethyl-1-isopropyltriptycene (**13**) afforded the rearranged alkene **42** as the sole product both in $CHCl_3$ and AcOH (Scheme 11). Structures



Scheme 12.



Scheme 13.

of these compounds were determined without difficulty by using ^{1}H NMR.

Possible mechanistic pathways are shown in Scheme 12. The three-center two-electron species **43** is again postulated as an intermediate. The σ-electrons of an α-C–H bond of the 1-alkyl group act as a nucleophile and attack the α-carbon of the diazonium ion in the *ap* rotamer to give **43**. Deprotonation of **43** (R = H) gives **38**, but this is not the predominant path. The benzylic cation **44** (R = H) is more stable than **36** in Scheme 9, and thus **43** rearranges to **44** more easily, which gives the acetate **39** and the alcohol **40** upon reaction with outer nucleophiles, and the alkene **41** upon deprotonation. In the deamination of the isopropyl compound **13**, the benzylic cation **44** (R = CH_3) is even more stable, and the entire reaction proceeds via this species. The sole formation of alkene **42** by deprotonation of **44** (R = CH_3) and the absence of substitution products, such as an acetate, may be due to the steric reasons: In **44** (R = CH_3), approach of AcO^- to the cationic center is more hindered than in **44** (R = H), and thus abstraction of proton from the methyl group is favored.

It should be noted that no products were observed that might be produced by way of the intermediate species **45**, which would form by the participation of the β-C–H bond of the 1-alkyl group. This is partly ascribed to the conformation of the 1-alkyl group. The conformation in which the α-hydrogen points toward the bridgehead substituent is most stable, and the β-hydrogens are located too far to participate in N_2 elimination.

Deamination of 9-aminomethyl-1-*t*-butyltriptycene (**14**) afforded a cyclized product, 3,3-dimethyl-2,3,7,11b-tetrahydro-7,11b-*o*-benzeno-1*H*-benzo[*d*,*e*]anthracene (**46**) as the sole product both in $CHCl_3$ and AcOH (Scheme 13). The molecular structure of **46** was confirmed by X-ray crystallography (Fig. 3).

A C–H bond of the *t*-butyl group that is located in a proper position assists in the elimination of N_2 to form a cationic species **47**, which will upon deprotonation afford **46**. If the reaction followed a different cleavage pathway in **47**, a tertiary benzylic cation **48** would be formed by rearrangement of a methyl group, which is often observed in a neophyl system. This does not occur even in AcOH.

The results for **14** may be compared with those in a previous report by Ōki et al.[12] that deamination of the ±*sc* rotamer of compound **49** in boiling benzene afforded the cyclization product **50** in 28% yield together many other products (Scheme 14).

Deamination of 9-(1-aminoethyl)-1-methyltriptycene (**15**) gave products as shown in Scheme 15. Irrespective of the solvent, no products in which the 1-methyl group participated were detected. In $CHCl_3$, 9-substituted 1-methyltriptycene derivatives **51** and **52** were the predominant products together with small amounts of homotriptycene derivatives **53** and **54**. In AcOH, the amounts of the homotriptycenes **53** and **54** increased at the expense of the triptycenes **51** and **52**.

Structures of **51** and **52** were unambiguously determined by NMR spectroscopy including the NOE experiments. The acetate **52** existed as two rotamers in an equilibrium ratio of 72:28 and the R^*-$(-sc)^*$ conformation was assigned to the major isomer with the similar reasoning as in the case of **15**. The homotriptycenes **53** and **54** were formed in a ratio of ca. 1:2 both in $CHCl_3$ and in AcOH. The mixture of these two isomers was easily separated from the other products, but the complete mutual separation of the two by chromatography could not be made. Fortunately, crystallization of the mixture from diethyl ether–hexane afforded single crystals of **54**. X-ray crystallographic analysis of **54** revealed that this compound is the 9,11-dimethyl isomer, and that two methyl groups are in the anti orientation, i.e. the configurations are $5R^*, 10R^*, 11R^*$ (Fig. 4). ^{1}H and ^{13}C NMR data of pure **54** could be obtained, while those of **53** were obtained for a sample of the homotriptycene mixture and by subtracting the signals of **54**. The proximity of the two methyl groups in **53** was clearly shown by NOE confirming that it is the 1,11-dimethyl isomer.

Plausible mechanistic pathways are shown in Scheme 16 for **15** with the (*R*)-configuration, though the racemic compound was used in the deamination reactions. It is reasonable to assume that secondary carbocations are formed from secondary alkanediazonium ions by spontaneous loss of N_2. Thus, rotameric diazonium ions *ap*-**15′** and *R*-(−*sc*)-**15′** afford rotameric carbocations **55** and **55a**, respectively, which then give rise to the alkene **51** and the acetate **52**, upon reaction with the outer nucleophile/base AcO^-, or rearrange to the homotriptycene cations **56** and **57**. The larger formation ratio of the homotriptycenes **53** and **54** in AcOH (15%) than in $CHCl_3$ (2%) is ascribed to the lower nucleophilicity/basicity of AcO^- in AcOH than in $CHCl_3$, as discussed before in the case of the deamination of the amine **11**. The skeletal rearrangement of **55** will form the tertiary cation **56**, which results in the acetate **53**, while that of **55a** will form **57** and finally **54**. Absence of the diastereomeric homotriptycene **58** in the products indicates that rotameric carbocation **55b** is not formed. There are two

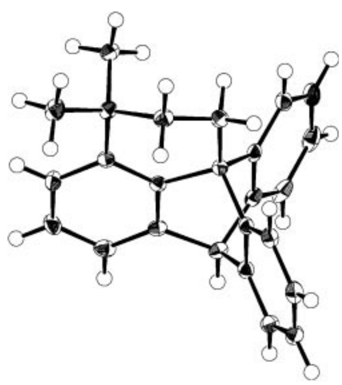
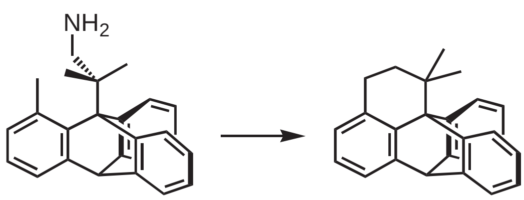


Fig. 3. ORTEP drawing of compound **46** with 50% probability thermal ellipsoids.



49 50

Scheme 14.

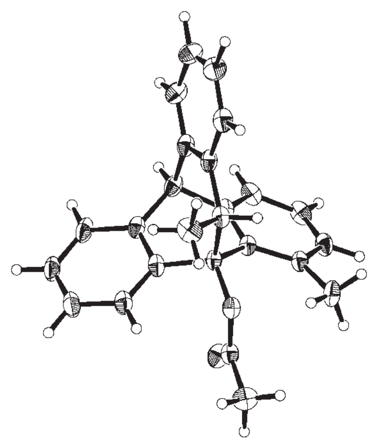
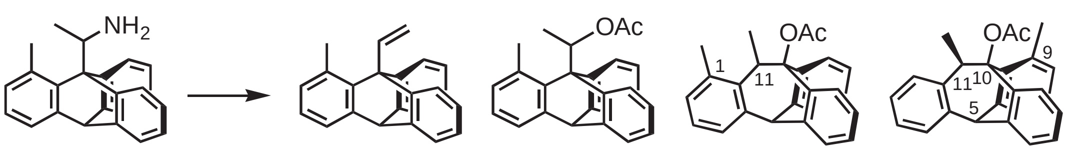


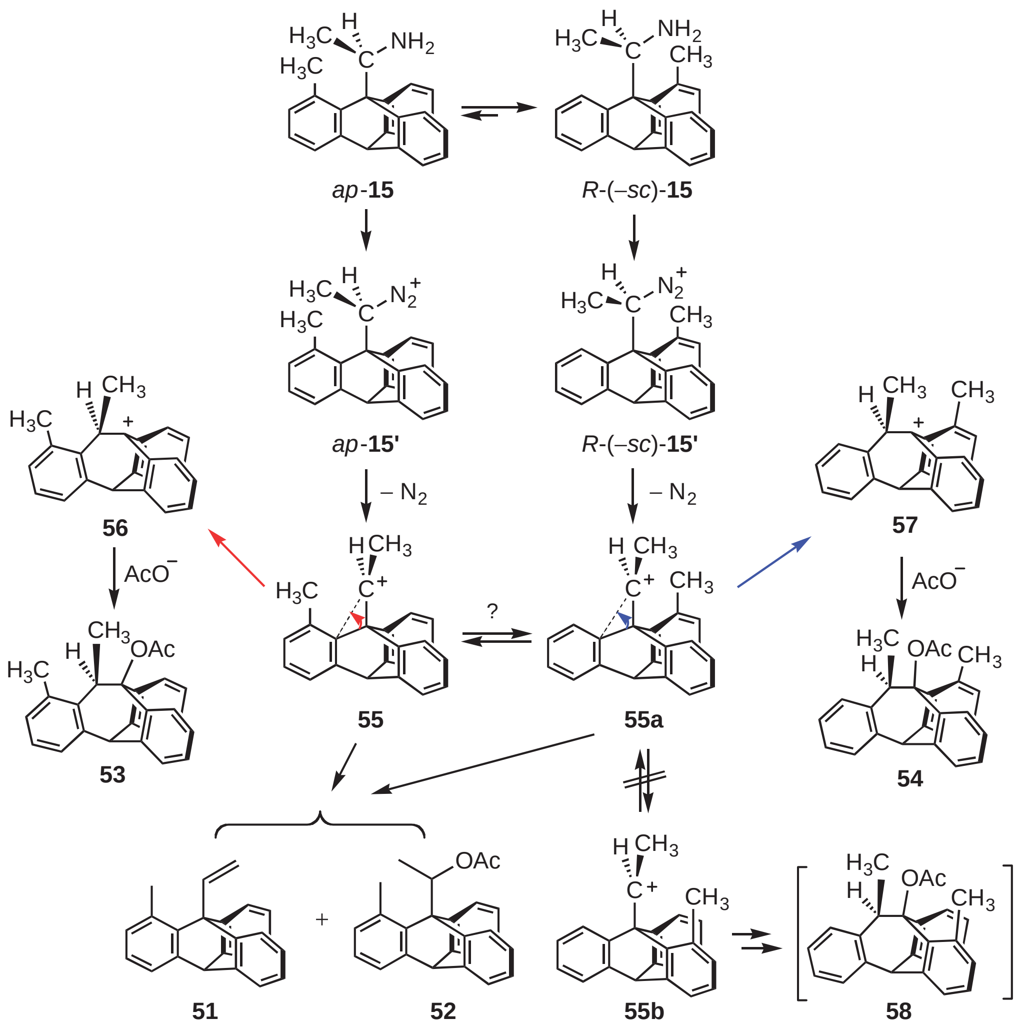
Fig. 4. ORTEP drawing of compound **54** with 50% probability thermal ellipsoids.



15

Solvent	**51**	**52**	**53**	**54**
$CHCl_3$	85%	13	0.7	1.3
AcOH	77	8	5	10

Scheme 15.



Scheme 16.

possible reasons: (1) the skeletal rearrangement takes place faster than the rotation of the bridgehead-to-cationic carbon bond, and (2) the cation **55b** is much less stable than **55** or **55a** probably due to the steric repulsion between the methyl groups. No definite conclusion on this point can be drawn at the present stage.

Conclusion

The results presented above indicate that elimination of N_2 from primary alkanediazonium ions predominantly occurs with concomitant formation of a nonclassical cationic species with a three-center two-electron bonding, through participation of the C–H bond from a neighboring 1-alkyl group, which then gives a cyclized product by a proton loss, or 1-acetoxymethyl or 1-vinyl derivatives of 9-methyltriptycene by way of a benzylic cation. On the other hand, N_2 elimination from a secondary alkanediazonium ion mostly takes place spontaneously to form a classical secondary carbocation, which then affords unrearranged 9-acetoxymethyl- or 9-vinyltriptycene derivatives, or skeletally rearranged homotriptycene derivatives. Solvent effects ($CHCl_3$ vs AcOH) are explained in terms of the lower nucleophilicity/basicity of AcO^- in AcOH than in $CHCl_3$ due to solvation.

Experimental

General. Melting points are not corrected. Mass spectra were obtained on a Hitachi M-2500 spectrometer in an EI mode. Preparative gel permeation chromatography (GPC) was performed on an LC-908 or an LC-918 apparatus of Japan Analytical Instruments Co., Ltd. using a series of JAIGEL 1H and 2H columns and $CHCl_3$ as the eluent. ^1H and ^{13}C NMR spectra were obtained on a Bruker ARX-300 spectrometer operating at 300.1 MHz for ^1H and 75.4 MHz for ^{13}C, respectively, or on a Bruker AVANCE II 600 spectrometer operating at 600.1 MHz for ^1H and 150.9 MHz for ^{13}C, respectively. Chemical shifts were referenced with internal tetramethylsilane (δ_H 0.0) or $CDCl_3$ (δ_C 77.0). Data of ^1H and ^{13}C spectra given below are obtained at 22–24 °C unless otherwise stated. Letters p, s, t, and q given with the ^{13}C chemical shifts denote primary, secondary, tertiary, and quaternary, respectively. In variable-temperature experiments, temperatures were calibrated using methanol[13] or ethylene glycol[14] and are reliable to ±1 °C.

9-Methoxymethylanthracene (16). To a solution of 9-hydroxymethylanthracene (5.0 g, 24 mmol) in tetrahydrofuran (100 mL) was added a solution of butyllithium in hexane (1.6 M, 15 mL, 24 mmol) at 0 °C and the mixture was stirred for 1 h at 0 °C. To this solution was added dropwise methyl iodide (2.24 mL, 36 mmol), and the mixture was allowed to warm up to room temperature and stirred overnight. The mixture was extracted with diethyl ether, and the extracts were washed with water and dried over $MgSO_4$, and the solvent was evaporated. Recrystallization from CH_2Cl_2–hexane gave 4.44 g (20 mmol, 82%) of **16**, mp 89–90 °C (lit.[15] 90–91 °C). ^{1}H NMR ($CDCl_3$) δ 3.542 (3H, s), 5.431 (2H, s), 7.24–7.57 (4H, m), 8.008 (2H, dd, $J = 8.4$, 0.6 Hz), 8.379 (2H, dd, $J = 8.4$, 0.6 Hz), 8.458 (1H, s). ^{13}C NMR ($CDCl_3$) δ 58.33 (1C, p), 66.57 (1C, s), 124.22 (2C, t), 124.92 (2C, t), 126.18 (2C, t), 128.36 (1C, t), 128.62 (1C, q), 129.00 (2C, t), 130.98 (2C, q), 131.40 (2C, q).

9-Methoxymethyltriptycene (17). A slurry of benzenediazonium-2-carboxylate,[16] prepared from anthranilic acid (13.5 g, 98 mmol), in $CHCl_3$ (100 mL) was added in small portions to a boiling solution of 9-methoxymethylanthracene (**16**) (5.70 g, 5.6 mmol) in $CHCl_3$ (100 mL) during the course of 2 h, and the mixture was heated under reflux for 2 h. After removal of the solvent, the residue was subjected to column chromatography on alumina with hexane–ethyl acetate (3:1) as the eluent affording 3.87 g (13.0 mmol, 51%) of **17**, mp 185–187 °C. Anal. Found: C, 88.50; H, 6.11%. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08%. ^{1}H NMR ($CDCl_3$) δ 3.813 (3H, s), 4.942 (2H, s), 5.361 (1H, s), 6.93–7.04 (6H, m), 7.32–7.48 (6H, m). ^{13}C NMR ($CDCl_3$) δ 53.25 (1C, q), 54.28 (1C, t), 59.51 (1C, p), 71.02 (1C, s), 122.31 (3C, t, br), 123.32 (3C, t), 124.99 (6C, t), 144.79 (3C, q), 146.50 (3C, q).

9-Methoxymethyl-1-methyltriptycene (18). A solution of butyllithium in hexane (16 M, 5.4 mL, 9.0 mmol) was added to a solution of **17** (0.90 g, 3.0 mmol) and tetramethylethylenediamine (TMEDA) (1.4 mL, 9.0 mmol) in diethyl ether (5 mL) at 0 °C, and the mixture was stirred for 5 h.[7] To the mixture was added methyl iodide (1.0 mL, 16.0 mmol) and $NiCl_2$(DPPP) [DPPP = 1,3-bis(diphenylphosphino)propane] (100 mg), and the mixture was stirred for 15 h at ambient temperature. The mixture was partitioned with diethyl ether and water, and the ether layer was washed with water, dried over $MgSO_4$ and evaporated. The residue was subjected to preparative GPC to afford 0.460 g (1.47 mmol, 49%) of **18**. Recrystallization from CH_2Cl_2–hexane gave a pure sample of **18**, mp 225–227 °C. Anal. Found: C, 88.23; H, 6.60%. Calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45%. ^{1}H NMR ($CDCl_3$) δ 2.59 (3H, br s), 3.753 (3H, s), 4.5–5.4 (2H, br), 5.287 (1H, s), 6.5–7.9 (11H, br m). ^{1}H NMR ($CDCl_3$) at −29 °C showed the presence of two rotamers, *ap* and ±*sc*, in a ratio of 59:41; the *ap* isomer: δ 2.552 (3H, s), 3.790 (3H, s), 5.221 (2H, s), 5.354 (1H, s), 6.69–7.54 (11H, m); the ±*sc* isomer: δ 2.669 (3H, s), 3.765 (3H, s), 4.794 (1H, d, $J = 9.8$ Hz), 5.096 (1H, d, $J = 9.8$ Hz), 5.354 (1H, s), 6.78–7.68 (11H, m).

9-Hydroxymethyl-1-methyltriptycene (19). To a solution of **18** (0.62 g, 2.0 mmol) in CH_2Cl_2 (20 mL) was added a 1.0 M solution of BBr_3 (18 mL, 18 mmol) in CH_2Cl_2 and the mixture was stirred for 1 h at ambient temperature. The mixture was partitioned between water and CH_2Cl_2 and the organic layer was washed with water and dried over $MgSO_4$, and the solvent was evaporated. The residue was recrystallized from CH_2Cl_2–hexane to give 0.54 g (1.8 mmol, 90%) of **19**, mp 174–175 °C. Anal. Found: C, 88.46; H, 6.13%. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08%. ^{1}H NMR ($CDCl_3$) δ 2.16 (1H, br), 2.47 (3H, br s), 5.313 (1H, s), 5.43 (2H, br s), 6.6–7.9 (11H, br m).

1-Methyltriptycene-9-carbaldehyde (20). To a solution of **19** (1.00 g, 3.35 mmol) in CH_2Cl_2 (40 mL) was added pyridinium chlorochromate (PCC) (2.25 g, 10 mmol) and the mixture was stirred at ambient temperature for 2 h. The mixture was extracted with diethyl ether and the extracts were subjected to column chromatography on silica gel with CH_2Cl_2 as the eluent affording 0.97 g (3.29 mmol, 98%) of **20**. Recrystallization from CH_2Cl_2–hexane gave a pure sample of **20**, mp 183–185 °C. Anal. Found: C, 88.88; H, 5.59%. Calcd for $C_{22}H_{16}O$: C, 89.16; H, 5.44%. ^{1}H NMR ($CDCl_3$) δ 2.464 (3H, s), 5.336 (1H, s), 6.807 (1H, dd, $J = 7.7$, 0.6 Hz), 6.944 (1H, t, $J = 7.5$ Hz), 7.02–7.05 (4H, m), 7.286 (1H, dm, $J = 7.2$ Hz), 7.397 (2H, m), 7.916 (2H, m), 11.319 (1H, s). ^{13}C NMR ($CDCl_3$) δ 23.12 (1C, p), 54.93 (1C, t), 61.90 (1C, q), 122.28 (1C, t), 123.23 (2C, t), 123.74 (2C, t), 125.14 (2C, t), 125.73 (2C, t), 126.02 (1C, t), 129.11 (1C, t), 132.03 (1C, q), 141.24 (1C, q), 142.50 (2C, q), 146.09 (2C, q), 146.41 (1C, q), 201.43 (1C, t).

1-Methyltriptycene-9-carbaldehyde Oxime (21). A mixture of **20** (0.75 g, 2.53 mmol) and hydroxylamine hydrochloride (1.00 g, 14.6 mmol) in pyridine (35 mL) was heated under reflux for 6 h. After neutralization of the mixture with dil HCl, the mixture was extracted with benzene. The extracts were washed with water and dried over $MgSO_4$, and the solvent was evaporated. Recrystallization from CH_2Cl_2–hexane gave 0.71 g (2.18 mmol, 95%) of **21**, mp 241–243 °C. Anal. Found: C, 84.80; H, 5.61; N, 4.37%. Calcd for $C_{22}H_{17}NO$: C, 84.86; H, 5.50; N, 4.50%. ^{1}H NMR ($CDCl_3$) δ 2.483 (3H, s), 5.338 (1H, s), 6.780 (1H, dm, $J = 7.7$ Hz), 6.905 (1H, t, $J = 7.5$ Hz), 6.97–7.08 (4H, m), 7.262 (1H, dd, $J = 7.2$, 0.8 Hz), 7.370 (2H, m), 7.64 (1H, br s, OH), 7.860 (2H, m), 8.891 (1H, s). ^{13}C NMR ($CDCl_3$) δ 23.67 (1C, p), 55.08 (1C, t), 55.23 (1C, q), 122.15 (1C, t), 123.45 (2C, t), 123.97 (2C, t), 124.94 (2C, t), 125.47 (2C, t), 125.68 (1C, t), 129.76 (1C, t), 132.75 (1C, q), 142.52 (1C, q), 144.29 (2C, q), 145.92 (2C, q), 146.26 (1C, q), 153.39 (1C, t).

9-Aminomethyl-1-methyltriptycene (11). To a suspension of $LiAlH_4$ (70 mg, 2.0 mmol) in diethyl ether (10 mL) was added dropwise a solution of the 1-methyl oxime **21** (100 mg, 0.32 mmol) in diethyl ether (20 mL), and the mixture was stirred for 5 h at ambient temperature. The mixture was quenched with ethyl acetate and water and extracted with diethyl ether. The extracts were washed with water and dried over $MgSO_4$, and the solvent was evaporated. The residue was recrystallized from CH_2Cl_2–hexane to give 69 mg (0.23 mmol, 72%) of **11**, mp 180–182 °C. Anal. Found: C, 88.66; H, 6.54; N, 4.69%. Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71%. ^{1}H NMR ($CDCl_3$) δ 1.679 (2H, br s, NH_2), 2.566 (3H, br s), 4.679 (2H, br s), 5.288 (1H, s), 6.5–7.8 (11H, br m).

In the NMR spectrum at −44 °C, rotation about the Tp-CH_2NH_2 bond is frozen and ca. 95% of **11** exist as the *ap*-rotamer: ^{1}H NMR ($CDCl_3$, −44 °C) δ 2.014 (2H, br s), 2.569 (3H, s), 4.695 (2H, s), 5.382 (1H, s), 6.703 (1H, dm, $J = 7.5$ Hz), 6.818 (1H, t, $J = 7.5$ Hz), 7.02–7.17 (4H, m), 7.201 (1H, dm, $J = 6.8$ Hz), 7.488 (2H, m), 7.610 (2H, m). For the minor ±*sc* isomer, the following signals were detected at −44 °C: δ 2.79 (3H, s), 4.32 (1H, d, $J = 12$ Hz). ^{13}C NMR ($CDCl_3$, −44 °C) δ 22.81 (1C, p), 41.35 (1C, s), 54.75 (1C, t), 58.59 (1C, q), 121.95 (1C, t), 123.06 (2C, t), 123.85 (2C, t), 124.71 (1C, t), 124.74 (2C, t), 125.25 (2C, t), 129.67 (1C, t), 132.23 (1C, q), 143.31 (1C, q), 143.81 (2C, q), 146.25 (2C, q), 148.93 (1C, q).

9-Aminomethyl-1-[D$_3$]methyltriptycene (11a): Compound **11a** was synthesized in the same manner as **11**, by reaction of lithiated **17** with CD_3I instead of CH_3I and the subsequent transformations as shown in Scheme 2. Mp 182–183 °C. ^{1}H NMR ($CDCl_3$) δ 1.716 (2H, br s, NH_2), 4.675 (2H, br s), 5.293 (1H, s), 6.5–7.8 (11H, br m). MS m/z 300 (M^+, 100%), 283 (70%).

General Procedure for the Preparation of *N*-(2-Alkylphenyl)-2-hydroxyiminoacetamides. To a solution of chloral hydrate (36 g, 0.22 mol) and sodium sulfate decahydrate (500 g) in 1.5 L of water was added successively a solution of *o*-alkylaniline (0.18 mol) and concd HCl (17 mL) in water (200 mL) and a solution of hydrazine hydrochloride (42 g, 0.60 mol) in water (100 mL) and the mixture was heated until boiling during the course of 1 h and heated under reflux for 2 min. Precipitated solids on standing overnight were collected by filtration, and were dissolved in aq NaOH. The solution was treated with activated charcoal, and neutralized with HCl. The precipitates were collected by filtration, air-dried, and recrystallized from ethanol.

***N*-(2-Ethylphenyl)-2-hydroxyiminoacetamide:** This compound was obtained in 69% yield, mp 107–108 °C (lit.[17] 105–106 °C). ^{1}H NMR ($CDCl_3$) δ 1.245 (3H, t, $J = 7.5$ Hz), 2.633 (2H, q, $J = 7.5$ Hz), 7.11–7.28 (3H, m), 7.617 (1H, s), 7.947 (1H, d, $J = 8.1$ Hz), 8.29 (1H, br), 8.53 (1H, br s). ^{13}C NMR ($CDCl_3$) δ 13.89 (1C, p), 24.29 (1C, s), 122.88 (1C, t), 125.71 (1C, t), 126.82 (1C, t), 128.72 (1C, t), 134.01 (1C, q), 134.67 (1C, q), 144.98 (1C, t), 160.13 (1C, q).

***N*-(2-Isopropylphenyl)-2-hydroxyiminoacetamide:** This compound was obtained in 89% yield, mp 109–110 °C (lit.[18] 104–108 °C). ^{1}H NMR ($CDCl_3$) δ 1.245 (6H, d, $J = 6.9$ Hz), 3.028 (1H, sept, $J = 6.9$ Hz), 7.16–7.26 (2H, m), 7.303 (1H, m), 7.606 (1H, s), 7.773 (1H, m), 8.33 (1H, br s), 9.32 (1H, br s). ^{13}C NMR ($CDCl_3$) δ 22.89 (2C, p), 28.11 (1C, t), 124.10 (1C, t), 125.80 (1C, t), 126.37 (1C, t), 126.49 (1C, t), 132.91 (1C, q), 140.36 (1C, q), 144.53 (1C, t), 160.82 (1C, q).

***N*-(2-*t*-Butylphenyl)-2-hydroxyiminoacetamide:** This compound was obtained in 47% yield, mp 156–157 °C (lit.[18] 151–152 °C). ^{1}H NMR ($CDCl_3$) δ 1.414 (9H, s), 7.166 (1H, td, $J = 7.8$, 1.5 Hz), 7.255 (1H, td, $J = 7.8$, 1.5 Hz), 7.409 (1H, dd, $J = 7.9$, 1.5 Hz), 7.640 (1H, s), 7.791 (1H, dd, $J = 7.8$, 1.5 Hz), 8.50 (1H, br s), 8.69 (1H, br). ^{13}C NMR ($CDCl_3$) δ 30.56 (3C, p), 34.49 (1C, q), 126.11 (1C, t), 126.21 (1C, t), 126.62 (1C, t), 126.88 (1C, t), 134.14 (1C, q), 141.84 (1C, q), 145.17 (1C, t), 160.00 (1C, q).

General Procedure for the Preparation of 7-Alkylisatins. To a stirred mixture of concd H_2SO_4 (110 mL) and water (15 mL) at 60 °C was gradually added an *N*-(2-alkylphenyl)-2-hydroxyiminoacetamide (0.155 mol) and the mixture was kept at 65–70 °C for 10 min. The mixture was poured onto ice-water and the precipitates were collected by filtration and washed thoroughly with water, air-dried, and recrystallized from dichloromethane.

7-Ethylisatin: This compound was obtained in 81% yield, mp 193–194 °C (lit.[17] 189–190 °C). ^{1}H NMR ($CDCl_3$) δ 1.291 (3H, t, $J = 7.6$ Hz), 2.637 (2H, q, $J = 7.6$ Hz), 7.081 (1H, t, $J = 7.6$ Hz), 7.431 (1H, dd, $J = 7.7$, 0.6 Hz), 7.479 (1H, d, $J = 7.5$ Hz), 9.37 (1H, br s). ^{13}C NMR ($CDCl_3$) δ 13.71 (1C, p), 22.66 (1C, s), 117.66 (1C, q), 123.16 (1C, t), 124.02 (1C, t), 128.10 (1C, q), 138.24 (1C, t), 147.45 (1C, q), 160.81 (1C, q), 183.85 (1C, q).

7-Isopropylisatin: This compound was obtained in 89% yield, mp 196–198 °C (lit.[18] 187–191 °C). ^{1}H NMR ($CDCl_3$) δ 1.306 (6H, d, $J = 6.9$ Hz), 2.940 (1H, sept, $J = 6.9$ Hz), 7.105 (1H, t, $J = 7.7$ Hz), 7.45–7.51 (2H, m), 8.97 (1H, br). ^{13}C NMR ($CDCl_3$) δ 22.27 (2C, p), 27.60 (1C, t), 117.75 (1C, q), 123.18 (1C, t), 124.18 (1C, t), 132.60 (1C, q), 135.48 (1C, t), 146.76 (1C, q), 160.80 (1C, q), 183.92 (1C, q).

7-*t*-Butylisatin: This compound was obtained in 98% yield, mp 236–238 °C (lit.[18] 227–230 °C). ^{1}H NMR ($CDCl_3$) δ 1.425 (9H, s), 7.073 (1H, t, $J = 7.8$ Hz), 7.491 (1H, d, $J = 7.5$ Hz), 7.559 (1H, d, $J = 8.1$ Hz), 8.944 (1H, br s). ^{13}C NMR ($CDCl_3$) δ 29.72 (3C, p), 34.06 (1C, q), 118.77 (1C, q), 123.36 (1C, t), 123.83 (1C, t), 134.41 (1C, q), 135.90 (1C, t), 146.75 (1C, q), 159.44 (1C, q), 183.61 (1C, q).

General Procedure for the Preparation of 3-Alkylanthranilic Acids. To a hot (ca. 80 °C) solution of 7-alkylisatin (0.10 mol) in 10% aqueous sodium hydroxide (80 mL) was added dropwise 23 mL of 30% hydrogen peroxide. After cooling to room temperature, the solution was treated with activated carbon and neutralized with hydrochloric acid. The precipitates were collected by filtration and purified by sublimation under reduced pressure.

3-Ethylanthranilic Acid (22b): Compound **22b** was obtained in 83% yield, mp 158–159 °C (lit.[17] 147–148 °C). ^{1}H NMR ($CDCl_3$) δ 1.283 (3H, t, $J = 7.4$ Hz), 2.577 (2H, q, $J = 7.3$ Hz), ca. 6.5 (3H, br), 6.664 (1H, t, $J = 7.5$ Hz), 7.256 (1H, d, $J = 6.6$ Hz), 7.864 (1H, d, $J = 7.7$ Hz). ^{13}C NMR ($CDCl_3$) δ 12.39 (1C, p), 23.67 (1C, s), 109.10 (1C, q), 115.90 (1C, t), 128.50 (1C, q), 129.95 (1C, t), 133.61 (1C, t), 149.22 (1C, q), 174.05 (1C, q).

3-Isopropylanthranilic Acid (22c): Compound **22c** was obtained in 72% yield, mp 99–100 °C (lit.[19] 98–99 °C). ^{1}H NMR ($CDCl_3$) δ 1.266 (6H, d, $J = 6.9$ Hz), 2.873 (1H, sept, $J = 6.9$ Hz), ca. 6.2 (3H, br), 6.685 (1H, t, $J = 7.8$ Hz), 7.314 (1H, dd, $J = 7.5$, 1.3 Hz), 7.873 (1H, dd, $J = 8.1$, 1.6 Hz). ^{13}C NMR ($CDCl_3$) δ 22.02 (2C, p), 27.20 (1C, t), 109.24 (1C, q), 115.99 (1C, t), 129.82 (1C, t), 131.01 (1C, t), 133.02 (1C, q), 148.68 (1C, q), 174.02 (1C, q).

3-*t*-Butylanthranilic Acid (22d): Compound **22d** was obtained in 75% yield, mp 185–187 °C (lit.[19] 190–192 °C). ^{1}H NMR ($CDCl_3$) δ 1.444 (9H, s), ca. 6.1 (3H, br), 6.628 (1H, t, $J = 7.8$ Hz), 7.412 (1H, dd, $J = 7.5$, 1.5 Hz), 7.900 (1H, dd, $J = 8.1$, 1.5 Hz). ^{13}C NMR ($CDCl_3$) δ 29.62 (3C, p), 34.27 (1C, q), 109.86 (1C, q), 115.53 (1C, t), 130.53 (1C, t), 132.32 (1C, t), 133.87 (1C, q), 150.18 (1C, q), 174.16 (1C, q).

General Procedure for the Preparation of 1-Alkyl-9-cyanotriptycenes (24–27). To a boiling solution of 9-cyanoanthracene (**23**) (3.00 g, 14.8 mmol) in $CHCl_3$ (30 mL) were added simultaneously a solution of 3-alkylanthranilic acid (40 mmol) in $CHCl_3$ (70 mL) and a solution of isopentyl nitrite (12 mL, 89 mmol) in $CHCl_3$ (70 mL) over the course of 4 h, and the mixture was stirred under reflux for 1 h. Column chromatography of the mixture on silica gel with hexane–benzene (5:1) as the eluent afforded a mixture of 1-alkyl-9-cyanotriptycene and its regioisomer, 1-alkyl-10-cyanotriptycene. GPC of the mixture afforded both isomers separately after at least 20 recycles. Recrystallization from chloroform–hexane gave pure samples.

9-Cyano-1-methyltriptycene (24): Compound **24** was obtained in 21% yield, mp 221–222 °C. Anal. Found: C, 89.77; H, 5.26; N, 4.81%. Calcd for $C_{22}H_{15}N$: C, 90.07; H, 5.15; N, 4.77%. ^{1}H NMR ($CDCl_3$) δ 2.831 (3H, s), 5.386 (1H, s), 6.829 (1H, d, $J = 7.7$ Hz), 6.939 (1H, t, $J = 7.5$ Hz), 7.08–7.18 (4H, m), 7.261 (1H, d, $J = 6.3$ Hz), 7.422 (2H, m), 7.805 (2H, m). ^{13}C NMR ($CDCl_3$) δ 20.26 (1C, p), 51.91 (1C, q), 53.73 (1C, t), 118.50 (1C, q), 122.25 (2C, t), 122.37 (1C, t), 123.75 (2C, t), 125.62 (2C, t), 126.26 (1C, t), 126.72 (2C, t), 129.37 (1C, t), 133.20 (1C, q), 137.69 (1C, q), 140.86 (2C, q), 143.50 (2C, q), 144.26 (1C, q).

10-Cyano-1-methyltriptycene (24a): Compound **24a** was obtained in 20% yield, mp 206–208 °C. Anal. Found: C, 90.40; H, 5.24; N, 4.81%. Calcd for $C_{22}H_{15}N$: C, 90.07; H, 5.15; N, 4.77%. ^{1}H NMR ($CDCl_3$) δ 2.523 (3H, s), 5.672 (1H, s), 6.91–7.03 (2H, m), 7.06–7.16 (4H, m), 7.422 (2H, m), 7.558 (1H, dm, $J = 7.3$ Hz), 7.701 (2H, m). ^{13}C NMR ($CDCl_3$) δ 18.45 (1C, p), 49.24 (1C, t), 53.91 (1C, q), 116.31 (1C, q), 119.61 (1C, t), 121.81 (2C, t), 123.89 (2C, t), 125.22 (1C, t), 125.64 (2C, t), 126.57 (2C, t), 128.21 (1C, t), 132.30 (1C, q), 140.34 (1C, q), 140.75 (2C, q), 141.45 (1C, q), 143.16 (2C, q).

9-Cyano-1-ethyltriptycene (25): Compound **25** was obtained in 16% yield, mp 181–191 °C. Anal. Found: C, 89.57; H, 5.54; N, 4.53%. Calcd for $C_{23}H_{17}N$: C, 89.87; H, 5.57; N, 4.56%. ^{1}H NMR ($CDCl_3$) δ 1.312 (3H, t, $J = 7.5$ Hz), 3.271 (2H, q, $J = 7.5$ Hz), 5.391 (1H, s), 6.861 (1H, dd, $J = 7.8$, 1.3 Hz), 6.974 (1H, t, $J = 7.5$ Hz), 7.08–7.18 (4H, m), 7.258 (1H, dd, $J = 7.2$, 1.4 Hz), 7.421 (2H, m), 7.817 (2H, m). ^{13}C NMR ($CDCl_3$) δ 17.47 (1C, p), 26.10 (1C, s), 51.67 (1C, q), 53.79 (1C, t), 118.32 (1C, q, CN), 122.25 (2C, t), 122.30 (1C, t), 123.72 (2C, t), 125.62 (2C, t), 126.41 (1C, t), 126.70 (2C, t), 128.04 (1C, t), 137.02 (1C, q), 139.66 (1C, q), 140.83 (2C, q), 143.47 (2C, q), 144.33 (1C, q).

10-Cyano-1-ethyltriptycene (25a): Compound **25a** was obtained in 18% yield, mp 156–158 °C. Anal. Found: C, 90.07; H, 5.70; N, 4.63%. Calcd for $C_{23}H_{17}N$: C, 89.87; H, 5.57; N, 4.56%. ^{1}H NMR ($CDCl_3$) δ 1.269 (3H, t, $J = 7.6$ Hz), 2.888 (2H, q, $J = 7.6$ Hz), 5.694 (1H, s), 6.945 (1H, dd, $J = 7.7$, 1.2 Hz), 7.029 (1H, t, $J = 7.6$ Hz), 7.06–7.16 (4H, m), 7.435 (2H, m), 7.570 (1H, dd, $J = 7.4$, 1.0 Hz), 7.702 (2H, m). ^{13}C NMR ($CDCl_3$) δ 15.82 (1C, p), 25.98 (1C, s), 48.95 (1C, t), 53.92 (1C, q), 116.32 (1C, q, CN), 119.68 (1C, t), 121.73 (2C, t), 123.75 (2C, t), 125.38 (1C, t), 125.56 (2C, t), 126.57 (2C, t), 126.84 (1C, t), 138.61 (1C, q), 140.37 (1C, q), 140.77 (2C, q), 141.04 (1C, q), 143.21 (2C, q).

9-Cyano-1-isopropyltriptycene (26): Compound **26** was obtained in 21% yield, mp 215–217 °C. Anal. Found: C, 89.38; H, 5.84; N, 4.39%. Calcd for $C_{24}H_{19}N$: C, 89.68; H, 5.96; N, 4.36%. ^{1}H NMR ($CDCl_3$) δ 1.303 (6H, d, $J = 6.7$ Hz), 4.480 (1H, sept, $J = 6.7$ Hz), 5.391 (1H, s), 6.98–7.07 (2H, m), 7.08–7.18 (4H, m), 7.248 (1H, dd, $J = 6.2$, 2.3 Hz), 7.412 (2H, m), 7.829 (2H, m). ^{13}C NMR ($CDCl_3$) δ 24.34 (2C, p), 27.71 (1C, t), 51.57 (1C, q), 54.02 (1C, t), 118.60 (1C, q, CN), 122.17 (1C, t), 122.35 (2C, t), 123.19 (1C, t), 123.73 (2C, t), 125.68 (2C, t), 126.53 (1C, t), 126.76 (2C, t), 136.63 (1C, q), 140.93 (2C, q), 143.61 (2C, q), 144.15 (1C, q), 144.17 (1C, q).

10-Cyano-1-isopropyltriptycene (26a): Compound **26a** was obtained in 19% yield, mp 251–253 °C. Anal. Found: C, 89.30; H, 6.08; N, 4.38%. Calcd for $C_{24}H_{19}N$: C, 89.68; H, 5.96; N, 4.36%. ^{1}H NMR ($CDCl_3$) δ 1.304 (6H, d, $J = 6.9$ Hz), 3.511 (1H, sept, $J = 6.9$ Hz), 5.798 (1H, s), 6.98–7.13 (6H, m), 7.424 (2H, m), 7.572 (1H, dd, $J = 6.6$, 2.0 Hz), 7.701 (2H, m). ^{13}C NMR ($CDCl_3$) δ 23.19 (2C, p), 29.68 (1C, q), 48.79 (1C, t), 54.08 (1C, q), 116.37 (1C, q, CN), 119.71 (1C, t), 121.90 (2C, t), 123.22 (1C, t), 123.85 (2C, t), 125.60 (1C, t), 125.70 (2C, t), 126.66 (2C, t), 140.29 (1C, q), 140.76 (1C, q), 140.98 (2C, q), 142.84 (1C, q), 143.33 (2C, q).

1-*t*-Butyl-9-cyanotriptycene (27): Compound **27** was obtained in 45% yield, mp 250–252 °C. Anal. Found: C, 89.58; H, 6.34; N, 4.14%. Calcd for $C_{25}H_{21}N$: C, 89.51; H, 6.31; N, 4.18%. ^{1}H NMR ($CDCl_3$) δ 1.651 (9H, s), 5.404 (1H, s), 6.984 (1H, dd, $J = 8.0$, 7.3 Hz), 7.08–7.20 (5H, m), 7.293 (1H, dd, $J = 7.3$, 1.2 Hz), 7.429 (2H, m), 7.903 (2H, m). ^{13}C NMR ($CDCl_3$) δ 34.31 (3C, p), 35.39 (1C, q), 53.51 (1C, q), 54.83 (1C, t), 119.82 (1C, q, CN), 122.95 (2C, t), 123.10 (1C, t), 123.61 (2C, t), 123.77 (1C, t), 125.72 (2C, t), 126.02 (1C, t), 126.88 (2C, t), 138.99 (1C, q), 140.63 (2C, q), 143.81 (2C, q), 145.71 (1C, q), 146.39 (1C, q).

1-*t*-Butyl-10-cyanotriptycene (27a): Compound **27a** was obtained in 23% yield, mp 269–270 °C. Anal. Found: C, 89.13; H, 6.46; N, 4.23%. Calcd for $C_{25}H_{21}N$: C, 89.51; H, 6.31; N, 4.18%. ^{1}H NMR ($CDCl_3$) δ 1.550 (9H, s), 6.248 (1H, s), 7.027 (1H, dd, $J = 8.1$, 7.5 Hz), 7.06–7.16 (5H, m), 7.440 (2H, m), 7.636 (1H, dd, $J = 7.5$, 1.2 Hz), 7.703 (2H, m). ^{13}C NMR ($CDCl_3$) δ 31.42 (3C, p), 35.47 (1C, q), 51.01 (1C, t), 54.34 (1C, q), 116.48 (1C, q, CN), 120.36 (1C, t), 121.86 (2C, t), 123.79 (2C, t), 124.00 (1C, t), 125.20 (1C, t), 125.70 (2C, t), 126.64 (1C, t), 141.14 (2C, q), 141.30 (1C, q), 141.99 (1C, q), 142.84 (2C. q), 145.33 (1C, q).

General Procedure for the Preparation of 1-Alkyl-9-aminomethyltriptycene (11–14). A mixture of 1-alkyl-9-cyanotriptycene (0.82 mmol) and $LiAlH_4$ (93 mg, 2.5 mmol) in THF (30 mL) under Ar was stirred for 15 h at 40–60 °C. The mixture was quenched with aq $NaHCO_3$ and extracted with diethyl ether. The extracts were washed with water and dried over $MgSO_4$, and the solvent was evaporated. The residue was recrystallized from benzene–hexane.

9-Aminomethyl-1-methyltriptycene (11): Compound **11** was obtained in 65%, mp 181–183 °C. Spectral data were completely identical with those for the sample of **11** synthesized by Route A, described above.

9-Aminomethyl-1-ethyltriptycene (12): Compound **12** was obtained in 59%, mp 144–146 °C. Anal. Found: C, 88.52; H, 6.87; N, 4.48%. Calcd for $C_{23}H_{21}N$: C, 88.71; H, 6.80; N, 4.50%. ^{1}H NMR ($CDCl_3$) δ 1.180 (3H, t, $J = 7.5$ Hz), 1.66 (2H, br s), 2.88 (2H, br q, $J = 7.5$ Hz), 4.72 (2H, br s), 5.292 (1H, s), 6.67–6.88 (2H, br m), 7.00–7.19 (5H, br m), 7.42 (2H, br d, $J \approx 8$ Hz), 7.60 (2H, br). ^{13}C NMR ($CDCl_3$) δ 17.95 (1C, p), 27.73 (1C, s), 41.25 (1C, s), 55.57 (1C, t), 58.96 (1C, q), 121.87 (1C, t), 123.16 (2C, t), 123.78 (2C, t), 124.85 (2C, t), 124.98 (1C, t), 125.46 (2C, t), 128.39 (1C, t), 139.08 (1C, q), 142.99 (1C, q), 144.24 (2C, q), 146.60 (2C, q), 149.34 (1C, q). The NMR spectra at −44 °C reveal that rotation about the Tp-CH_2NH_2 bond is frozen and that ca. 96% of **12** exist as the *ap*-rotamer: ^{1}H NMR ($CDCl_3$, −44 °C) δ 1.185 (3H, t, $J = 7.3$ Hz), 1.987 (2H, br s), 2.881 (2H, q, $J = 7.3$ Hz), 4.732 (2H, s), 5.382 (1H, s), 6.740 (1H, dd, $J = 7.8$, 1.3 Hz), 6.860 (1H, t, $J = 7.6$ Hz), 7.03–7.16 (4H, m), 7.191 (1H, dd, $J = 7.2$, 1.3 Hz), 7.494 (2H, m), 7.598 (2H, m). For the minor ±*sc* isomer, the following signals were detected at −44 °C: δ 1.118 (3H, t, $J = 7.3$ Hz), 4.323 (1H, d, $J = 12.4$ Hz), 4.574 (1H, d, $J = 12.4$ Hz), 5.329 (1H, s).

9-Aminomethyl-1-isopropyltriptycene (13): Compound **13** was obtained in 93% yield, mp 108–109 °C. Anal. Found: C, 88.85; H, 6.83; N, 4.37%. Calcd for $C_{24}H_{23}N$: C, 88.57; H, 7.12; N, 4.30%. ^{1}H NMR ($CDCl_3$) δ 1.204 (6H, d, $J = 6.3$ Hz), 1.65 (2H, br s), 3.70 (1H, m), 4.748 (2H, br s), 5.282 (1H, s), 6.82–6.98 (2H, br m), 7.00–7.16 (5H, br m), 7.43 (2H, br d, $J \approx 6$ Hz), 7.58 (2H, br d, $J \approx 6$ Hz). ^{13}C NMR ($CDCl_3$) δ 24.76 (2C, p), 28.85 (1C, t), 41.73 (1C, s), 55.70 (1C, t), 59.11 (1C, q), 121.82 (1C, t), 123.15 (2C, t), 123.37 (1C, t), 123.81 (2C, t), 124.89 (2C, t), 125.04 (1C, t), 125.38 (2C, t), 142.28 (1C, q), 144.01 (3C, q), 146.55 (2C, q), 149.07 (1C, q).

1-*t*-Butyl-9-phthalimidomethyltriptycene (30). To a boiling solution of 9-phthalimidomethylanthracene[20] (0.30 g, 0.89 mmol) in 1,2-dichloroethane (5 mL) were added simultaneously a solution of isopentyl nitrite (0.83 mL, 6.2 mmol) in of 1,2-dichloroethane (50 mL) and a solution of 3-*t*-butylanthranilic acid (**22d**) (0.86 g, 4.5 mmol) in THF (50 mL) during the course of 3 h, and the mixture was stirred under reflux for 2 h. Column chromatography on silica gel with benzene–hexane (1:1) as the eluent afforded a mixture of **30** and its regioisomer, 1-*t*-butyl-10-phthalimidomethyltriptycene (**30a**) in a ratio of ca. 2:3. Each isomer was isolated by GPC of the mixture. Compound **30** was obtained in 9% yield, mp 254–255 °C (from ethyl acetate). Anal. Found: C, 84.79; H, 5.75; N, 3.05%. $C_{33}H_{27}NO_2$: C, 84.41; H, 5.80; N, 2.98%. ^{1}H NMR ($CDCl_3$) δ 1.661 (9H, s), 5.356 (1H, s), 5.944 (2H, s), 6.823 (1H, dd, $J = 8.1$, 7.1 Hz), 6.907 (2H, td, $J = 7.6$, 1.3 Hz), 7.040 (2H, td, $J = 7.4$, 1.0 Hz), 7.144 (1H, dd, $J = 8.2$, 1.3 Hz), 7.207 (1H, dd, $J = 7.1$, 1.3 Hz), 7.278 (2H, d, $J = 7.6$ Hz), 7.451 (2H, dd, $J = 7.3$, 1.0 Hz), 7.60–7.72 (4H, m). ^{13}C NMR ($CDCl_3$) δ 35.12 (3C, p), 35.42 (1C, q), 46.42 (1C, s), 53.57 (1C, t), 56.79

(1C, q), 122.30 (2C, t), 122.94 (1C, t), 123.12 (2C, t), 123.42 (2C, t), 124.27 (1C, t), 124.29 (1C, t), 124.66 (2C, t), 125.46 (2C, t), 131.80 (2C, q), 133.83 (2C, t), 143.58 (2C, q), 145.19 (1C, q), 145.70 (2C, q), 147.09 (1C, q), 150.56 (1C, q), 168.00 (2C, q).

Compound **30a** was obtained in 9% yield, mp 189–191 °C (from $CHCl_3$–hexane). Anal. Found: C, 84.21; H, 5.55; N, 3.02%. Calcd for $C_{33}H_{27}NO_2$: C, 84.41; H, 5.80; N, 2.98%. ^{1}H NMR ($CDCl_3$) δ 1.594 (9H, s), 5.237 (2H, s), 6.251 (1H, s), 6.890 (1H, t, $J = 7.7$ Hz), 6.92–7.03 (4H, m), 7.054 (1H, d, $J = 7.9$ Hz), 7.194 (1H, d, $J = 7.6$ Hz), 7.274 (2H, m), 7.429 (2H, m), 7.724 (2H, m), 7.826 (2H, m). ^{13}C NMR ($CDCl_3$) δ 31.63 (3C, p), 35.45 (1C, q), 43.05 (1C, s), 51.13 (1C, t), 51.86 (1C, q), 119.74 (1C, t), 121.48 (2C, t), 122.43 (1C, t), 123.33 (2C, t), 123.37 (2C, t), 124.10 (1C, t), 124.75 (2C, t), 125.05 (2C, t), 131.94 (2C, q), 134.02 (2C, t), 144.21 (1C, q), 144.32 (1C, q), 144.84 (2C, q), 146.24 (2C, q), 146.51 (1C, q), 168.01 (2C, q).

1-*t*-Butyl-9-aminomethyltriptycene (14). A mixture of **30** (300 mg, 0.32 mmol) and hydrazine hydrate (240 µL, 4.93 mmol) in THF (3 mL) and ethanol (2 mL) was heated under reflux for 7 h. The solvent was evaporated and the residue was extracted with $CHCl_3$. The $CHCl_3$ solution was washed with water and dried over $MgSO_4$ and the solvent was evaporated. Recrystallization from hexane gave 173 mg (81%) of **14**, mp 159–162 °C. Anal. Found: C, 88.50; H, 7.12; N, 4.21%. Calcd for $C_{25}H_{25}N$: C, 88.45; H, 7.42; N, 4.13%. ^{1}H NMR ($CDCl_3$) δ 1.530 (9H, s), 1.60 (2H, br s), 4.901 (2H, s), 5.285 (1H, s), 6.801 (1H, dd, $J = 8.1$, 7.1 Hz), 7.01–7.13 (5H, m), 7.155 (1H, dd, $J = 7.1$, 1.3 Hz), 7.435 (2H, m), 7.540 (2H, m). ^{13}C NMR ($CDCl_3$) δ 34.85 (3C, p), 35.32 (1C, q), 42.91 (1C, s), 56.83 (1C, t), 59.17 (1C, q), 122.79 (1C, t), 123.50 (2C, t), 123.88 (2C, t), 124.02 (1C, t), 124.22 (1C, t), 125.00 (2C, t), 125.54 (2C, t), 143.94 (2C, q), 145.24 (1C, q), 146.83 (2C, q), 147.35 (1C, q), 150.97 (1C, q).

9-(1-Iminoethyl)-1-methyltriptycene (28). To a solution of **24** (0.60 g, 1.95 mmol) in anhydrous diethyl ether (30 mL) was added under argon 1 M methyllithium (12 mL, 12 mmol) in diethyl ether, and the mixture was stirred for 3 h at room temperature. After quenching with water, the mixture was extracted with diethyl ether. The extracts were dried over $MgSO_4$ and the solvent was evaporated. Recrystallization from dichloromethane–hexane gave 0.56 g (1.81 mmol, 93%) of **28**, mp 192–194 °C. Anal. Found: C, 88.95; H, 6.13; N, 4.57%. Calcd for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53%. ^{1}H NMR ($CDCl_3$) at ambient temperature gave broadened signals, presumably because of syn–anti isomerization of the NH moiety: δ 2.44 (3H, br s), 2.54 (3H, br s), 5.26 (1H, s), 6.81 (1H, d, $J = 7.7$ Hz), 6.91 (1H, t, $J = 7.4$ Hz), 6.98–7.03 (4H, m), 7.23 (1H, d, $J = 7.0$ Hz), 7.35 (2H, br d, $J = 6.5$ Hz), 8.10 (2H, br), 10.22 (1H, br, NH). At ca. −30 °C, two isomers were observed in a ratio of 78:22. The major isomer: δ 2.473 (3H, s), 2.535 (3H, s), 5.319 (1H, s), 6.837 (1H, d, $J = 7.5$ Hz), 6.947 (1H, t, $J = 7.5$ Hz), 6.97–7.07 (4H, m), 7.273 (1H, d, $J = 7.5$ Hz), 7.382 (2H, d, $J = 7.0$ Hz), 8.111 (2H, d, $J = 7.0$ Hz), 10.225 (1H, s, NH). The minor isomer: δ 2.317 (3H, s), 2.862 (3H, s), 5.32 (1H, s), 6.8–7.6 (11H, m), 9.957 (1H, s, NH).

9-(1-Aminoethyl)-1-methyltriptycene (15). To a solution of **28** (220 mg, 0.71 mmol) in dry THF (20 mL) was added 270 mg (7.11 mmol) of $LiAlH_4$ under argon and the mixture was heated under reflux for 24 h. After quenching with aq $NaHCO_3$, the mixture was extracted with diethyl ether. The extracts were washed with water and dried over $MgSO_4$ and the solvent was evaporated. The residue was recrystallized from diethyl ether–hexane to afford 122 mg (0.39 mmol, 55%) of **15**, mp 191–193 °C. Anal. Found: C, 88.31; H, 6.82; N, 4.50%. Calcd for $C_{23}H_{21}N$: C, 88.71; H, 6.80; N, 4.50%. ^{1}H NMR ($CDCl_3$) revealed the presence of two rotamers, R^*-($-sc$)* and *ap*, in a ratio of 64:36; the R^*-($-sc$) isomer: δ 1.90 (2H, br, NH_2), 1.968 (3H, d, $J = 6.5$ Hz), 2.786 (3H, s), 5.164 (1H, q, $J = 6.5$ Hz), 5.217 (1H, s), 6.73–7.50 (10H, m), 8.274 (1H, d, $J = 7.7$ Hz); the *ap* isomer: δ 1.90 (2H, br), 2.090 (3H, d, $J = 6.5$ Hz), 2.566 (3H, s), 5.209 (1H, q, $J = 6.5$ Hz), 5.221 (1H, s), 6.74–7.59 (10H, m), 8.046 (1H, d, $J = 7.7$ Hz). ^{13}C NMR ($CDCl_3$): the R^*-($-sc$) isomer: δ 21.74 (1C, p), 22.58 (1C, p), 46.12 (1C, s), 56.32 (1C, t), 62.14 (1C, q), 122.05 (1C, t), 123.44 (1C, t), 123.48 (1C, t), 123.52 (1C, t), 123.95 (1C, t), 124.51 (1C, t), 124.62 (1C, t), 124.67 (1C, t), 125.48 (1C, t), 128.06 (1C, t), 130.37 (1C, t), 132.34 (1C, t), 142.16 (1C, q), 144.03 (1C, q), 145.69 (1C, q), 146.69 (1C, q), 148.31 (1C, q), 149.34 (1C, q); the *ap* isomer: δ 23.09 (1C, p), 24.38 (1C, p), 46.27 (1C, s), 56.34 (1C, t), 62.91 (1C, q), 121.74 (1C, t), 122.48 (1C, t), 123.78 (1C, t), 123.80 (1C, q), 124.11 (1C, t), 124.50 (1C, t), 124.94 (1C, t), 125.57 (1C, t), 126.96 (1C, t), 130.29 (1C, t), 132.64 (1C, t), 142.28 (1C, q), 144.29 (1C, q), 146.16 (1C, q), 146.82 (1C, q), 148.48 (1C, q), 149.18 (1C, q), one tertiary peak missing.

Deamination Reactions. The reactions were systematically run as follows. To a magnetically stirred solution of the amine (2 mmol) in the appropriate solvent ($CHCl_3$ containing 1.2 molar amount of AcOH or AcOH) (10 mL) was added 1.1 molar amount of isopentyl nitrite at 23 °C and the solution was stirred for 4 h. After the starting amine was completely consumed, the mixture was extracted with diethyl ether, and the extracts were washed with water and brine, and dried over $MgSO_4$. After evaporation of the solvent, the residue was submitted to NMR analysis to determine the product ratio. The product ratios reported are the averages from two or three experiments under the same conditions. The mixture was then submitted to preparative GPC to isolate and characterize each product. Characterization of the products was mainly made by analysis of the ^{1}H and ^{13}C NMR spectra. Elemental analysis was made when a sufficient amount of the sample was obtained.

1,2,6,10b-Tetrahydro-6,10b-*o*-benzenoaceanthrylene (31): Mp 207–209 °C. Anal. Found: C, 94.20; H, 5.82%. Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75%. ^{1}H NMR ($CDCl_3$) δ 3.25 (2H, m, 1-H), 3.35 (2H, m, 2-H), 5.462 (1H, s), 6.869 (1H, dd, $J = 7.6$, 0.8 Hz), 6.90–7.03 (5H, m), 7.189 (1H, dd, $J = 7.0$, 0.7 Hz), 7.31–7.44 (4H, m). ^{13}C NMR ($CDCl_3$) δ 22.83 (1C, s, 1-C), 33.18 (1C, s, 2-C), 53.75 (1C, t), 60.05 (1C, q), 120.32 (1C, t), 120.37 (2C, t), 121.24 (1C, t), 123.98 (2C, t), 124.58 (2C, t), 124.74 (2C, t), 126.37 (1C, t), 136.47 (1C, q), 141.72 (1C, q), 146.33 (2C, q), 147.64 (2C, q), 152.37 (1C, q).

1,2,6,10b-Tetrahydro-6,10b-*o*-benzenoaceanthrylene-2,2-d_2 (31a): MS m/z 282 (M^+). ^{1}H NMR ($CDCl_3$) δ 3.25 (2H, m), 5.462 (1H, s), 6.869 (1H, dd, $J = 7.6$, 0.8 Hz), 6.90–7.03 (5H, m), 7.189 (1H, dd, $J = 7.0$, 0.7 Hz), 7.31–7.44 (4H, m). ^{13}C NMR ($CDCl_3$) δ 22.60 (1C, s), 32.54 (1C, quint, $J = 18.8$ Hz), 53.72 (1C, t), 60.04 (1C, q), 120.33 (1C, t), 120.35 (2C, t), 121.27 (1C, t), 123.97 (2C, t), 124.57 (2C, t), 124.73 (2C, t), 126.34 (1C, t), 136.34 (1C, q), 141.69 (1C, q), 146.31 (2C, q), 147.64 (2C, q), 152.43 (1C, q).

1-Acetoxymethyl-9-methyltriptycene (32): Oil. ^{1}H NMR ($CDCl_3$) δ 2.077 (3H, s), 2.652 (3H, s), 5.382 (1H, s), 5.391 (2H, s), 6.92–7.08 (6H, m), 7.34–7.43 (5H, m). ^{13}C NMR ($CDCl_3$) δ 16.18 (1C, p), 21.12 (1C, p), 51.25 (1C, q), 54.94 (1C, t), 65.18 (1C, s), 121.38 (2C, t), 123.19 (2C, t), 124.73 (1C, t), 125.03 (2C, t), 125.22 (1C, t), 125.24 (2C, t), 129.51 (1C, t), 130.54 (1C, q), 144.99 (1C, q), 145.99 (2C, q), 147.33 (2C, q), 148.47 (1C, q), 170.68 (1C, q).

1-Acetoxy(methyl-d_2)-9-(methyl-d)triptycene (32a): MS m/z 343 (M^+). ^{1}H NMR ($CDCl_3$) δ 2.079 (3H, s), 2.636 (2H, s), 5.386 (1H, s), 6.92–7.08 (6H, s), 7.34–7.43 (5H, m).

10-Acetoxy-10,11-dihydro-1-methyl-5,10-*o*-benzeno-5*H*-dibenzo[*a,d*]cycloheptene (33): Mp 273–286 °C. ^{1}H NMR ($CDCl_3$) δ 2.035 (3H, s), 2.462 (3H, s, OAc), 3.116 (2H, br s), 4.895 (1H, s), 6.901 (1H, d, $J = 7.0$ Hz), 6.972 (1H, t, $J = 7.0$ Hz), 7.12–7.26 (7H, m), 7.365 (2H, m). ^{13}C NMR ($CDCl_3$) δ 19.74 (1C, p), 22.04 (1C, p), 42.30 (1C, s), 54.63 (1C, t), 122.25 (2C, t), 124.99 (1C, t), 125.11 (2C, t), 126.30 (1C, t), 126.42 (2C, t), 127.24 (2C, t), 128.90 (1C, t), 131.20 (1C, q), 137.69 (2C, q), 138.80 (1C, q), 139.13 (2C, q), 140.34 (1C, q), 168.49 (1C, q). At room temperature, the methylene proton signal appeared as a broad singlet ($W_{1/2} \approx 20$ Hz in $CDCl_3$) together with some broadening of the other signals. The methylene signal sharpened upon either elevating or lowering the temperatures ($W_{1/2} \approx 3$ Hz at 60 and −35 °C), presumably reflecting the rotation of the C–OAc bond. At 60 °C the rotation is fast on the NMR timescale, while at −35 °C the rotation is slow but the rotamer equilibrium is almost shifted to the *ap* rotamer.

2-Methyl-1,2,6,10b-tetrahydro-6,10b-*o*-benzenoaceanthrylene (38): Mp 165–167 °C. ^{1}H NMR ($CDCl_3$) δ 1.425 (3H, d, $J = 7.1$ Hz), 2.792 (1H, dd, $J = 14.2, 5.4$ Hz), 3.509 (1H, dd, $J = 14.2, 8.7$ Hz), 3.717 (1H, m), 5.468 (1H, s), 6.851 (1H, d, $J = 7.7$ Hz), 6.92–7.04 (5H, m), 7.205 (1H, d, $J = 7.7$ Hz), 7.33–7.43 (4H, m). ^{13}C NMR ($CDCl_3$) δ 21.78 (1C, p), 32.66 (1C, s), 41.37 (1C, t), 53.68 (1C, t), 59.07 (1C, q), 120.28 (1C, t), 120.35 (1C, t), 120.47 (1C, t), 120.59 (1C, t), 123.93 (1C, t), 124.00 (1C, t), 124.55 (2C, t), 124.72 (1C, t), 124.82 (1C, t), 126.45 (1C, t), 141.23 (1C, q), 141.70 (1C, q), 146.12 (1C, q), 146.42 (1C, q), 147.36 (1C, q), 148.35 (1C, q), 151.74 (1C, q).

1-(1-Acetoxyethyl)-9-methyltriptycene (39): Mp 201–202 °C. Anal. Found: C, 84.51; H, 6.19%. Calcd for $C_{25}H_{22}O_2$: C, 84.72; H, 6.26%. ^{1}H NMR ($CDCl_3$) δ 1.457 (3H, d, $J = 6.6$ Hz), 2.014 (3H, s), 2.740 (3H, s), 5.345 (1H, s), 6.93–7.08 (6H, m), 7.187 (1H, dd, $J = 8.1, 1.4$ Hz), 7.282 (1H, dd, $J = 7.2, 1.4$ Hz), 7.32–7.50 (4H, m). ^{13}C NMR ($CDCl_3$) δ 18.07 (1C, p), 21.32 (1C, p), 24.00 (1C, p), 51.19 (1C, q), 55.07 (1C, t), 67.87 (1C, t), 121.22 (1C, t), 121.72 (1C, t), 123.04 (1C, t), 123.17 (1C, t), 123.43 (1C, t), 123.87 (1C, t), 125.01 (1C, t), 125.11 (1C, t), 125.20 (1C, t), 125.24 (1C, t), 125.40 (1C, t), 138.59 (1C, q), 141.59 (1C, q), 145.70 (1C, q), 146.19 (1C, q), 147.14 (1C, q), 147.59 (1C, q), 147.67 (1C, q), 170.36 (1C, q).

1-(1-Hydroxyethyl)-9-methyltriptycene (40): Mp 207–208 °C. Anal. Found: C, 88.20; H, 6.52%. Calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45%. ^{1}H NMR ($CDCl_3$) δ 1.460 (3H, d, $J = 6.3$ Hz), 1.578 (1H, br s), 2.688 (3H, s), 5.359 (1H, s), 5.920 (1H, q, $J = 6.3$ Hz), 6.98–7.10 (5H, m), 7.292 (1H, dd, $J = 7.2, 1.3$ Hz), 7.34–7.43 (5H, m). ^{13}C NMR ($CDCl_3$) δ 18.01 (1C, p), 25.90 (1C, p), 51.21 (1C, q), 55.14 (1C, t), 65.10 (1C, t), 121.22 (1C, t), 121.47 (1C, t), 122.88 (1C, t), 123.14 (1C, t), 123.18 (1C, t), 123.36 (1C, t), 124.96 (1C, t), 124.99 (1C, t), 125.21 (1C, t), 125.28 (1C, t), 125.52 (1C, t), 141.68 (1C, q), 142.26 (1C, q), 146.00 (1C, q), 146.16 (1C, q), 147.38 (1C, q), 147.53 (1C, q), 147.77 (1C, q).

9-Methyl-1-vinyltriptycene (41): Mp 194–195 °C. Anal. Found: C, 93.67; H, 6.26%. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16%. ^{1}H NMR ($CDCl_3$) δ 2.567 (3H, s), 5.24–5.30 (2H, m, =CH_2), 5.357 (1H, s), 6.883 (1H, dd, $J = 7.8, 2.0$ Hz), 6.924 (1H, dd, $J = 7.9, 7.1$ Hz), 6.97–7.07 (4H, m), 7.297 (1H, dd, $J = 7.1, 2.0$ Hz), 7.33–7.40 (4H, m), 7.462 (1H, m, –CH=). The signals of the vinyl group were "deceptively simple," and spectral simulation (LAOCN3[21]) was necessary for the analysis: $\delta_a = 7.465$, $\delta_b = 5.275$, $\delta_c = 5.287$, $J_{ab} = 10.9$ Hz, $J_{ac} = 17.0$ Hz, and $J_{bc} = 1.8$ Hz for $–CH^a{=}CH^bH^c$. ^{13}C NMR ($CDCl_3$) δ 18.21 (1C, p), 51.33 (1C, q), 54.82 (1C, t), 116.67 (1C, s), 121.34 (2C, t), 123.12 (2C, t), 123.40 (1C, t), 124.89 (2C, t), 125.08 (2C, t), 125.17 (2C, t), 127.28 (1C, t), 136.04 (1C, q), 138.49 (1C, t), 142.55 (1C, q), 146.14 (2C, q), 147.39 (1C, q), 147.65 (2C, q).

1-Isopropenyl-9-methyltriptycene (42): Mp 160–162 °C. Anal. Found: C, 93.84; H, 6.26%. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54%. ^{1}H NMR ($CDCl_3$) δ 2.057 (3H, t, $J = 1.0$ Hz), 2.524 (3H, s, 9-Me), 4.808 (1H, m), 5.212 (1H, m), 5.357 (1H, s, 10-H), 6.643 (1H, dd, $J = 7.7, 1.4$ Hz), 6.878 (1H, t, $J = 7.5$ Hz), 6.95–7.04 (4H, m), 7.252 (1H, dd, $J = 7.2, 1.3$ Hz), 7.31–7.40 (4H, m). ^{13}C NMR ($CDCl_3$) δ 16.06 (1C, p), 27.38 (1C, p), 50.80 (1C, q), 54.88 (1C, t), 115.50 (1C, s), 121.10 (1C, t), 121.29 (1C, t), 122.51 (1C, t), 123.11 (1C, t), 123.16 (1C, t), 124.47 (1C, t), 124.91 (1C, t), 129.92 (1C, t), 125.01 (1C, t), 125.02 (1C, t), 127.39 (1C, t), 140.16 (1C, q), 141.81 (1C, q), 146.04 (1C, q), 146.19 (1C, q), 146.79 (1C, q), 147.47 (1C, q), 147.69 (1C, q), 147.91 (1C, q).

3,3-Dimethyl-2,3,7,11b-tetrahydro-7,11b-*o*-benzeno-1*H*-benzo[*d,e*]anthracene (46): Mp 154–157 °C. Anal. Found: C, 93.23; H, 6.70%. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88%. ^{1}H NMR ($CDCl_3$) δ 1.300 (6H, s), 2.000 (2H, m, 2-H), 3.035 (2H, m, 1-H), 5.362 (1H, s), 6.927 (1H, dd, $J = 7.8, 7.2$ Hz), 6.95–7.04 (5H, m), 7.192 (1H, dd, $J = 7.2, 1.2$ Hz), 7.360 (2H, dd, $J = 7.2, 1.2$ Hz), 7.380 (2H, d, $J = 7.8$ Hz). ^{13}C NMR ($CDCl_3$) δ 20.14 (1C, s), 30.09 (2C, p), 33.63 (1C, q), 36.01 (1C, s), 49.47 (1C, q), 54.17 (1C, t), 120.92 (2C, t), 122.07 (1C, t), 123.53 (2C, t), 124.78 (2C, t), 124.81 (3C, t), 124.91 (1C, t), 140.85 (1C, q), 143.50 (2C, q), 145.42 (1C, q), 146.82 (2C, q), 146.95 (1C, q).

1-Methyl-9-vinyltriptycene (51): Mp 163–164 °C. Anal. Found: C, 93.62; H, 6.30%. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16%. ^{1}H NMR ($CDCl_3$) δ 2.583 (3H, s), 5.322 (1H, s), 5.801 (1H, dd, $J = 18.3, 1.2$ Hz), 6.151 (1H, dd, $J = 11.7, 1.2$ Hz), 6.730 (1H, dm, $J = 7.6$ Hz), 6.836 (1H, t, $J = 7.5$ Hz), 6.98–7.04 (4H, m), 7.202 (1H, dm, $J = 6.8$ Hz), 7.394 (2H, m), 7.396 (1H, dd, $J = 18.3, 11.7$ Hz), 7.642 (2H, m). ^{13}C NMR ($CDCl_3$) δ 23.99 (1C, p), 55.39 (1C, t), 58.32 (1C, q), 120.84 (1C, s, =CH_2), 121.97 (1C, t), 123.42 (2C, t), 123.66 (2C, t), 124.57 (2C, t), 124.89 (1C, t), 125.21 (2C, t), 129.89 (1C, t), 133.10 (1C, q), 134.52 (1C, t, –CH=), 144.32 (1C, q), 145.99 (2C, q), 146.00 (2C, q), 147.44 (1C, q).

9-(1-Acetoxyethyl)-1-methyltriptycene (52): Mp 214–216 °C. ^{1}H NMR ($CDCl_3$) showed the presence of two rotamers, R^*-($-sc$)* and *ap*, in a ratio of 72:28; the R^*-($-sc$)* isomer: δ 2.054 (3H, d, $J = 5.9$ Hz), 2.251 (3H, s), 2.381 (3H, s), 5.258 (1H, s), 6.666 (1H, q, $J = 5.9$ Hz), 6.69–7.47 (11H, m), 7.881 (1H, d, $J = 7.7$ Hz); the *ap* isomer: δ 2.126 (3H, s), 2.189 (3H, d, $J = 6.4$ Hz), 2.578 (3H, s), 5.258 (1H, s), 6.75–7.47 (11H, m), 6.944 (1H, q, $J = 6.1$ Hz), 7.902 (1H, d, $J = 7.9$ Hz).

10-Acetoxy-10,11-dihydro-1,11-dimethyl-5,10-*o*-benzeno-5*H*-dibenzo[*a,d*]cycloheptene (53): ^{1}H NMR ($CDCl_3$) δ 1.439 (3H, d, $J = 6.9$ Hz), 2.404 (3H, s, OAc), 2.549 (3H, s), 3.369 (1H, q, $J = 6.9$ Hz), 4.809 (1H, s), 6.90–7.40 (11H, m). ^{13}C NMR ($CDCl_3$) δ 19.12 (1C, p), 21.44 (1C, p), 22.37 (1C, p), 46.32 (1C, t), 55.80 (1C, t), 85.49 (1C, q), 123.03 (1C, t), 124.27 (1C, t), 124.30 (1C, t), 126.14 (1C, t), 126.34 (1C, t), 126.66 (1C, t), 126.79 (1C, t), 126.98 (1C, t), 127.11 (1C, t), 131.20 (1C, t), 131.70 (1C, t), 133.46 (1C, q), 135.19 (1C, q), 138.58 (1C, q), 138.65 (1C, q), 139.26 (1C, q), 140.38 (1C, q), 140.97 (1C, q), 169.05 (1C, q).

Table 1. Crystal Data and Parameters for Data Collection, Structure Determination, and Refinement

	26	**30**	**46**	**54**
Empirical formula	$C_{24}H_{19}N$	$C_{33}H_{27}NO_2$	$C_{25}H_{22}$	$C_{25}H_{22}O_2$
Formula weight	321.40	469.56	322.43	354.45
Crystal system	monoclinic	trigonal	monoclinic	monoclinic
Space group	$P2_1/c$	$R\bar{3}$	$P2_1/n$	$P2_1/a$
a/Å	10.8472(14)	29.2779(9)	10.2269(9)	10.075(5)
b/Å	13.2857(14)	29.2779(9)	10.0974(7)	17.790(6)
c/Å	12.4932(13)	15.1293(5)	16.5762(11)	10.915(6)
$\alpha/^\circ$	90.00	90.00	90.00	90.00
$\beta/^\circ$	100.5072(17)	90.00	90.7078(14)	106.86(4)
$\gamma/^\circ$	90.00	120.00	90.00	90.00
V/Å^3	1770.2(3)	11231.3(6)	1711.6(2)	1872(1)
Z	4	18	4	4
D_{calcd}/g cm^{-3}	1.206	1.250	1.251	1.257
μ(Mo Kα)/cm^{-1}	0.069	0.077	0.070	0.078
Temp/K	293(2)	113(2)	113(2)	296(2)
$2\theta_{\mathrm{max}}/^\circ$	55.0	55.0	55.0	55.0
No. of reflections measured				
Total	3178	5004	3110	4676
Unique	3052	4440	2909	4289
No. of refinement variables	229	337	229	245
Final R_1;[a] wR_2[b]	0.0592; 0.1565	0.0518, 0.1516	0.0443, 0.1158	0.071; 0.104
GOF	1.114	1.053	1.096	1.206

a) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. b) $wR_2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

(5*R,10*R**,11*R**)-10-Acetoxy-10,11-dihydro-9,11-dimethyl-5,10-*o*-benzeno-5*H*-dibenzo[*a*,*d*]cycloheptene (54):** Mp 231–234 °C. ^{1}H NMR ($CDCl_3$) δ 1.228 (3H, d, $J = 6.9$ Hz), 2.397 (3H, s, OAc), 2.499 (3H, s), 3.550 (1H, q, $J = 6.9$ Hz), 4.786 (1H, s), 6.90–7.40 (11H, m). ^{13}C NMR ($CDCl_3$) δ 18.99 (1C, p), 21.28 (1C, p), 21.92 (1C, p), 42.59 (1C, t), 55.50 (1C, t), 84.47 (1C, q), 122.83 (1C, t), 125.37 (1C, t), 125.44 (1C, t), 125.61 (1C, t), 126.27 (1C, t), 126.79 (2C, t), 126.94 (1C, t), 127.30 (1C, t), 130.94 (1C, t), 131.93 (1C, t), 133.41 (1C, q), 135.44 (1C, q), 135.91 (1C, q), 138.24 (1C, q), 138.86 (1C, q), 141.09 (1C, q), 141.32 (1C, q), 168.29 (1C, q).

X-ray Crystallography. Crystals of compounds **26**, **30**, **46**, and **54** were grown from diethyl ether–hexane. The crystal data and the parameters for data collection, structure determination, and refinement are summarized in Table 1. Diffraction data were collected on a Rigaku AFC7R or a Rigaku/MSC Mercury CCD diffractometer and calculations were performed using the SHELXL97 program.[22] The structures were solved by direct methods followed by full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and all hydrogen atoms isotropic. Reflection data with $|I| > 2.0\sigma(I)$ were used.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-609632 to CCDC-509635 for compounds **26**, **30**, **46**, and **54**, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

References

1 J. T. Keating, P. S. Skell, in *Carbonium Ions*, ed. by G. A. Olah, P. von R. Schleyer, **1970**, Vol. 2, Chap. 15; L. Friedman, in *Carbonium Ions*, ed. by G. A. Olah, P. von R. Schleyer, **1970**, Vol. 2, Chap. 16.

2 S. J. Cristol, D. K. Pennelle, *J. Org. Chem.* **1970**, *35*, 2357.

3 J. W. Wilt, T. P. Malloy, *J. Org. Chem.* **1972**, *37*, 2781.

4 G. Yamamoto, M. Ōki, *Chem. Lett.* **1987**, 1163.

5 See for example: K. Hiraoka, R. Kebarle, *J. Am. Chem. Soc.* **1976**, *98*, 6119; L. I. Yeh, J. M. Price, Y. T. Lee, *J. Am. Chem. Soc.* **1989**, *111*, 5597; J. W. de M. Carneiro, P. von R. Schleyer, M. Saunders, R. Remington, H. F. Schaefer, III, A. Rauk, T. S. Sorensen, *J. Am. Chem. Soc.* **1994**, *116*, 3483; A. L. L. East, Z. F. Liu, C. McCague, K. Cheng, J. S. Tse, *J. Phys. Chem. A* **1998**, *102*, 10903.

6 A part of the results has been reported in a preliminary form: G. Yamamoto, H. Mochida, *Chem. Lett.* **2000**, 454.

7 T. Kawase, N. Asai, T. Ogawa, M. Oda, *J. Chem. Soc., Chem. Commun.* **1990**, 339.

8 E. C. Kornfeld, P. Barney, J. Blankley, W. Faul, *J. Med. Chem.* **1965**, *8*, 342.

9 U. Berg, J. Sandström, *Adv. Phys. Org. Chem.* **1989**, *25*, 1.

10 See for example: J. E. Anderson, R. W. Franck, W. L. Mandella, *J. Am. Chem. Soc.* **1972**, *94*, 4608; M. S. Newman, R. Kannan, *J. Org. Chem.* **1976**, *41*, 3356; G. Yamamoto, M. Suzuki, M. Ōki, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 306; G. Yamamoto, M. Ōki, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3597; G. W. Gribble, D. J. Keavy, S. E. Branz, W. J. Kelly, M. A. Pals, *Tetrahedron Lett.* **1988**, *29*, 6227.

11 For the stereochemical descriptors for the conformational isomers, see: W. Klyne, V. Prelog, *Experientia* **1960**, *16*, 521; M. Ōki, *Top. Stereochem.* **1983**, *14*, 1; G. Yamamoto, C. Agawa, T. Ohno, M. Minoura, Y. Mazaki, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1801.

12 M. Ōki, Y. Taguchi, T. Miyasaka, M. Kitano, S. Toyota, T. Tanaka, K. Yonemoto, G. Yamamoto, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1485.

13 A. L. Van Geet, *Anal. Chem.* **1970**, *42*, 679.
14 H. Friebolin, G. Schilling, L. Pohl, *Org. Magn. Reson.* **1979**, *12*, 569.
15 F. H. C. Stewart, *Aust. J. Chem.* **1960**, *13*, 478.
16 F. M. Logullo, A. H. Seitz, L. Friedman, *Org. Synth.* **1973**, Coll. Vol. *V*, 54.
17 N. S. Newman, M. W. Logue, *J. Org. Chem.* **1971**, *36*, 1398.
18 C. A. Demerson, L. G. Humber, A. H. Philipp, R. R. Martel, *J. Med. Chem.* **1976**, *19*, 391.
19 M. Boyd, H. H. Lee, R. F. Anderson, W. A. Denny, *J. Chem. Soc., Perkin Trans. 2* **1994**, 291.
20 E. Teodori, S. Dey, P. Quidu, R. Budriesi, A. Chiarini, A. Garnier-Suillerot, F. Gualtieri, D. Manetti, M. N. Romanelli, S. Scapecchi, *J. Med. Chem.* **1999**, *42*, 1687.
21 A. A. Bothner-by, S. Castellano, *QCPE Program No. 111*.
22 G. M. Sheldrick, *SHELXL97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.